Author's 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 SO_2 *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* $7*10^{11}$ *molec* cm^{-3} *sec (5 days at [OH] =* $1.5*10^{6}$ 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 ~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]

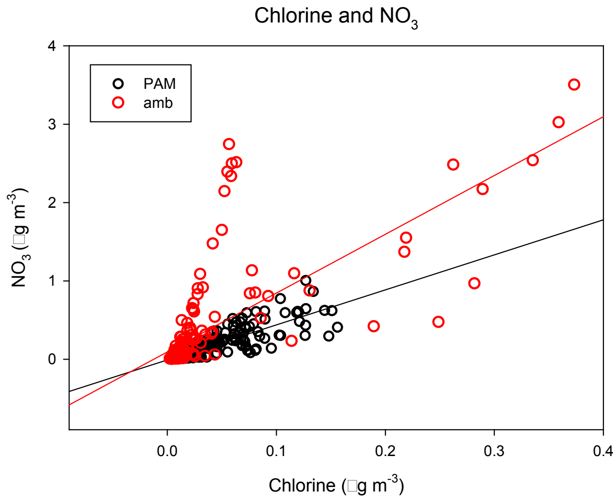
Page 4 Line 100: Added the sentence: In previous studies, sulfate and organic aerosols were measured in Baengnyeong Island, showing the influence of pollution plumes transported from eastern China and the Korean Peninsula (Choi et al., 2016; Lee et al., 2015).

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 O_3, 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 10^{11} 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 10^6 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 how 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?*

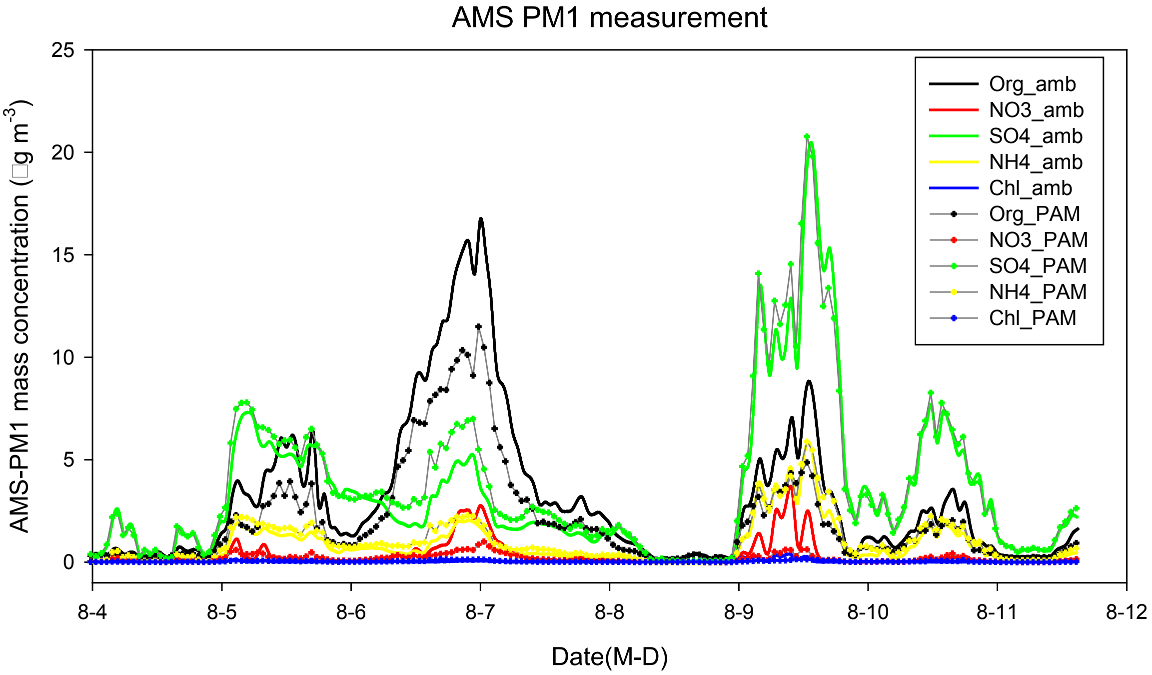
[Response]

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 ~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 ~3 – 7 μg m^{-3} was an error and should be -3 ~ 7 μg m^{-3}. Second, the mass concentration of -3~7 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 (~ 30 cm) from PM1.0 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 ℃ 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 ℃ 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 O_3 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 SO_2 to sulfate, causing the aerosols to become acidic and causing particulate nitrate ($HNO_3(p)$) 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 ~1 μg m−3 (Fig. 4). Thus, in both cases the aerosol mass measured by AMS was ~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 10^{11} molecules cm^{-3} s, for which the CE comes close to 0.5 (Ortega et al., 2016). In addition, the equivalent ratio of ($[NH_4]/(2x[SO_4]+[NO_3])$) was 0.7~1.2 for ambient and PAM aerosol, respectively. According to Middlebrook et al. (2012), the CE would fall into the range of 0.45~0.5 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 0.01~0.22 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.

	Organic-dominant		**Sulfate-dominant**	
	(Aug. 6, 11 AM~ Aug. 7, 9 AM)		(Aug. 9, 1 AM~ Aug. 9, 2 PM*)	
Meteorological parameters				
Temp(°C)	26 ± 0.8		20 ± 0.6	
Relative humidity (%)	84 ± 7.7		96 ± 0.2	
Wind speed (m/s)	5 ± 1.6		8 ± 1.7	
Wind direction	easterly		southwesterly	
Weather mark	Cloudy		Fog	
Gaseous species				
SO_2 (ppbv)	3.1 ± 0.3		3.4 ± 0.2	
NO_2 (ppbv)	2.4 ± 0.8		0.9 ± 0.3	
CO (ppmv)	0.2 ± 0.0		0.4 ± 0.1	
O_3 (ppbv)	46 ± 22		54 ± 8	
Aerosol species#				
	Ambient	**PAM**	**Ambient**	**PAM**
Mass&	14.04±4.49	16.31±5.14	25.00±6.41	27.48 ± 7.32
10~50nm	0.03±0.03	0.66±0.30	0.01±0.01	0.24±0.10
50~200nm	5.55±2.33	4.73±1.99	7.78±2.01	7.83±2.09
200~500nm	8.45±2.27	10.92±3.15	17.21±5.49	19.41±6.65
Sulfate	2.95 ± 1.31	4.19 ± 1.81	11.45 ± 4.65	12.37 ± 4.68
Nitrate	1.16 ± 0.85	0.47 ± 0.21	1.56 ± 1.01	0.38 ± 0.18
Ammonium	1.03 ± 0.62	1.38 ± 0.63	3.44 ± 1.36	3.44 ± 1.37
Organics	10.59± 3.71	7.33 ± 2.54	5.34 ± 1.85	3.36 ± 0.95
m/z 43	0.66 ± 0.04	0.29 ±0.01	0.24 ± 0.02	0.09 ± 0.02
m/z 44	1.47 ± 0.08	1.76 ± 0.01	0.93 ± 0.06	0.86 ± 0.05

* Data from 9 AM to 12 AM, August 9 were excluded because of rain.

Units are μg cm^{-3}.

& Aerosol mass concentrations were obtained from SMPS measurements with an aerosol density of 1.2 μg cm^{-3} and sulfate, nitrate, ammonium and organics were from HR-ToF-

AMS measurements.

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, SO_2, NO_2, CO, O_3, 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 (O_3), 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?

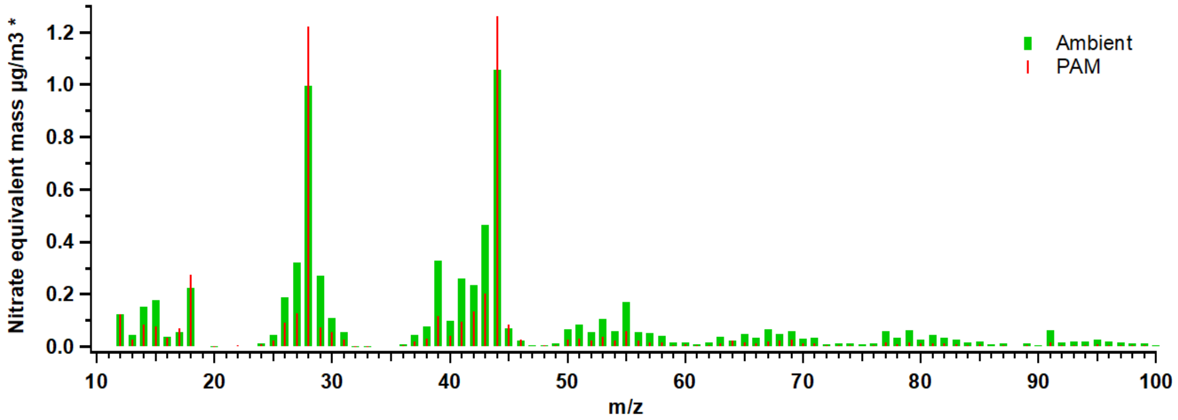
[Response]

While O_2 gives major signal to m/z 32, there is also the contribution from organics (CH_4O) 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.

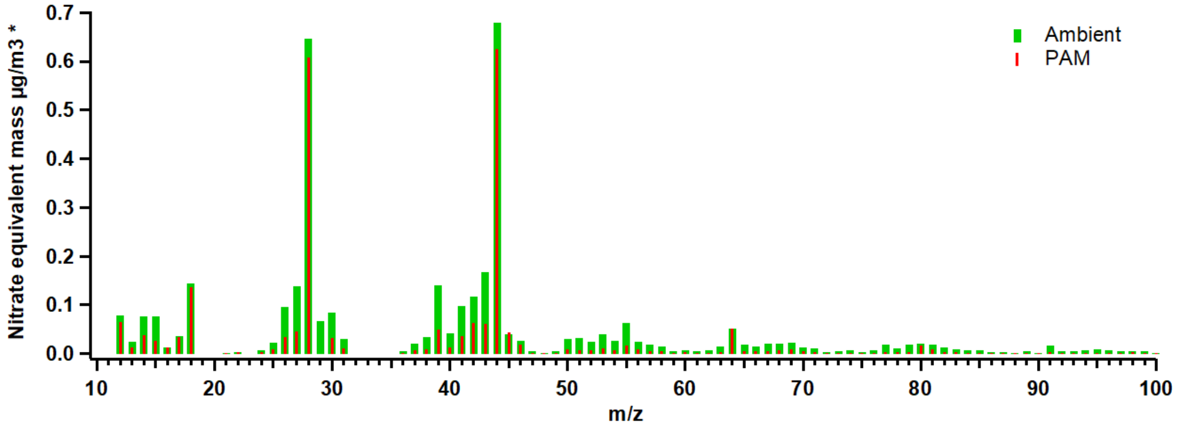
[Manuscript revision]

Figure 5 is replaced with a new one shown below.

Organic dominant



Sulfate dominant



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?

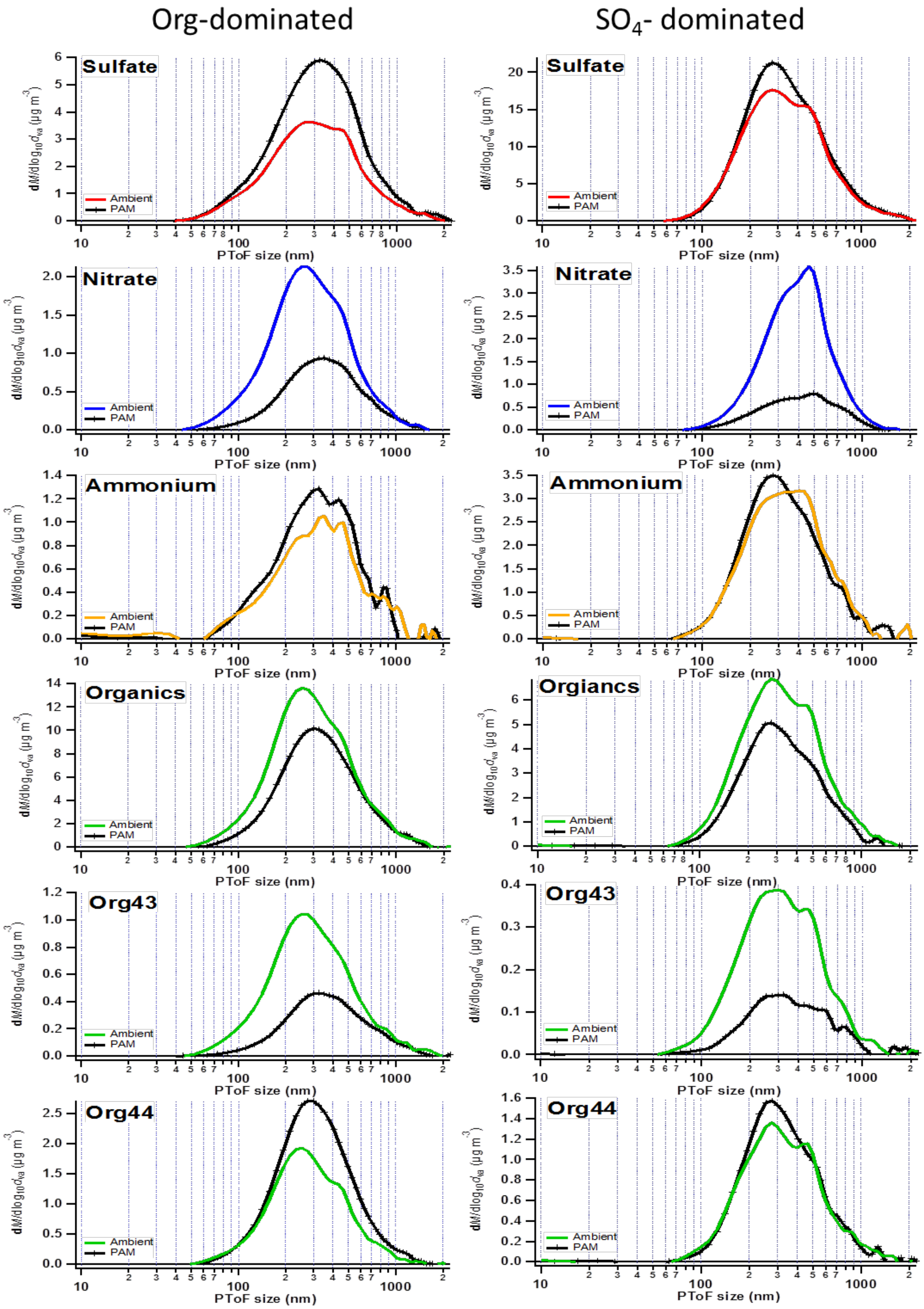
[Response]

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.



References

P. F. DeCarlo, J. G. Slowik, D. R. Worsnop, P. Davidovits, and J. L. Jimenez. Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory. Aerosol Science and Technology, 38:1185–1205, 2004.

A. M. Middlebrook, R. Bahreini, J. L. Jimenez, and M. R. Canagaratna. Evaluation of CompositionDependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Science and Technology, 46:258–271, 2012.

A.M. Ortega, P.L. Hayes, Z. Peng, B.B. Palm, W. Hu, D.A. Day, R. Li, M.J. Cubison, W.H. Brune, M. Graus, C. Warneke, J.B. Gilman, W.C. Kuster, J. de Gouw, and J.L. Jimenez. Real-time Measurements of Secondary Organic Aerosol Formation and Aging from Ambient Air in an Oxidation Flow Reactor in the Los Angeles Area. Atmospheric Chemistry and Physics, 16, 7411- 7433, 2016.

B.B. Palm, P. Campuzano-Jost, A.M. Ortega, D.A. Day, L. Kaser, W. Jud, T. Karl, A. Hansel, J.F. Hunter, E.S. Cross, J.H. Kroll, A. Turnipseed, Z. Peng, W.H. Brune, and J.L. Jimenez. In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor. Atmospheric Chemistry and Physics, 16, 2943-2970, 2016.

D. S. Tkacik, A. T. Lambe, S. Jathar, X. Li, A. A. Presto, Y. Zhao, D. R. Blake, S. Meinardi, J. T. Jayne, P. L. Croteau, and A. L. Robinson, Secondary organic aerosol formation from in-use motor vehicle emissions using a Potential Aerosol Mass reactor. Environmental Science and Technology, 48, 11235-11242, 2014.

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.

Middlebrook, A.M., R. Bahreini, J.L. Jimenez, and M.R. Canagaratna. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass

Spectrometer using Field Data. Aerosol Sci. Technol., 46, 258–271, 2012.

Choi J., Kim, J., Lee, T., Choi, Y., Park, T., Oh, J., Park, J., Ahn, J., Jeon, H., Koo, Y., Kim, S., Hong, Y., and Hong, J.: A Study on Chemical Characteristics of Aerosol Composition at West Inflow Regions in the Korean Peninsula I. Characteristics of PM Concentration and Chemical Components, J.KOSAE., 32(5), 469-484, 2016

Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutiérrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, doi:10.5194/acp-16-7411-2016, 2016.

Zhang, J., Wang, Y., Huang, X., Liu, Z., Ji, D., Sun, Y.: "Characterization of organic aerosols in Beijing using an aerodyne high-resolution aerosol mass spectrometer", Adv. Atmos. Sci., 32(6), 877-888, 2015.

Author’s Response to Reviewer 2

Reviewer 2 comments

This paper describes measurements of ambient aerosol and resulting aerosol after photochemical processing of ambient air with a PAM reactor on an island in the Yellow Sea. Measurements were made using an SMPS and high-resolution AMS. Only a 1-week period is shown. Two 1-day periods are compared in more detail, which show large differences in OA/sulfate ratios and air mass origin (SE China vs the Korean Peninsula). Bulk composition, chemically-resolved size distributions, two AMS fragment tracers (m/z 43, m/z 44), and organic elemental ratios were compared between the two periods and between PAM-processed and unperturbed ambient air. Generally, sulfate tended to increase in the PAM, while nitrate and OA decreased. With PAM aging, O/C increased, m/z 43 decreased, and m/z 44 was relatively unchanged. The authors conclude that SO2 and sulfate production play a key role in controlling secondary aerosol formation and CCN in East Asia based on this analysis. This paper is one of just a few that have explored the transformation of ambient aerosols (and ambient aerosol precursors that may form new aerosols) upon exposure to OH in near real-time with a fast flow reactor. The topic is relevant to current atmospheric chemistry research and ACP is a good fit for it. However, the analyses in the paper completely ignore important aspects of the chemistry and physics going on in the reactor, which have been discussed in the published literature over the past several years. Analysis critical to the credibility of the results, such as a comparison of the amount of sulfate produced in the reactor vs. that predicted by a simple kinetic model, are completely missing.

The conclusions of the study about dominance of sulfate formation in this region are biased due to the consistently high photochemical aging used in this study, which is known to suppress OA formation from several published studies, which is not appropriately discussed or even mentioned in the abstract and conclusions. The paper may be eventually acceptable into ACP, but only after a thorough revision that addresses the major problems below.

[Response]

The result of this study emphasizes the role of sulfate in northeast Asia in high summer

(August), when sulfur emission is at its minimum level. It was not stated in the text but ammonia was thought to play a critical role in stabilizing sulfate aerosol because its concentrations are high in the study region during summer. As seen in Figure 6, ammonium loss was not considerable for both episodes. The lost in sulfate dominated episode is likely to be coupled with nitrate loss. Therefore, the main conclusion of this study does not necessarily underestimate the importance of organic aerosol. It is also stated in the conclusion that organic aerosols are relatively more important near source region. To avoid misunderstanding, however, the following sentence was added to the conclusion P17 L423. "Note that caution needs to be exerted when interpreting the results of the present study, considering that only one OH exposure was used in the PAM reactor, and so that maximum organic SOA mass may not have been observed."

The manuscript was thoroughly revised, including re-calculation of OH exposure, wall loss, and AMS collection efficiency as suggested by reviewers. The point-by-point response to each of the comments is given below.

[Manuscript revision]

- Page 17, Line 423. The following sentence was added. Note that caution needs to be exerted when interpreting the results of the present study, considering that only one OH exposure was used in the PAM reactor, and so that maximum organic SOA mass may not have been observed."

Major Problems

(1) Line 81 states: "...the PAM reactor is not vulnerable to wall losses...". Neither a citation nor experimental results (when the lights were turned off) are given for this statement. This statement is contradictory to results published in Palm et al. (2016) for both gas and particle losses to the walls. While particle losses are often of the order of a few percent of the mass and can more easily be corrected for, losses of low-volatility vapors to the walls and outlet (due to the limited residence time in the reactor) can be very important. This is especially true for the low residence time used in this study (100 s, L293). For example Figure 5 of Palm et al. (2016) shows that between 25-80% of the condensable gases did not condense onto particles in their experiment, due to losses to the reactor walls or lack of sufficient time in the reactor. Note that this model was validated using

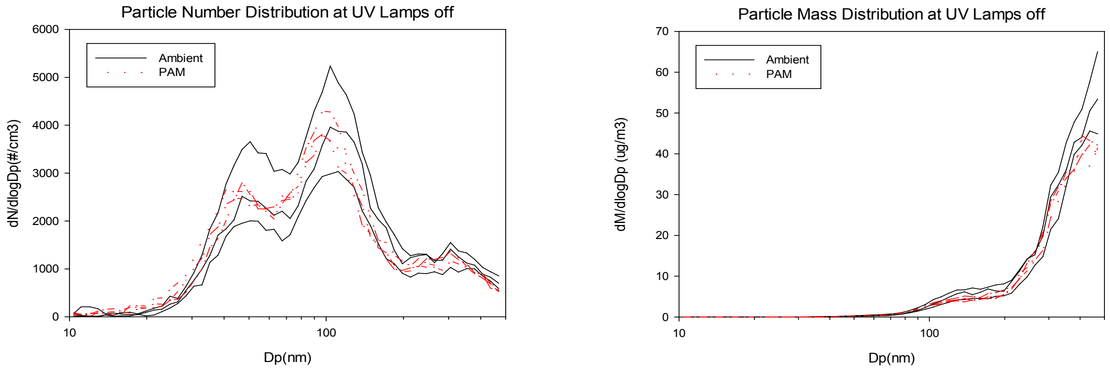
sulfate formation from ambient SO 2 (see Fig. 6 of the same study). This effect depends on reactor residence time and aerosol surface area. Residence time is shorter in this study while mass concentration (as a surrogate of surface area) varies and is at times lower and at times higher than in Palm et al. One would expect fractional losses of the 1 same order of magnitude, i.e. losses of the order of 50% of the condensable gases, given those differences. The method of Palm. et al. can be applied in this study, and in fact the computer program used in that peer-reviewed study has been made available publicly at https://sites.google.com/site/pamwiki/hardware/estimation-equations . The correction will be highly variable in time depending on the aerosol concentration. These effects need to be discussed in the paper and the published correction method should be applied, or it should be demonstrated why that is not relevant to the present study.

[Response]
We conducted the loss test for 1) ambient aerosol and 2) SO_2 during the experiment in 2011. Its results are discussed below and the LVOCs fate is calculated using the method in Palm et al. (2016).

First, PAM reactor was run for ambient air without lamp-on and the SMPS signals of air entering and exiting the PAM reactor were compared to estimate the physical loss of aerosol to the wall. In experimental setup, ambient air entering the PAM reactor was introduced into SMPS alternately with air exiting the PAM reactor. For the test, this cycle was repeated three times.

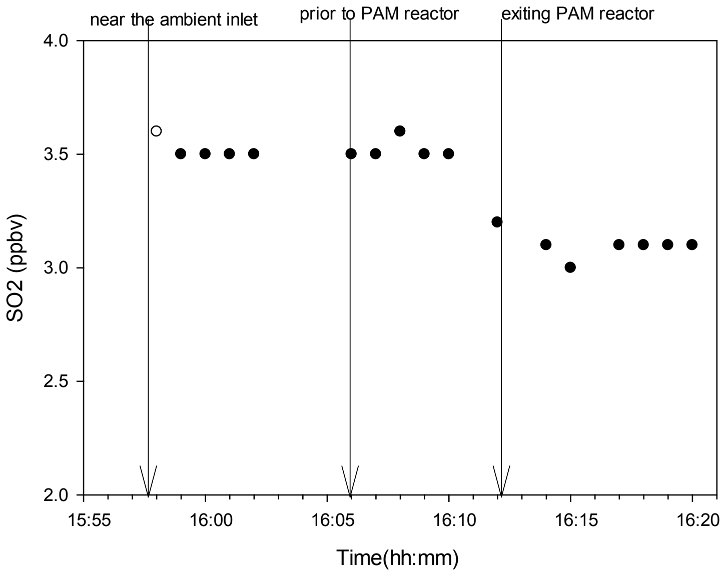
Because entering and exiting air was not simultaneously measured, there could be some error caused by the variation of ambient air. However, there was no detectable variation in ambient air, judged from gaseous concentrations for less than an hour of test period.

The mass of ambient aerosol and aerosol exiting the PAM reactor (without lamps on) was 13.1 ± 2.06 μg m^{-3} and 11.6 ± 0.46 μg m^{-3}, respectively, resulting in about 12 % of aerosol mass in the PAM reactor (Figure below). However, the decrease in mass was due to the loss of pre-existing aerosols but not newly formed secondary aerosols from condensable gases.



[Figure. SMPS particle number distribution (left) and mass distribution (right) for wall loss test. Red and black color indicate air exiting and entering the PAM reactor.]

Second, we have tested SO_2 loss by the wall during the experiment. For this test, we used ambient air instead of standard SO_2 mixtures in a wide range of concentrations. When air was pulled through the PAM reactor inlet plate, SO_2 was measured first for ambient air in front of the inlet, and then before it entered and after it exited the PAM reactor (Figure below). SO_2 concentrations prior to and after the PAM reactor were 3.5 ppbv and 3.1 ppbv, respectively, leading to SO_2 loss of 11 ± 7 %. There was loss in the sampling inlet line. The detailed information on SO_2 measurement is given below.



[Figure. SO_2 loss test results in PAM reactor]

In addition, we estimated the loss of condensable gases by wall deposition, exiting the reactor, and further OH reaction competing with condensation on existing particles, based on Palm et al. (2016) and model posted in https://sites.google.com/site/pamwiki/hardware/estimation-equations. Although the model calculating the possible loss of condensable gases was developed a couple of years after this experiment was performed, the physical setup of our PAM reactor was very similar to the ones used in Palm et al. (2016), Ortega et al. (2013), and (2016).

We used the same constants as those in Palm et al. (2016) for our PAM condition (residence time of 100 s and aging time of 4.6 days), which was estimated by the photochemistry model (corresponding response is given in the following question). In our experiment, 27~33% of condensable organic gases were not condensed while they passed through the PAM reactor. In addition, 1~3% and 6~7% of organic gases were lost by exiting the reactor and walls, respectively. In total, 57~66% of condensable organic gases were estimated to be condensed on existing particles, contributing to mass increase in PAM reactor. It is similar to the case of high condensation sink (CS) shown in figure 5 of Palm et al. (2016). In our study, the calculated CS is in the range of 0.021~0.028 and more than half of organic gases were condensed on the existing aerosols at 4.6 days of aging. The fraction of low-volatility gases that were not condensed in the PAM reactor was higher for organic-dominated case (33%) than sulfate-dominated case (27%) because of greater CS in latter than former.

For conversion of SO_2 to sulfate, the fraction of additional OH reaction-induced loss was set to 0 because of no more reactions between SO_2 and OH as described in Palm et al. (2016). The estimated fraction of sulfate condensation on existing particles was in the range of 62~81% and the rest were expected to be lost by walls and exit the reactor without being condensed.

[Manuscript revision]

- Page 4 Line 80. Modified: " --- for the equivalent of a week or more."
- Page 4 Line 81. Modified: In particular, the PAM reactor has less wall loss mainly due to much shorter residence time compared to conventional chambers.
- Page 5 Line 106. Added these sentences: The ambient air was introduced into the PAM reactor through an inlet plate and endcap. During the experiment, the loss associated with PAM reactor and inlet was determined. The SO_2 loss through a cyclone and inlet plate was 11±7% and aerosol loss in the PAM reactor was about 12 %. The aerosol loss

was measured as difference in mass concentration between ambient air and air pulled through PAM reactor with UV lights off.

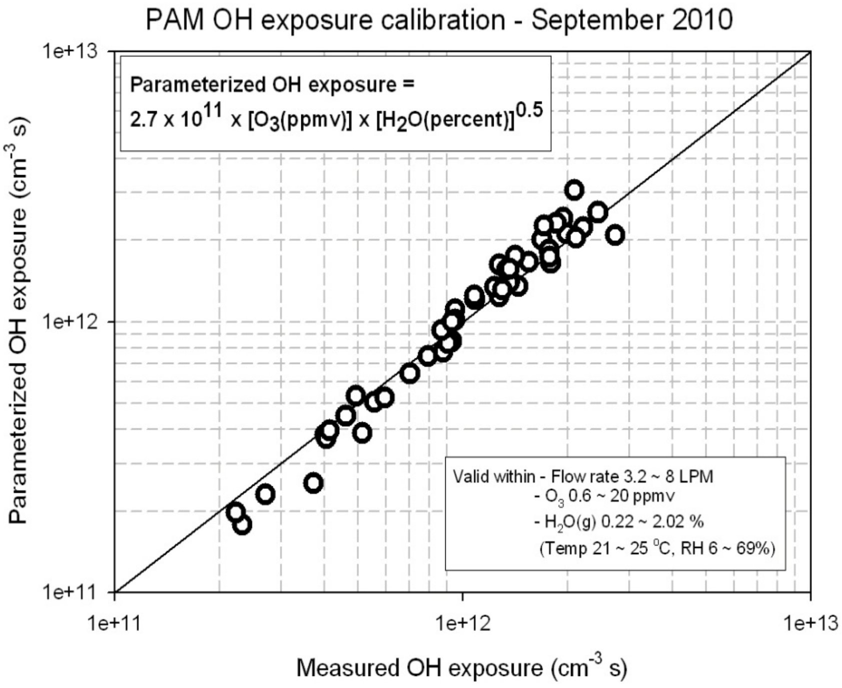
•Page 7 Line 159. Added the following paragraph: The measurement result of PAM experiment include uncertainty associated with losses of condensable gases and aerosols in PAM reactor and sampling system. The condensable gases fate model for PAM reactors (Palm et al., 2016) predicts 57~66% and 62~81% of organic gases and sulfates to be condensed on the existing aerosols, respectively at 4.6 days of equivalent aging time. We used the constants same as those in Palm et al. (2016) for our PAM condition (residence time of 100 s and aging time of 4.6 days). The fraction of low-volatility gases that were not condensed in the PAM reactor was higher for organic-dominated case (33%) than sulfate-dominated case (27%) because of greater CS in latter than former. Previous studies showed that the SOA formation from VOCs including Semi/Intermediate Volatile Compounds (S/IVOCs) could be enhanced up to a few times greater than SOAs from VOCs only (Hayes et al., 2015; Palm et al., 2016). In our experiment set up, about 1-day aged air masses transported from the Korean Peninsula or from east China were sampled in the PAM reactor, thus it is likely that S/IVOCs were already partitioned into the aerosol phase, if existed and the loss of S/IVOCs or their contribution to SOA formation would be much less significant than it was reported in previous studies. Nonetheless, S/IVOCs could be lost to the reactor inlet plate as well as reactor wall due to their low saturation vapor pressures, leading to the underestimation of their contribution to SOA formation in the PAM reactor of this study.

(2) Line 119-122: More details are needed describing the OH exposure calculation. Was it done offline or online while sampling ambient air? What SO2, water vapor, and light level ranges were used, and how do they compare to the ambient levels? The figures that document the calibration of the OH exposure for this experiment should be shown in Supp. Info. Were ambient water vapor, output O3, or the decay of any OH-reacting gases measured during the field study? If the calibrations were done offline, consideration for the important effects of changes in water vapor concentrations and for OH suppression from ambient VOC and other OH-reactive gases should be discussed and accounted for. It has been shown in the literature that such effects can be large and that just using offline calibration without accounting for variations of ambient water vapor concentration and OH reactivity can lead to substantial errors in OH exposure (Li et al., 2015; Peng et al., 2015; 2016). Estimation equations for OH exposure have been published in those peer-

reviewed papers and made available in easily-usable form at the PAM Wiki web site (same link given above). The authors need to document their OH exposure in more detail and make use of the tools available, or state why those methods are not applicable to the present study.

[Response]

We used the OH exposure calibration which was done with a mixture of pure air and SO_2(g) in the laboratory by Kang et al. (2011a), which is shown below. In this OH exposure calibration, the possible OH suppression by ambient OH-reactive gases is not taken into consideration. Thus, the effective OH exposure was calculated by applying the external OH reactivity by VOCs (30 s^{-1}). With measured ozone of 1.5 ppm and water vapor of 1.5%, the OH exposure was decreased by about 25%, resulting in 4.6 days of aging time. Therefore, we revised the manuscript with effective aging time of 4.6 days. Details of effective OH exposure calibration are given in supplementary information.



The model used to estimate the OH exposure depression due to OH reactivity is essentially identical to the one used by the University of Colorado group (Li et al., 2015; Peng et al., 2016). We adjusted the photolysis to match the oxidant conditions observed in the chamber and then ran the model with and without the 30 s^{-1} external OH reactivity, which is about the maximum measured at towers in environments similar to this site.

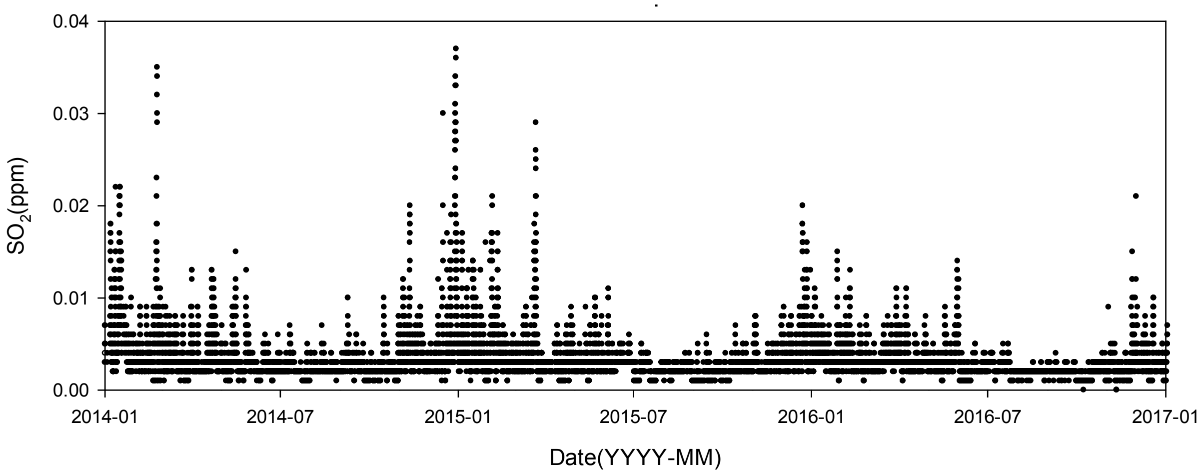
[Manuscript Revision]

- Page 2, Line 24. 4.6 days.
- Page5, Lines 113-122. Rewritten: 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 O_3, 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., 2011a), giving 7 x 10^{11} 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 10^6 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 how the air masses reaching Baegnyeong Island were further oxidized during the effective aging time of 4.6 days, which is consistent with transport time from China but slightly longer than typical maximum SOA production from aging (Ortega et al., 2016) under OH diel-mean of 1.5 x 10^6 molecules cm^{-3}.

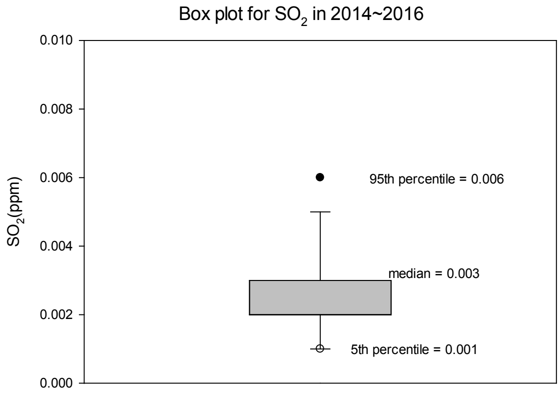
(3) ***A very important comment.*** *Related to major problem #2, calculations comparing the measured SO4 increase to that predicted based on OH exp and ambient SO2 concentrations (both of which are given in the paper) are critical to evaluate whether the OH exp estimates and the losses of condensable vapors are reasonably accurate. For example see Fig. 6 in Palm et al. (2016) for a similar analysis. These calculations are easy to do and very important to understand the quality and uncertainties of the measurements, so there is no excuse for not including them in the paper.*

[Response]

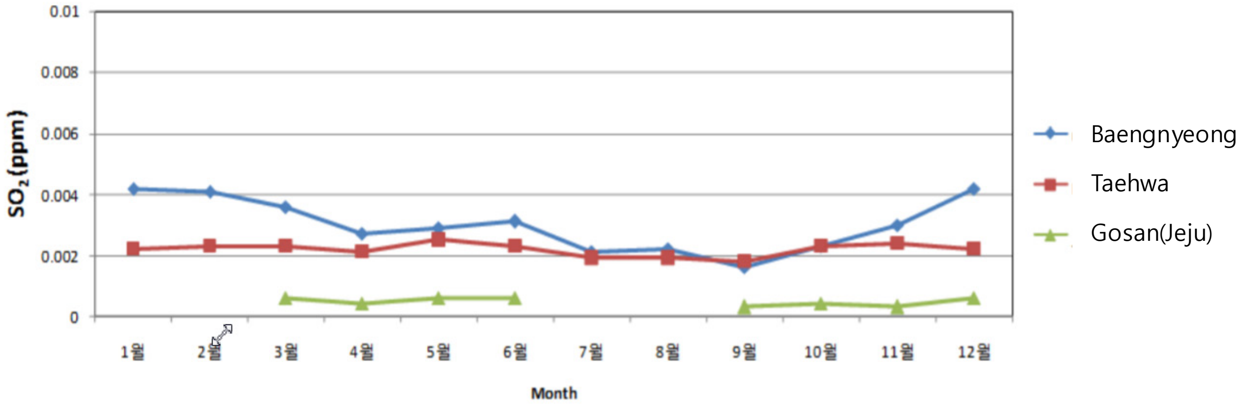
In Korea, SO_2 concentration is reported as hourly average in ppm unit. Baengnyeong measurement data are available from 2012 (1 ppb unit) and recently released for the three years of 2014, 2015, and 2016 (0.1 ppb unit) through the website (www.airkorea.or.kr). Now, all air quality measurement data are released to the public through website. The SO_2 variation for the three years is presented below. The nominal detection limit of SO_2 measurement is 1 ppb, which corresponds to the 5th percentile for the three years. The time series plot shows clear seasonal variation with high and low concentrations during cold and warm season, respectively. In all Korean sites, SO_2 concentrations are at its minimum levels during wet summer from July to September.



[Figure. SO_2 concentrations at Baengnyeong Island during 2014~2016. Source: www.airkorea.or.kr]

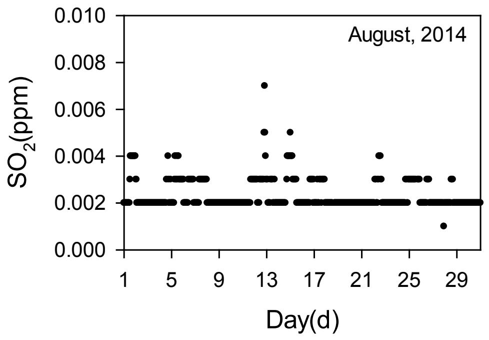


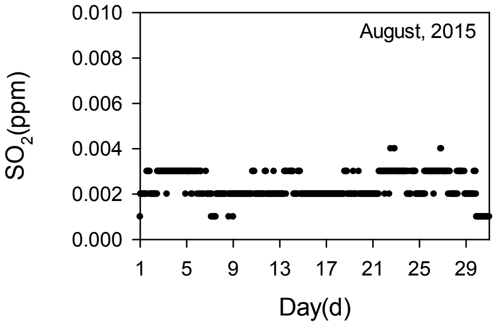
[Figure. Box plot for SO2 measurement during 2014-2016]

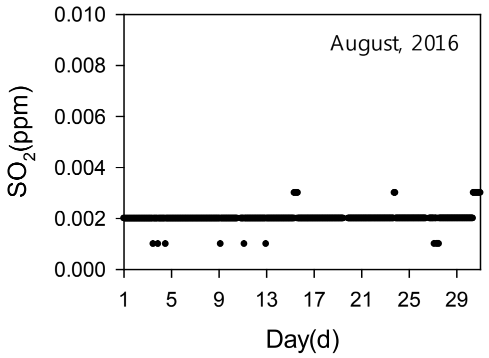


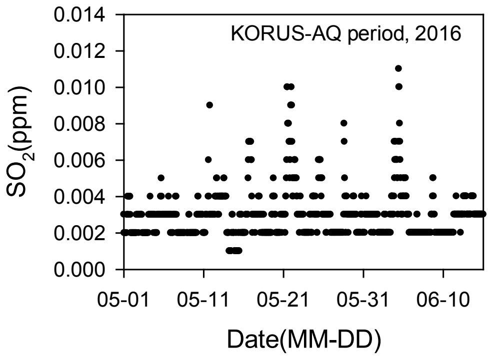
[Figure. SO_2 monthly averaged concentrations at three background sites of Korea in 2015. Blues for Baengnyeong Island. source: NIER Annual Report for Atmospheric Environment in 2015. GP-2016-122]

For the experiment period in 2011, the SO_2 remained unchanged around 3 ppbv. When a strong typhoon passed through the Yellow Sea, it rained all day and the daily precipitation was up to 30 mm on August 8, during which the minimum SO_2 concentration was 2.5 ppbv. When it rained, SO_2 concentration used to get down below detection limit. In monthly variation of the three background sites, the SO_2 concentrations are similar at Baengnyeong and Taehwa (in the East Sea) sites with ~ 2 ppb minimum during July ~ August. For Baengnyeong site, SO_2 concentrations are shown for every August from 2014 to 2016 and during the KORUS campaign (May-June 2016) below. Concentrations varied in a narrow range and it rarely went down below 2 ppbv.







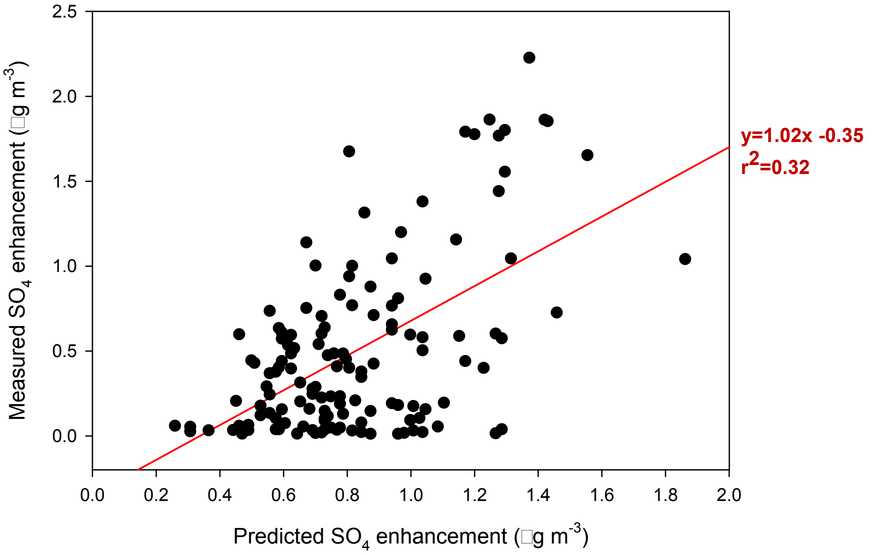


When we conducted the PAM experiment at Baengnyeong Island, we were able to have access to measurement data, but the whole data were given several months after getting a permission from government. Unfortunately, we were not able to get detailed information on calibration. SO_2 measurements have reported with 1 ppb digit until a couple of months ago. Considering all factors mentioned above, it is quite likely that the calibration offset is around 2 ppbv at Baengnyeong site.

We calculated the predicted sulfate formation with measured SO_2 concentrations, assuming that all SO_2(g) was converted to sulfate(p) by reaction with OH inside the PAM reactor. For this estimation, we adopted 2 ppbv offset for ambient SO_2 measurement, SO_2 gas loss of 11 % in the PAM reactor, and condensable sulfate loss by wall and exiting the reactor of 38%. The measured SO_4 enhancement was obtained by the SO_4 concentration in PAM reactor subtracted by the SO_4 concentration measured in ambient air. For this comparison, AMS measurements were hourly averaged in accordance with SO_2 measurement. The figure below compares the measured and predicted SO_4 enhancement, showing that the measured explained well the expected (slope = 1.02 and r= 0.57 (r^2 = 0.32).

The correlation between the two was deteriorated by the very low measured SO_4 enhancement against a wide range of sulfate expected to be enhanced. It is mainly because the comparison was made for hourly averaged concentrations of AMS even thought measurement was alternately made every 6 minutes between the ambient and PAM air. Not to mention, uncertainty was involved in the measurement of SO_2 concentration, loss assessment of SO_2 and condensable sulfate, and the AMS measurement of particles smaller than 50 nm.

We modified the manuscript and provide the following figure as supplementary information.



[Figure. Measured SO_4 enhancement vs. predicted SO_4 enhancement. The negative values of measured SO_4 enhancement were excluded.]

[Manuscript revision]

- We added the figure above and relevant explanations to the supplements as follows.

S 1. Comparison between predicted and measured sulfate formation in PAM reactor

We calculated the predicted sulfate formation with measured SO_2 concentrations, assuming that all SO_2(g) was converted to sulfate(p) by reaction with OH inside the PAM reactor. For this estimation, we adopted 2 ppbv offset for ambient SO_2 measurement, SO_2 gas loss of 11 % in the PAM reactor, and condensable sulfate loss by wall and exiting the reactor of 38%. The measured SO_4 enhancement was obtained by the SO_4 concentration in PAM reactor subtracted by the SO_4 concentration measured in ambient air. For this comparison, AMS measurements were hourly averaged in accordance with SO_2 measurement. The figure below compares the measured and predicted SO_4 enhancement, showing that the measured explained well the expected (slope = 1.02 and r= 0.57 (r^2 = 0.32).

The correlation between the two was deteriorated by the very low measured SO_4 enhancement against a wide range of sulfate expected to be enhanced. It is mainly because the comparison was made for hourly averaged concentrations of AMS even thought measurement was alternately made every 6 minutes between the ambient and PAM air. Not to mention, uncertainty was involved in the measurement of SO_2 concentration, loss assessment of SO_2 and condensable sulfate, and the AMS measurement of particles smaller than 50 nm.

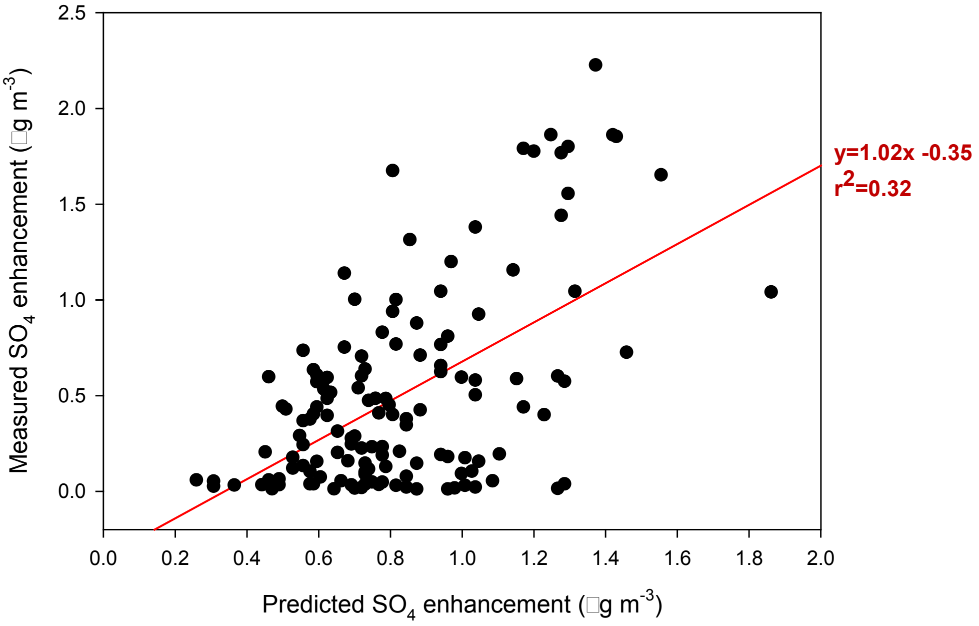


Figure S1. Measured SO_4 enhancement vs. predicted SO_4 enhancement. The negative values of measured SO_4 enhancement were excluded.

(4) Why were the lights constantly ran at 5 days worth of oxidation and not cycled between different times? Prior studies (e.g., Kang et al., 2011; Lambe et al., 2012; Chen et al., 2013; Ortega et al., 2016; Palm et al., 2016) have shown that the OA enhancement is maximized at OH exp lower than 5 equivalent days. In particular, the conclusion that SO 2 is the key for increasing East Asian aerosol mass may be biased by this experimental limitation. OA may be just as important, but that was not observed in this study because the OH exp was constant and too high.

[Response]

Our PAM experiment was done at Baengnyeong Island in 2011 as the first field measurement coupled with the AMS 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 3-4 days of ambient aging. As you recommended, it would be better if PAM reactor would have been operated at lower 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 lower and various OH exposure levels to observe the progress of SOA formation, growth and fragmentation in northeast Asian region.

[Manuscript revision]

Page 5, line 121: In the present study, therefore, we examined how the air masses reaching Baegnyeong Island were further oxidized during the effective aging time of 4.6 days, which is consistent with transport time from China but slightly longer than typical maximum SOA production from aging (Ortega et al., 2016) under OH diel-mean of 1.5 x 10^6 molecules cm^{-3}.

(5) Line 126 indicates that the tubing and endcap were removed from the PAM for these measurements. However, Line 101 indicates that air was sampled through a PM 1 cyclone for both ambient and PAM measurements. These statements are contradictory, given that the tubing and endcap would be needed to connect the PAM to a cyclone. Please clarify.

[Response]

We sampled ambient air through a PM1.0 cyclone and flowed through the PAM reactor every 6 minutes before being measured by SMPS and AMS. As you pointed out, we clarified it and provided information on SO_2 gas loss by the inlet plate in the revised manuscript as follows.

[Manuscript revision]

- Page 5, Line 103: For another 6 minutes, the sampled ambient air was directly pumped into the analytical instruments, bypassing the PAM reactor.
- Page 5, Line 106: The ambient air was introduced into the PAM reactor through an inlet plate and endcap. During the experiment, the loss associated with PAM reactor and inlet was determined. The SO_2 loss through a cyclone and inlet plate was 11±7% and aerosol loss in the PAM reactor was about 12 %. The aerosol loss was measured as difference in mass concentration between ambient air and air pulled through PAM reactor with UV lights off.

(5b) If the ambient air was sampled through a PM 1 cyclone and the PAM air was not, then the ambient concentrations should be lower than when sampling through PAM, as the PM 1 cyclone will remove particles within the AMS size range. The time series in Fig. 2 would suggest that both lines sampled through a cyclone, and thus the statement that the PAM sampled without tubing and endcap is incorrect.

[Response]

Yes. We sampled both ambient and PAM air through PM1 cyclone. Please see the response for 5b above.

(5c) Quantitative comparison of results when sampling ambient air through the ambient inlet and through the PAM with the lights off (which seem to be have been done, given the statement in L233) need to be shown in order to support statements of no particle losses.

[Response]

As addressed in the response for major problem (1), we compared the ambient aerosol and aerosol exiting PAM reactor without lamps on to examine the physical loss of ambient aerosol by the PAM reactor wall. The detailed results of this test are described above. The aerosol mass of ambient air and exiting PAM reactor (without lamps on) was 13.1 ± 2.06 μg m^{-3} and 11.6 ± 0.46 μg m^{-3}, respectively, resulting in about 12% of the loss by the PAM reactor itself.

[Manuscript Revision]

Page 5, Line 103-106. Rewritten: For another 6 minutes, the sampled ambient air was directly pumped into the analytical instruments, bypassing the PAM reactor. The ambient and PAM aerosols were alternately measured every 6 minutes thereafter, producing pseudo-simultaneous measurements. The ambient air was introduced into the PAM reactor through an inlet plate and endcap. During the experiment, the loss associated with PAM reactor and inlet was determined. The SO_2 loss through a cyclone and inlet plate was experimentally tested, giving 11±7% of loss. Experimentally tested existing aerosol loss due to the PAM reactor inlet and through the PAM was about 12% by measuring aerosol mass concentration from ambient air and PAM reactor through air with the lights off.

(5d) Additionally, if the PAM was sampled through a cyclone and substantial inlet tubing length, loss of semi- and intermediate-volatility compounds may have been substantial and played a major role in suppressing SOA formation in the PAM. S/IVOC compounds have been implicated as potentially making larger contributions to SOA formation both in

the atmosphere and in OFRs than VOCs (e.g., Robinson et al., 2007; Palm et al. 2016). Such an effect would affect the apparent relative importance of sulfate vs OA formation, which is highlighted as a major conclusion in this study. Please include a discussion of potential biases from this effect if indeed the PAM sampled through an inlet.

[Response]
We tested the loss of SO_2 gas and existing aerosols through the inlet plate and estimated the possible loss of condensable organic gases through the wall, exiting the reactor and further OH reaction by model calculation. However, we were not able to measure semi- and intermediate-VOCs.

Previous study (Palm et al., 2016) demonstrated that the measured SOA formation was a factor of 4.4 greater than the predicted SOA formation from measured VOCs, which means the S/IVOCs significantly contributed SOA formation in PAM reactor at a highest SOA formation optimized aging time of 0.4~1.5 equivalent days (Palm et al., 2016; Hayes et al., 2015). As the saturation vapor pressures of S/IVOCs were lower than SO_2 or VOCs, the loss of S/IVOCs would result in underestimation of secondary organic formation in the PAM reactor.

In our experiment, the length of inlet tubing from PM1.0 cyclone to the PAM reactor was less than 30 cm and the air masses were sampled in the PAM reactor after being transported for at least 1-day from the Korean Peninsula or from east China. Therefore, it is likely that S/IVOCs were already partitioned into the aerosol phase, if existed and the loss of S/IVOCs or their contribution to SOA formation would be much less significant than it was reported in previous studies. Due to the lack of VOCs and S/IVOCs measurements in this study, however, we added the statement on the potential underestimation of their contribution to SOA formation in revised manuscript.

[Manuscript Revision]
- Page 6 Line 159: The measurement results of PAM experiment include uncertainty associated with losses of condensable gases and aerosols in PAM reactor and sampling system. The condensable gases fate model for PAM reactors (Palm et al., 2016) predicts 57~66% and 62~81% of organic gases and sulfates to be condensed on the existing aerosols, respectively at 4.6 days of equivalent aging time. We used the constants same

as those in Palm et al. (2016) for our PAM condition (residence time of 100 s and aging time of 4.6 days). The fraction of low-volatility gases that were not condensed in the PAM reactor was higher for organic-dominated case (33%) than sulfate-dominated case (27%) because of greater CS in latter than former. Previous studies showed that the SOA formation from VOCs including Semi/Intermediate Volatile Compounds (S/IVOCs) could be enhanced up to a few times greater than SOAs from VOCs only (Hayes et al., 2015; Palm et al., 2016). In our experiment set up, about 1-day aged air masses transported from the Korean Peninsula or from east China were sampled in the PAM reactor, thus it is likely that S/IVOCs were already partitioned into the aerosol phase, if existed and the loss of S/IVOCs or their contribution to SOA formation would be much less significant than it was reported in previous studies. Nonetheless, S/IVOCs could be lost to the reactor inlet plate as well as reactor wall due to their low saturation vapor pressures, leading to the underestimation of their contribution to SOA formation in the PAM reactor of this study.

(6) Was the PAM housed outside or in a building or trailer where the temperature was different from ambient temperature? A presentation at the recent PAM User's Meeting (http://tinyurl.com/z2pags4 , slide #28) showed if there is a temperature differential between the ambient temperature and the PAM temperature, nitrate and organic mass is lost through evaporation and can lead to a similar increase in m/z 44 and decrease in m/z 43 for organics. This is not surprising given the literature on the volatility of these species. The location and temperature of the PAM, relative to ambient temperature, must be documented in the paper. If the PAM was housed in a building, please show the difference between the ambient and PAM temperature throughout the campaign. The large decreases in nitrate in the PAM seem to suggest that this may be an important factor; however with the current information provided, it is impossible to assess this.

[Response]

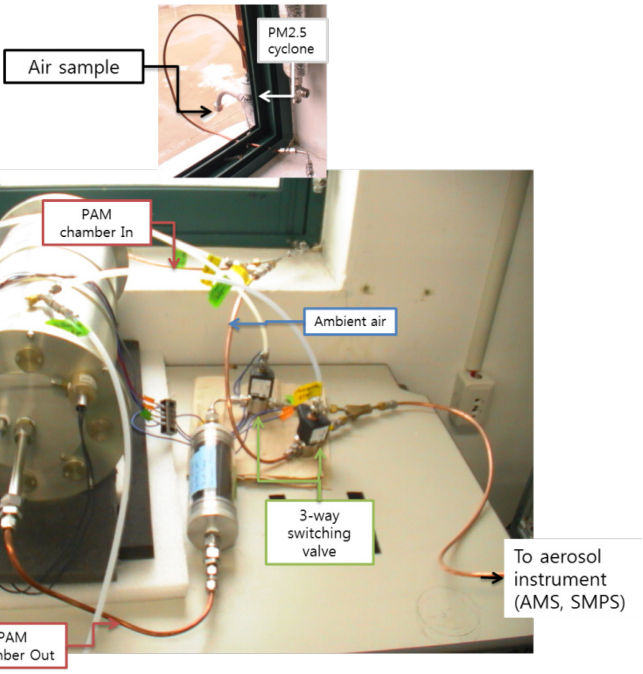
In our experimental setup, the PAM reactor was installed beside the window in the laboratory and ambient air was pulled through a Teflon tubing (~ 30 cm) from PM1.0 cyclone outside the laboratory. In the PAM reactor, the two UV lamps were housed in Teflon tubing being purged by nitrogen gas. In the previous 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 ℃ 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.

In addition, the average ambient temperature was 26 °C and 20 °C in the organics and sulfate dominated episode, respectively. The laboratory was set to 20°C with air conditioning. If measurement is made in summer, condensation is of more concern than evaporation. Nitrate was lost in PAM reactor during both sulfate dominated (75%) and organic dominated (56%) episode under similar levels of SO_2 and NO_2. Thus, the loss of nitrate was primarily associated with the buildup of sulfate in the PAM reactor.

[Manuscript revision]

- Page 5 Line 114. "… 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 O_3 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 ℃ inside the PAM reactor and its effect on evaporation of OA or nitrate was insignificant.



[Figure: The sampling setup of PAM reactor]

(7) Was a comparison between the SMPS and AMS done, both for ambient concentrations and for the enhancements observed in the PAM reactor, similar to Palm et al. (2016) or Ortega et al. (2016), to ensure the story is consistent between the two instruments about the loss of mass at different sizes?

[Response]

The result of this study was similar in the formation of particles at nuclei mode smaller than the AMS-detection-size to that of Ortega et al. (2016) and Palm et al. (2016). Palm et al. (2016) stated that the possible sources of nuclei mode particles would be SO_2 and VOCs, especially Extremely Low Volatile Organic Carbons (ELVOCs). Palm et al. (2016) measured SOA enhancement in accumulation mode when the equivalent aging time was less than 1 day or when the condensation sink (CS) was small at accumulation mode of ambient aerosol. However, Ortega et al. (2016) did not observe the shift of accumulation mode regardless of equivalent ages. Thus, the accumulation mode enhancement or depletion was likely affected by preexisting aerosols and precursor sources as well as equivalent ages. Under about 4.6 days of equivalent ages and high CS of ambient aerosol, we observed the particles enhanced at both nuclei and accumulation mode. In contrast, the particle loss was observed at 60~200 nm in this study but not reported in other studies, which was due to the loss of organics and nitrate surpassing the enhancement of sulfate in that size range.

[Manuscript Revision]

•Page 6 Line 151. Modified: " … increased at sizes larger than 200 nm diameter were either lost or produced in the PAM reactor, …"

• Page 6 Line 153. The formation of nuclei mode particles in PAM reactor were also observed in previous studies (Ortega et al., 2016; Palm et al., 2016). The enhancement of accumulation mode particles was dependent on the equivalent ages in PAM reactor and condensation sink (CS) of preexisting aerosols.

(8) The collection efficiency (CE) used to correct AMS measurements for the effect of particle bounce is not discussed at all. Was the method of Middlebrook et al. (2012) used? Importantly, the correction very likely varied between ambient and PAM-processed air, due to changes in 3 sulfate acidity. This is important for quantification of the AMS data and needs to be thoroughly discussed.

[Response]

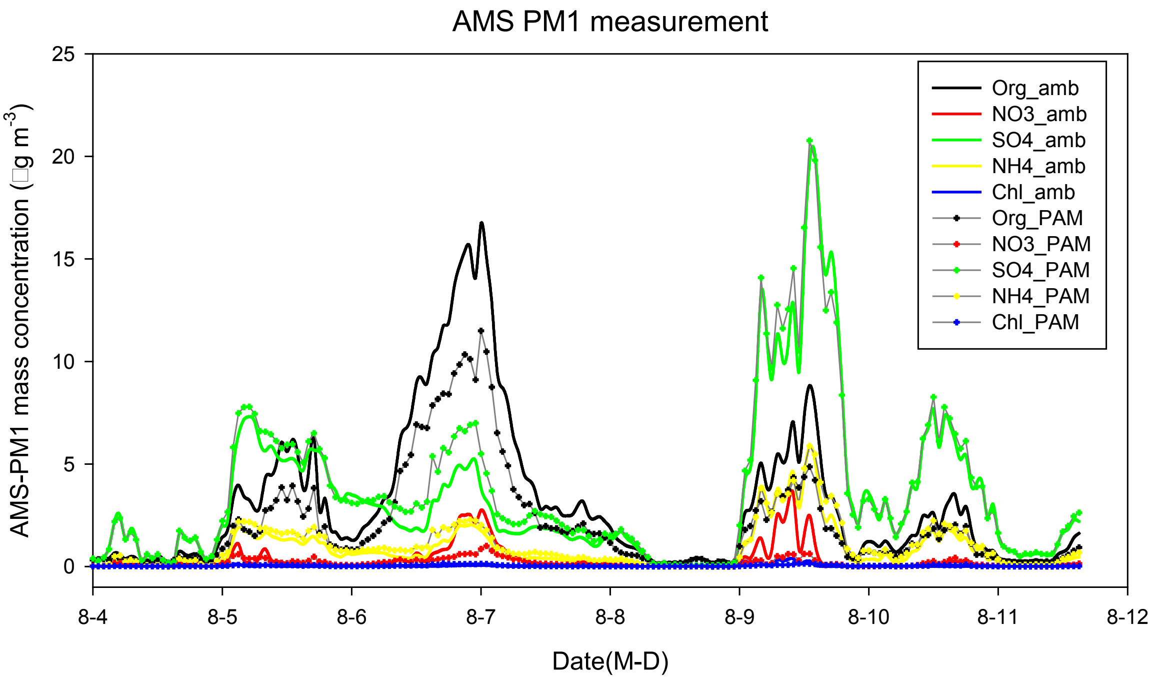
Composition dependent CE is especially important when the particles are acidic or contain large amount of nitrate and when the OH exposure of PAM reactor is very high (Middlebrook et al., 2012; Ortega et al., 2016). In this study, the OH exposure was about 7 x 10^{11} molecules cm^{-3} s, for which the CE comes close to 0.5 (Ortega et al., 2016). In addition, the equivalent ratio of ($[NH_4]/(2x[SO_4]+[NO_3])$) was 0.7~1.2 for ambient and PAM aerosol, respectively. According to Middlebrook et al. (2012), the CE would fall into the range of 0.45~0.5 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 0.01~0.22 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.

[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).

Figure 2(b):



(9) In Section 4.2, the differences in the OA chemistry between SV-OOAs and LV-OOAs are described. How were these two classes of OA determined? In this manuscript, it appears that the mass measured at m/z 43 and m/z 44 are interpreted as being analogous to SV-OOA and LV-OOA, which is not an accurate conclusion. Is there a reason that PMF analysis was not conducted on the ambient and/or PAM results? Evidence for the distinction between these two classes needs to be given, or the conclusions regarding these classes (e.g., line 215-216 on the size dependence of the two classes) should be withdrawn. Also, why do the authors use unit-mass resolution tracers when high-resolution AMS measurements were collected?

Additionally, in this section, the apparent connection being made between mass loss in the 100-200 nm range with higher SV-OOA concentrations and their oxidation in the PAM is not clear. In fact, in this section the point is made that SV-OOA may be oxidized to lower volatility products (which would add mass not subtract it).

[Response]

In this study, the single mass fragment 43 and 44 were used because their size distributions were available from unit mass data produced by HR-ToF-AMS, as shown in Figure 6. We want to see the volatility of OOA with m/z 43 and 44 simply based on Ng et al., (2011) instead of the more complicated PMF analysis for SV-OOA and LV-OOA. The terms of SV-OOA and LV-OOA were introduced to interpret particle loss at 100-200 nm size range in PAM reactor with reference to OA types described in Mohr et al., (2012). In PAM processed aerosols, the loss of 100~200 nm particles was associated with the enhancement of sulfate and decrease in organics and nitrate relative to those of ambient air. The amounts of organics decreased in that size range was greater than that of sulfate increased in PAM reactor during organic dominated episode. We modified the manuscript to avoid the confusion of SV-OOA and LV-OOA from PMF analysis.

[Manuscript Revision]

- Page 9, line 212. Rewritten: The SMPS mass size distributions highlight the size range of 100~200 nm, where PAM aerosol was reduced in mass only for organic-dominated episode (Fig. 5). Mohr et al. (2012) observed that the ambient Semi-Volatile Oxygenated Organic Aerosols (SV-OOAs) and Low-Volatile Oxygenated Organic Aerosols (LV-OOAs) were mostly found in the range of 100–200 nm and greater than 200 nm, respectively. In addition, the concentration of organic m/z 43 was higher in SV-OOAs than LV-OOAs. In the present study, the contribution of m/z 43 to total organics was greater in organics dominated episode than sulfate dominated episode. So was the loss of organics in PAM reactor. Volatility of organics with m/z 43 and 44 were previously described in Ng et al., (2011).
- Page 9 Line 223. Modified: "… including more less-oxidized OAs …"
- Page 16 Line 416-417. Modified: "… partitioning of less oxidized OAs into …", "As the concentration of mz/ 43 and total organics decreased upon …", "… fragmentation in gas phase, less oxidized OAs were evaporated away …"
- Page 17 Line 426. Modified: "… OAs were transformed from less oxidized OAs to further oxidized OAs, as …"

(10) Several interpretations and conclusions appear to be unjustified, highly-speculative, in some instances overly broad or exaggerated in the context of the evidence and discussions provided in this paper. In particular it cannot be concluded based on this study that sulfate is more important than OA as a secondary aerosol species in this

region, since the conditions used are biased against the formation of OA due to the use of a single and high OH exp, given the results of previous PAM ambient studies. Moreover, statements that broadly generalize the conclusions to NE Asia based on analysis of two 1-day case studies are inappropriate. The abstract and conclusions need to be thoroughly revised to report statements that are consistent with the evidence shown and the prior peer-reviewed literature.

[Response]

To interpret the PAM measurement results, we need to employ background knowledge that has been accumulated in the study region. The role of sulfate in secondary aerosol formation is emphasized in view of the fact that Asian outflow plumes used to be transported across the Pacific Ocean for about a week. As suggested, introduction, abstract, and conclusion were rewritten with more references added.

[Manuscript revision]

- Page 2 Line 24-36. Modified: Inside the PAM reactor, O_3 and OH levels were equivalent to approximately five days of integrated OH exposure at typical atmospheric conditions. During this period, two types of air masses were distinguished on the basis of the chemical composition and the degree of aging. Air from China contained was more aged with high levels of sulfate while air from the Korean Peninsula was less aged with more organics than sulfate. For air aged in the PAM reactor, sulfate was constantly formed, resulting in the increase of particle mass for particles with diameters between 200–400 nm, while particle mass was lost in the organic component for particles with diameters between 100-200 nm. This loss was especially evident for the m/z 43 component representing semi-volatile organics. Conversely, the fraction the m/z 44 component corresponding to low-volatile organics increased with a shift toward larger sizes during the organics-dominated episode. This oxidation of semi-volatile organics was likely facilitated by gas-phase oxidation and partitioning for re-equilibrium between the gas and particle phases, with heterogeneous oxidation occurring for more aged particles.
- Page 2 Line 43. Add a sentence: Note that 4.6 days of integrated OH exposure in this study emphasized the role of SO_2 on secondary aerosol because SOA formation were maximized near the source and further oxidation leading to the loss of OAs were favored at couple days of aging.
- Page 2 Line 44. “highlighting the potential role of secondary organic aerosol (SOA) …”

•Page 3 Line 59. Add a sentence: Recently, the aerosol chemical composition was directly measured for long-range transported air mass from eastern China, which exhibits the high contribution of sulfate to secondary aerosols and abundance of more oxidized OAs in Asian pollution plumes (Lee et al., 2015).
•Page 6 Line 141. Modified: Although the PAM aerosol masses were generally greater than the ambient aerosol masses, sometimes it was not. The difference in mass concentrations between the PAM aerosols and the ambient aerosols either a gain or loss of particle mass in the range of ~3–7 μg m^{-3}, indicating that photo-oxidation ----.
• Page 15 Line 384. Added a sentence: The formation yield of sulfate from SO_2 is greater than that of organic aerosols during 3~4 days of aging in the Asian pollution plume because of fast depletion of SOA precursors (Dunlea et al., 2009), which is consistent to our results.
• Page 17 Line 423. Added a sentence: Note that caution needs to be exerted when interpreting the results of the present study, considering the high photochemical aging in the PAM reactor.

(11) There are several published studies very similar to this one, in which ambient air was processed using a PAM reactor, with ambient air sampled by an HR-AMS, SMPS, and other instruments (for example Ortega et al., 2016; Palm et al., 2016; Hu et al., 2016; Palm et al., 2017). Those studies have discussed several effects and performed additional analyses that are very relevant to this study, and they should be cited and their results compared to the present study. This omission is particularly puzzling given that there are some shared coauthors between this paper and some of those papers. Specific examples are given above and below. Additional relevant literature is compiled at https://sites.google.com/site/pamwiki/publications.

[Response]
We cited and discussed the results from previous studies done with PAM reactors in revised manuscript. The revised part of the introduction is given below and those of discussion are given in responses of related questions.

[Manuscript revision]
• Page 4 Line 86, Add sentences: Recently, PAM reactor has been used to examine secondary aerosol formation and evolution from ambient air masses (Hu et al., 2016;

Ortega et al., 2016; Palm et al., 2016) and emission sources (Ortega et al., 2013; Link et al., 2017; Timonen et al., 2017). The wall losses of aerosols and condensable gases and photochemistry of the PAM reactors have been studied (Lamb et al., 2015; Palm et al., 2016; 2017; Peng et al., 2015; 2016) to more quantitatively understand the experimental results using PAM reactor.

Other significant comments

(12) What was the experimental setup? A figure showing the flow diagram for the AMS and SMPS for sampling PAM and ambient is needed, including flow rates, tubing lengths and inner diameters and materials, as well as residence times in all parts of the system, to allow the reader to fully interpret the measurements shown and to allow a full comparison with other studies in the literature. For example the losses of semivolatile and intermediate volatility 4 precursors of SOA will depend strongly on inlet materials and residence times, and whether the flow was laminar or turbulent.

[Response]

All details are added to the method section in revised manuscript.

[Manuscript revision]

- Page 5, Line 101 to page 6 line 129. Method section was thoroughly revised.

To study the secondary aerosol formation and evolution of pre-existing ambient aerosol under the photochemical oxidizing condition, we used a Potential Aerosol Mass (PAM) reactor. PAM reactor is a small flow-through aluminum cylinder equipped with Hg lamps to create a highly oxidizing environment. Detailed descriptions of the PAM reactors were given in previous publications (Kang et al., 2007; Kang et al., 2011b; Lambe et al. 2011; Ortega et al., 2016; Palm et al., 2016). The PAM reactor employed in this study is the same version as that described in Lambe et al. (2011), which was also used for laboratory studies of SOA aging (Lambe et al. 2012; 2015). In the present study, air was pulled through 1 cm diameter tubing into the enclosed reactor and rapidly dispersed before entering the chamber through a Silconert-coated (Silcotech, Inc.) stainless steel screen. All sampling tubes were made from copper or stainless steel to minimize the particle loss on the tubing walls. The residence time in the PAM reactor was obtained by the measured flow rate and the volume inside to 100 s.

Ambient air sampled using a PM1.0 cyclone was pulled through the PAM reactor for 6 minutes, during which time the ambient aerosols were oxidized (hereafter referred to as "PAM aerosols"). For another 6 minutes, the sampled ambient air was directly pumped into the analytical instruments, bypassing the PAM reactor. The ambient and PAM aerosols were alternately measured every 6 minutes thereafter, producing pseudo-simultaneous measurements. The ambient air was introduced into the PAM reactor through an inlet plate and endcap. The SO_2 loss through a cyclone and inlet plate was experimentally tested, giving 11±7% of loss. Experimentally tested existing aerosol loss due to the PAM reactor inlet and through the PAM was about 12% by measuring aerosol mass concentration from ambient air and PAM reactor through air with the lights off. The chemical composition of aerosol was measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, hereafter referred to as "AMS") and their number concentration was determined in the mobility diameter range of 10.4–469.8 nm with a scanning mobility particle sizer (SMPS 3034, TSI) (Jayne et al., 2000; Jimenez et al., 2003; DeCarlo et al., 2006; Drewnick et al., 2006). The aerosol mass concentration was obtained from the volume concentration multiplied by an assumed particle density of 1.2 g cm^{-3}. Detailed descriptions of the HR-ToF-AMS and the sampling site can be found elsewhere (Lee et al., 2015). For concentrations measured by AMS, composition dependent collection efficiency was applied by adopting the result of Middlebrook et al. (2012).

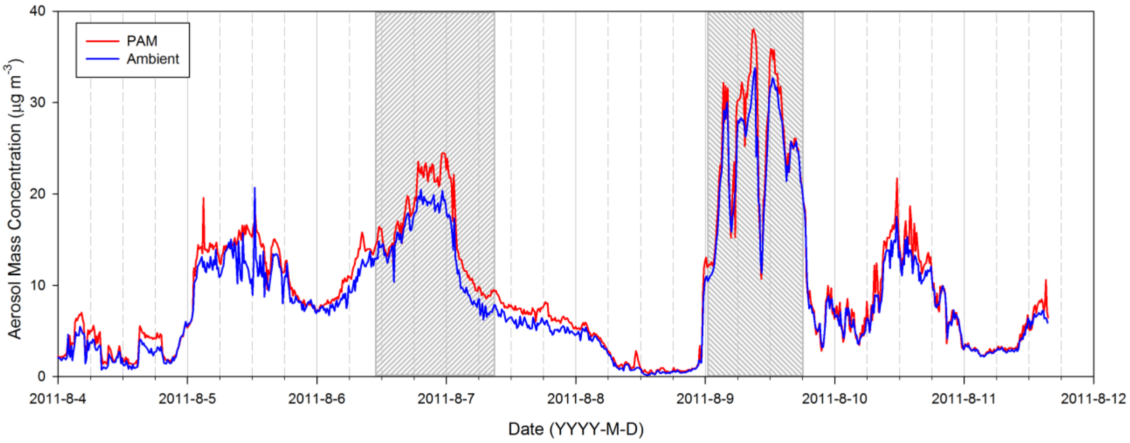
To produce large amounts of OH and O_3, creating a highly oxidizing environment, the PAM reactor is equipped with long Hg lamps (model no. 82-9304-03, BHK Inc., 185 nm and 254 nm emission. We obtained the OH exposure by calibrating the OH exposure against sulfur dioxide decay (Kang et al., 2011a) in a laboratory with a SO_2 mixture in pure air, giving 7 x 10^{11} molecules cm^{-3} s. The effective OH exposure in PAM reactor when ambient air is sampled is affected by VOCs and other OH-reactive gases (Peng et al., 2015; 2016). Thus, OH suppression from VOC and other OH-reactive gases in this study was estimated based on the oxidation chemistry model with 30 s^{-1} of external OH reactivity for maximum OH reactivity in rural areas, which is similar to comparable forested rural areas (Feiner et al., 2016; Lee et al., 2008; Peng et al., 2016; Yoshino et al., 2006). At a typical diel-mean concentration of $1.5x10^6$ molecules cm^{-3}(Mao et al., 2010), the effective aging time was equivalent to an integrated OH concentration over 4.6 days, which is a 25% decrease from OH exposure calculated from SO_2 decay, due to the external OH suppression. The effective aging time of 4.6 days is consistent with transport time from China but slightly longer than typical maximum SOA production from aging (Ortega et al., 2016) under OH diel-mean of 1.5 x 10^6 molecules cm^{-3}.

The Hg lamps were housed in Teflon sleeves being purged by nitrogen to prevent heat and O_3 from building up. The results of Ortega et al. (2016) using the same PAM reactor as that used in the present study, demonstrated that the increase in temperate by lamp irradiation was only 2 °C inside the PAM reactor and its effect on evaporation of OA or nitrate was insignificant.

(13) Fig. 2a does not allow seeing periods when PAM mass was less than ambient mass. A different format should be used that allows clearly seeing such periods.

[Response]
Figure 2a is re-plotted to clearly show the difference in SMPS mass between PAM-processed and ambient mass.

[Manuscript revision]
Figure 2a replaced.

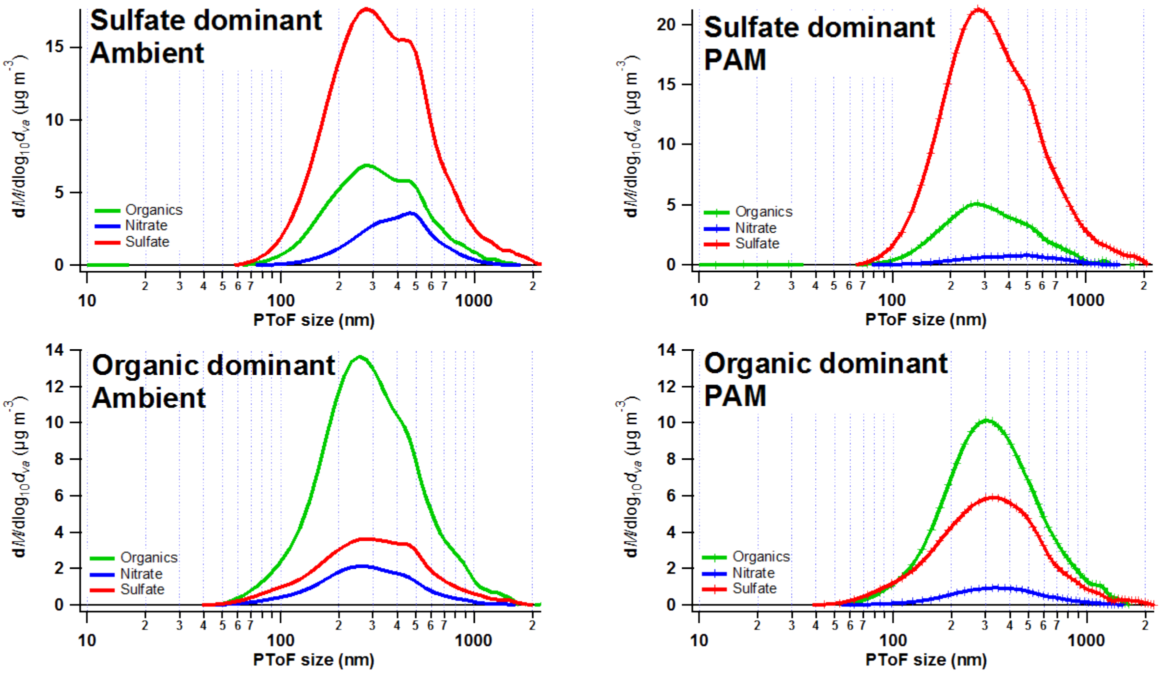


(14) Line 110-111. The reasoning for assuming a particle density of 1.2 is needed. This seems quite low considering that sometimes the aerosol is dominated by ammonium sulfate (with a density of 1.78, unnessarily introducing errors of nearly 50% in mass). The composition is also quite variable so a composition-dependant density would be more appropriate, and can be easily calculated with the information available. See for example:

http://tinyurl.com/FAQ-AMS-Data

[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.



[Figure. Size distribution of major aerosol species]

(15) Lines 155-158 and elsewhere: Statement: "In general, sulfate and ammonium concentrations were generally higher or lower in the PAM reactor compared to ambient air depending on the air masses" is not clear. It does not appear (Fig 2) that sulfate is ever lower for the PAM reactor measurements? Also, use of "general" twice makes this statement seem particularly vague. It is also not clear from this plot that nitrate is always less, it seems to be similar to ambient nitrate much of the time. An additional presentation of the time series of nitrate, as well as scatter plots of the PAM output vs

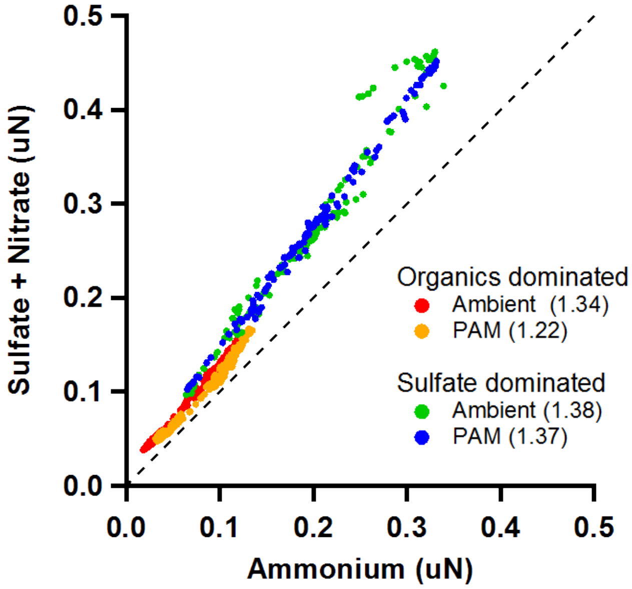
ambient concentrations would be very useful to illustrate and quantify these statements. Also histograms of the ratios or differences would be very useful.

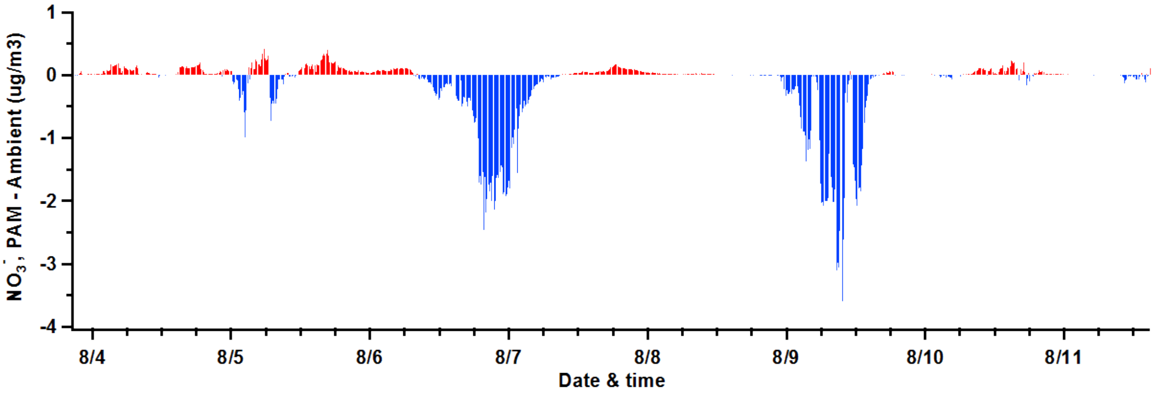
[Response]

In the Figure below, the balance between ammonium and sulfate+nitrate was examined for ambient and PAM aerosol in different two episodes, where chloride was not included because its concentration was below 0.4 μg m^{-3} (less than 1/10 of nitrate concentration). Overall, the inorganic aerosols were acidic. In sulfate dominated episode, the acidity of the PAM aerosol was similar to that of ambient aerosol. It is because sulfate enhancement was accompanied with nitrate loss in PAM reactor. In organics dominated episode, sulfate and ammonium was enhanced while nitrate was lost in PAM reactor, leading to slight decrease in acidity.

We observed nitrate loss in both organics dominated and sulfate dominated episode. When air was clean, nitrate was sometimes enhanced in PAM reactor. However, the enhanced mass was less than 0.5 μg m^{-3}, which is insignificant.

This part was reworded in revised manuscript.





[Figure. Balance between sulfate+nitrate (μN) and ammonium (μN) (top). Difference in nitrate concentration between PAM aerosol and ambient aerosol (bottom).]

[Manuscript revision]

- Page 7 Line 155. Sulfate and ammonium concentrations in the PAM reactor were mostly higher or similar to those in the ambient air. In contrast, total organics and nitrate were mostly lower in the PAM aerosols than ambient aerosols.
- Page 13 Line 321. Modified: In addition, the equivalent ratios of sulfate and nitrate to ammonium indicated that the ambient particles were mostly acidic.
- Page 13 Line 322. A sentence starting with "The aerosol was neutralized by formation …" was removed because it was thoroughly explained in the next paragraphs.
- Page 14 Line 347-354. Modified. In the organic dominated episode, the balance of ammonium with sulfate and nitrate [sulfate+nitrate(μN)]/[ammonium(μN)] was 1.34 in ambient aerosol, which was reduced to 1.22 in PAM aerosol because of enhanced sulfate and ammonium with nitrate being lost. In the sulfate dominated episode, however, this balance was 1.38 in ambient aerosol and not significantly changed in PAM aerosol. The acidity of the PAM aerosol remained constant due to an equivalent loss of nitrate over the condensation mode and its mode being shifted toward larger size. These results illustrate the role of sulfate in determining chemical compositions and mass loadings of aerosols in northeast Asia.

Figure 2 was modified with chloride being added to figure 2(b).

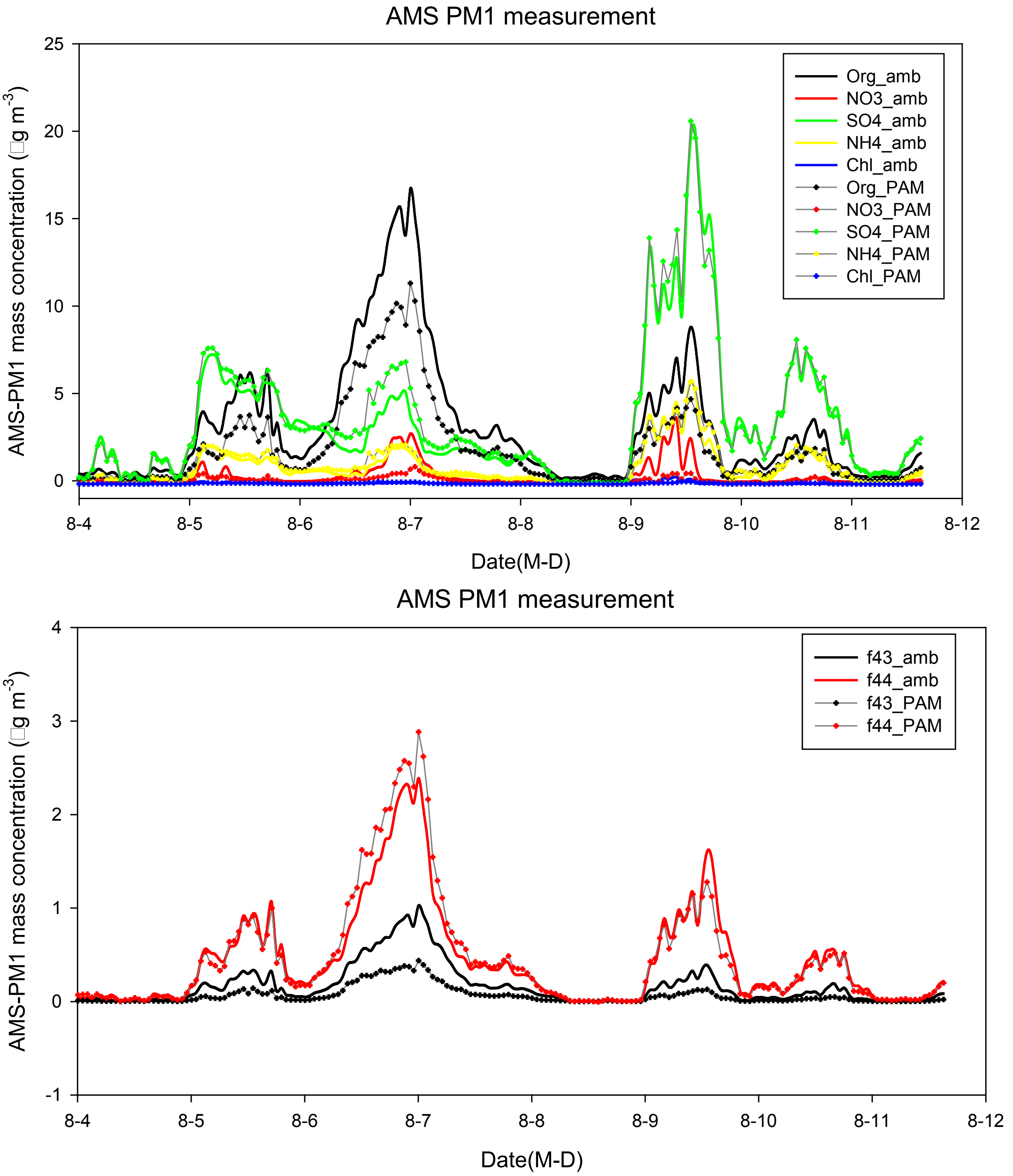


Figure 2. (a) Aerosol mass concentrations from SMPS measurements for ambient and PAM aerosols. (b) Mass concentrations of major components measured by HR-ToF-AMS including organics, nitrate, sulfate, ammonium, chloride, and organic m/z 43 and m/z 44. Solid lines and lines with markers represent ambient aerosols and PAM aerosols, respectively. Shaded periods represent the organics-dominated episode (August 6, 11 AM to August, 7 9 AM) and the sulfate-dominated episode (August 9, 1 AM to August 9, 2 PM). The lowest mass concentration observed on August 8 was due to rain.

(16) Figures 2 and 5 appear to contradict each other and some of the text: Figure 2 shows enhancements in m/z 44 during the organic period and decreases during the sulfate period. However, Figure 5 shows that m/z 44 stays constant in the organic period.

[Response]

Figure 2 is revised with a new figure presenting the time-series variation of m/z 44 and m/z 43 of PAM and ambient aerosol (shown above), which is consistent with what is shown in Figure 5.

(17) Lines 247-253: The interpretation of a slight change in H/C vs O/C in the PAM for the organic-dominated period indicating that "fragmentation is thought to play a major role in loss of organics" is an example of the exaggerated and unsupported conclusions in this manuscript.

(18) The discussion section (e.g., line 267 and 292) concludes that changes in the organic aerosol were due to gas-phase oxidation and subsequent repartitioning of semivolatile compounds, and that heterogeneous oxidation was not playing a substantial role. A detailed study of heterogeneous oxidation of ambient aerosols in the PAM reactor has been published (Hu et al., 2016), as have previous studies using similar reactors (George and Abbatt, 2010).Fig 6a in Hu et al. shows the loss of 20% of a type of SOA not formed in the PAM (IEPOX-SOA) at an OH exp of 7 x 10 11 molec. cm^{-3} s (the value used here). Can the authors provide a more quantitative analysis of these processes that uses the results available from the literature as part of the interpretation, rather than just speculate?

[Response]

The following is the response for the question (17) and (18). The above discussion was the most plausible explanation based on our results compared with those from previous studies. In revised manuscript, the main results of Lambe et al. (2012) and Hu et al. (2016) were included to explain our OA mass loss in PAM reactor. While their experimental conditions including PAM reactor setup and OH exposure were similar to ours, the measurement sites and aerosol compositions were quite different.

[Manuscript Revision]

- Page 10 Line 247-253. Figure 7 demonstrates that PAM OAs are shifted toward higher O:C and lower H:C ratio compared to ambient aerosols, leading to the Van Krevelen slope (Δ(H:C)/Δ(O:C)) of -0.6 for both organics and sulfate dominated episodes. In a laboratory PAM experiment, Lambe et al. (2012) observed a similar tendency and explained that as SOA oxidized, the Van Krevelen slope changed from minor fragmentation of carbonyl and acids/alcohol to major fragmentation of acids. Recently, Hu et al. (2016) reported that fragmentation became an important pathway of OAs oxidation involving heterogeneous reactions at OH exposure greater than 10^{11} molecules cm^{-3} s. At OH exposure of 7 x 10^{11} molecules cm^{-3} s, they observed 20% of OA mass lost by the fragmentation. Under similar OH exposure of 7 x 10^{11} molecules cm^{-3} s in the present study, the OA mass was lost in PAM reactor by about 22 % and 37 % for organic and sulfate dominated episodes, respectively (Table 1).

(19) L345-352: this discussion of condensation / evaporation of inorganic species and acidity would be enhanced by showing the AMS ammonium balance for ambient and PAM observations in the different periods. Some of those features are discussed in words, but there is no reason to not include the figures in Supp. Info., which will be useful to readers and also for comparison with other studies.

[Response]

The ammonium balance with sulfate and nitrate is explained and shown as the response (15).

[Manuscript revision]

- Page 7 Line 155. Modified: Sulfate and ammonium concentrations in the PAM reactor were mostly higher or similar to them in the ambient air. In contrast, total organics and nitrate were mostly lower in the PAM aerosols than ambient aerosols.
- Page 14 Line 347-354. Modified. In the organic dominated episode, the balance of ammonium with sulfate and nitrate [sulfate+nitrate(μN)]/[ammonium(μN)] was 1.34 in ambient aerosol, which was reduced to 1.22 in PAM aerosol because of enhanced sulfate and ammonium with nitrate being lost. In the sulfate dominated episode, however, this balance was 1.38 in ambient aerosol and not significantly changed in PAM aerosol. The acidity of the PAM aerosol remained constant due to an equivalent loss of nitrate over the condensation mode and its mode being shifted toward larger size. These results

illustrate the role of sulfate in determining chemical compositions and mass loadings of aerosols in northeast Asia.

- The following figure is provided as supplementary information as follows.

S2. Ammonium balance with sulfate and nitrate

The balance between ammonium and sulfate+nitrate was examined for ambient and PAM aerosol in different two episodes, where chloride was not included because its concentration was below 0.4 μg m^{-3} (less than 1/10 of nitrate concentration). Overall, the inorganic aerosols were acidic. In sulfate dominated episode, the acidity of the PAM aerosol was similar to that of ambient aerosol. It is because sulfate enhancement was accompanied with nitrate loss in PAM reactor. In organics dominated episode, sulfate and ammonium was enhanced while nitrate was lost in PAM reactor, leading to slight decrease in acidity.

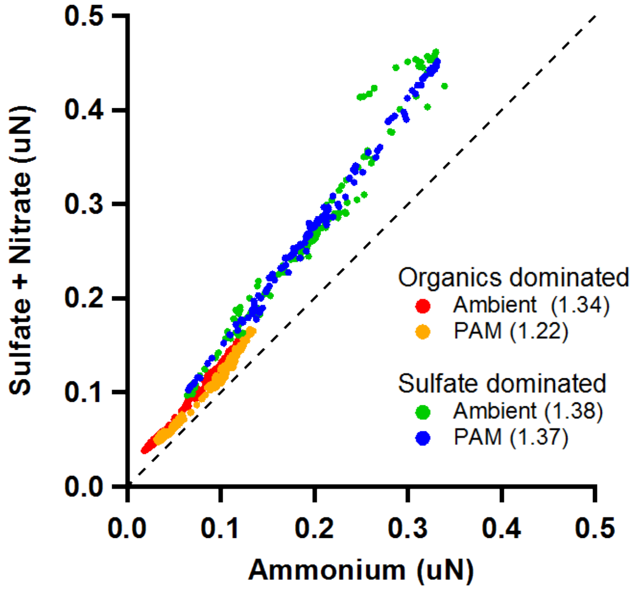


Figure S2. The normality of ammonium against sulfate and nitrate for ambient and PAM aerosol in organics and sulfate dominated episodes. The numbers in parentheses on the legend indicate the ratio of [sulfate+nitrate (μN)]/[ammonium(μN)].

(20) Line 339 and elsewhere (including abstract): Conclusions are drawn regarding the role of photooxidation in the formation of CCN. Presumably the authors are referring to the increase in hygroscopicity due to addition of sulfate? However, it appears that there is similar loss of nitrate (which is attributed to the nitrate being thermodynamically driven

out by sulfuric acid condensation) which would appear to approximately cancel out this effect. Likely the organic component is becoming increasingly hygroscopic during aging as well, which has nothing to do with SO2 oxidation to sulfate. Therefore, a more detailed analysis is needed to support broad statements about the link between photooxidation and CCN. For example the kappa value of the aerosols can be estimated from literature values for individual components using the ZSR approximation. However, large generalizations to NE Asia based on a few days of measurements at one location are not warranted.

[Response]

The CCN activation of organic particles was due to the growth of particle size to the condensation mode. In Figure 6, m/z 44 of PAM aerosol was increased in condensation mode (PToF size >200nm) where sulfate was also enhanced. In other words, the further oxidized OAs were formed together with sulfate at condensation mode in the PAM reactor. We modified the manuscript with more clear expression and background information about the regional characteristics to support the CCN contribution.

[Manuscript revision]

- Page 13, Line 338. The following sentence was added to the line 338. "In Figure 6, m/z 44 of PAM aerosol was increased in condensation mode (PToF size >200nm) where sulfate was also enhanced. In other words, the further oxidized OAs were formed together with sulfate at condensation mode in the PAM reactor."

(21) Section: 4.1 is underdeveloped and under referenced. It is not clear what point the authors are trying to make. As written, it appear to simply restate the observations pointed out in the results section that small particle concentrations were observed to increase in the PAM.

[Response]

The discussion about the nuclei mode particle formation was supplemented by adding the non-linear oscillatory nucleation in detail.

[Manuscript revision]

- Page 8 Line 199. Add sentence: Palm et al. (2016) also observed the nuclei mode particles formed, competing for the role of condensation sink (CS) with preexisting accumulation mode particles.

- Page 9 Line 207. The following discussion was added: 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.

(22) Section 4.4: When discussing the atmospheric implications of your measurements, what role would, e.g., aqueous chemistry and particle phase reactions have? Is there enough time in the reactor for these processes to take place, as they would in the atmosphere after 5 days of transport? What about coagulation, photolysis, etc? A discussion of these processes is needed in order to interpret a comparison between changes in aerosol properties (e.g., O:C ratios shown in Fig. 8) between these experiments and ambient air. In other words, please discuss how the aerosol aged 5 days in the PAM would compare to ambient aerosol that has been transported for 5 days.

[Response]

Hu et al. (2016) reported that photolysis negligibly contributes to formed SOA depletion during the aging because SOAs contain mainly hydroxyl and carbonyl groups and their quantum yields in aerosol phase are low. When the organic aerosols in the ambient air transport and experience the photochemical reaction, the photolysis would be less important. In the present study, the O:C ratio of ambient OAs were greater than 0.4 , indicating moderately aged OAs such as SV-OOAs and LV-OOAs containing carbonyl groups (Ng et al., 2011).

In East Asia, sulfate dominated aerosol is a distinguished feature of the air pollution plumes (Dunlea et al., 2009). The overall yield of sulfate formation from SO_2 is greater than organic aerosols during the transport across the Pacific Ocean because of shorter lifetime of SOA precursors than SO_2 and fragmentation loss of OAs. In addition, sulfate fraction against total sulfur increases during the transport, resulting in particle growth. In the ambient air, sulfate particles are scavenged by washout. When relative humidity is high, the oxidized OAs and acidic inorganic aerosols could be scavenged by heterogeneous reaction, acting as fog droplet nuclei and impacting on the droplets (Gilardoni et al., 2014).

Note that in PAM reactor the aerosol scavenging mechanism such as air mass lifting to the free troposphere (Dunlea et al., 2009) and new particle formation due to entrainment of free tropospheric air (Song et al. 2010) is not reproduced.

We modified the manuscript by adding supporting references.

[Manuscript revision]

- Page 15 Line 377. In the real atmosphere, the fate and evolution of secondary aerosols could be affected by scavenging of oxidized OAs and inorganic aerosols on the cloud droplets by aqueous aerosol surface reaction (Dunlea et al., 2009), nucleation of new particles due to the entrainment of free tropospheric air (Song et al., 2010), or dry deposition on the dust particles (Dunlea at al., 2009).
- Page 15, Line 379. Modified: "… which is possibly due to the omission of these scavenging processes in PAM reactor."
- Page 15 Line 384. Add sentence: The formation yield of sulfate from SO_2 is greater than that of organic aerosols during 3~4 days of aging in the Asian pollution plume because of fast depletion of SOA precursors (Dunlea et al., 2009), which is consistent to our results.
- Page 15 Line 386. Modified: "… this study indicates that …"
- Page 15 Line 387. Modified: "… of less oxidized OAs was carried out, …"

(23) Line 343: Could the evaporation of NO3 aerosol be due to heating or dilution of the air in sampling lines prior to measurement?

[Response]

In our experimental setup, there is no heating or dilution prior to measurement because air continuously flew through the inlet to the instruments. The residence time delay occurred inside of the PAM reactor. It was reported that in the PAM reactor, ~ 2°C increased due to the irradiation of UV lamps. However, this temperature difference will be not significant to evaporate NO_3 (Ortega et al., 2016). Thus, the evaporation of NO_3 due to heating or dilution would be negligible.

[Manuscript Revision]

- Page 5 Line 114. Modified: The Hg lamps were housed in Teflon sleeves being purged by nitrogen to prevent heat and O_3 from building up. The results of Ortega et al. (2016) using the same PAM reactor as that used in the present study, demonstrated that the increase in temperate by lamp irradiation was only 2 ℃ inside the PAM reactor and its effect on evaporation of OA or nitrate was insignificant.

Minor comments

Line 84: Which Kang et al. paper are you referencing?

[Response]

Kang et al. (2011a), which is listed in the references.

Kang, E., Brune, W. H., Kim, S., Yoon, S. C., Jung, M., and Lee, M.: A preliminary PAM measurement of ambient air at Gosan, Jeju to study the secondary aerosol forming potential, Journal of Korean Society for Atmospheric Environment, 27, 11, 2011a.

Line 99. "Asian" not needed.

[Response]

We modified the manuscript.

[Manuscript revision]

- Page 4, Line 99. "… to observe dust and pollution plume transported from China."

Line 101: consider changing "collected" to "sampled" as to not imply collection for offline analysis.

[Response]

We modified the manuscript as suggested.

[Manuscript revision]

- Page 5 Line 101. “Ambient air sampled using a PM1.0 …”

Line 107: Please add a reference(s) for the AMS instrument.

[Response]

We added references to the manuscript, as suggested.

[Manuscript revision]

- Page 5, Line 109. ”… a scanning mobility particle sizer (SMPS 3034, TSI) (Jayne et al., 2000; Jimenez et al., 2003; DeCarlo et al., 2006; Drewnick et al., 2006).

Line 169: air mass BACK-TRAJECTORIES

[Response]

It was changed in revised manuscript.

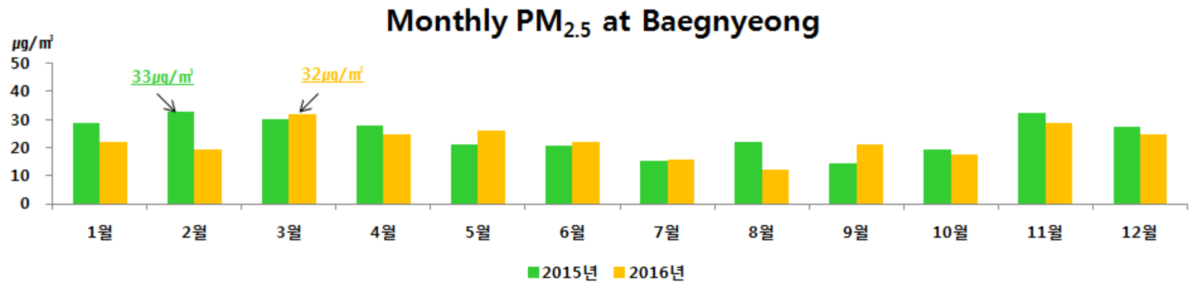
[Manuscript revision]

- Page 7, Line 169. ”… distinguished by the air masses backward-trajectories (Fig. 1b).”
- Page 6, Line 134. ” … used to examine the history of the sampled air masses (Wang et al., 2009).”

Line 140: How does the aerosol mass compare to other measurements in Eastern Asia?

[Response]

The ambient aerosol mass concentration measured in this study varied from 0.5 to 38 µg m^{-3} (in Figure 4). Choi et al. (2016) reported AMS measurements (PM1.0) during March-April, 2012 and November-December, 2013 in the same site, where PM1.0 varied from almost 0 to approximately 100 µg m^{-3}. The AMS PM1.0 measured in Changdao, China was in the range from 4.40 to 245 µg m^{-3} in spring and summer, 2011, which was much higher than those of Baengnyeong Island (Hu et al., 2013; Choi et al., 2016). Tokyo PM1.0 measured by AMS was 8.3 and 18.3 µg m^{-3} (25th-75th percentile) in summer, 2003 (Takegawa et al., 2006). Lee et al. (2015) also demonstrated the influence of air pollution plumes transported from eastern China and the Korean Peninsula on enhanced sulfate and organics. In revised manuscript, more information was added regarding Baengnyeong site to emphasize its role as regional background station in eastern Asia. The following figure shows the monthly variations of $PM_{2.5}$ concentrations measured at the same site during 2015~2016.



[Manuscript revision]

- Page 4, Line 112: 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 6 Line 140. "$PM_{1.0}$ aerosol mass concentrations ..."
- Page 6, Line 141. Add sentences: Choi et al. (2016) reported AMS measurements (PM1.0) during March-April, 2012 and November-December, 2013 in the same site, where PM1.0 varied from almost 0 to approximately 100 µg m^{-3}. These PM1.0 concentrations were comparably lower compared with those measured in Changdao that is located in Bohai Sea (Hu et al., 2013; Choi et al., 2016; Lee et al., 2015).

Line 326-329: It is incorrect to directly attribute the changes in the aerosol mass or size distributions to m/z 44 or m/z 43. Those are signals produced in the AMS and are not constituents of the particles. Moreover, those signals only constitute small fractions of the total organic signal measured by the AMS.

[Response]

As we mentioned in response above, we simply used f44 and 43 to interpret the volatility of SV-OOA and LV-OOA. We also presented the mass change of organics with the concentration of total organics in figure and manuscript.

Line 347: "Heterogenous reaction of NO 2 on the particle surfaces" producing particle *nitrate? To what process are the authors referring? I am not aware of any such process that could compete with OH + NO 2 in the gas phase. Please provide references.*

[Response]

It was meant to suggest one of the possible pathways of HNO_3(p) production but not to point out specific reaction of OH+NO_2. To avoid confusion, we modified the manuscript.

[Manuscript revision]

- Page 14, Line 345. A plausible source of HNO_3(p) in the PAM reactor is the deposition of gaseous HNO_3(g) or heterogeneous reaction of NO_2 on the particle surfaces (Underwood et al., 2001), even though the latter is not clearly understood.

Fig. 3 caption: What is dW/dlogDp?

[Response]

dW/dlogDp is a normalized particle concentration. dW is the mass of particles in the range (total concentration) and dlogDp is the difference in the log of the channel width. SMPS we used has 64 channels from 10 to 500 nm in particle diameter.

References

George, I. J. and Abbatt, J. P. D.: Heterogeneous oxidation of atmospheric aerosol particles by gas-phase radicals, Nature Chemistry, 2, 713–722, 2010.

Hu, W., Palm, B. B., Day, D. A., Campuzano-Jost, P., Krechmer, J. E., Peng, Z., de Sá, S. S., Martin, S. T., Alexander, M. L., Baumann, K., Hacker, L., Kiendler-Scharr, A., Koss, A. R., de Gouw, J. A., Goldstein, A. H., Seco, R., Sjostedt, S. J., Park, J.-H., Guenther, A. B., Kim, S., Canonaco, F., Prévôt, A. S. H., Brune, W. H., and Jimenez, J. L.: VolFatility and lifetime against OH heterogeneous reaction of ambient isoprene-epoxydiols-derived secondary organic aerosol (IEPOX-SOA), Atmos. Chem. Phys., 16, 11563-11580, doi:10.5194/acp-16-11563-2016, 2016.

Li, R., W.H. Brune, B.B. Palm, A.M. Ortega, J. Hlywiak, W. Hu, Z. Peng, D.A. Day, C. Knote, J. de Gouw, and J. L. Jimenez. Modeling the radical chemistry in an Oxidation Flow Reactor: radical formation and recycling, sensitivities, and OH exposure estimation *equation. J. Phys. Chem. A, 119, 4418–4432, 2015. doi:10.1021/jp509534k.*

Middlebrook, A.M., R. Bahreini, J.L. Jimenez, and M.R. Canagaratna. Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data. Aerosol Sci. Technol., 46, 258–271, 2012.

Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutiérrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, doi:10.5194/acp-16-7411-2016, 2016.

Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., Cross, E. S., Kroll, J. H., Peng, Z., Brune, W. H., and Jimenez, J. L.: In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, Atmos. Chem. Phys., 16, 2943-2970, doi:10.5194/acp-16-2943-2016, 2016.

Palm, B. B., Campuzano-Jost, P., Day, D. A., Ortega, A. M., Fry, J. L., Brown, S. S., Zarzana, K. J., Dube, W., Wagner, N. L., Draper, D. C., Kaser, L., Jud, W., Karl, T., Hansel, A., Gutiérrez-Montes, C., and Jimenez, J. L.: Secondary organic aerosol formation from in situ OH, O3, and NO3 oxidation of ambient forest air in an oxidation flow reactor, Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1080, in review, 2017.

Peng, Z., Day, D. A., Stark, H., Li, R., Lee-Taylor, J., Palm, B. B., Brune, W. H., and Jimenez, J. L.: HOx radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling, Atmos. Meas. Tech., 8, 4863-4890, doi:10.5194/amt-8-4863-2015, 2015.

Peng, Z., Day, D. A., Ortega, A. M., Palm, B. B., Hu, W., Stark, H., Li, R., Tsigaridis, K., Brune, W. H., and Jimenez, J. L.: Non-OH chemistry in oxidation flow reactors for the study of atmospheric chemistry systematically examined by modeling, Atmos. Chem. Phys., 16, 4283-4305, doi:10.5194/acp-16-4283-2016, 2016.

Robinson, A. L. Donahue, N. M. Shrivastava, M. K. Weitkamp, E. A. Sage, A. M. Grieshop, A. P. Lane, T. E. Pierce, J. R. and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259-1262, 2007.

The list of newly added references to the manuscript and responses.

Choi J., Kim, J., Lee, T., Choi, Y., Park, T., Oh, J., Park, J., Ahn, J., Jeon, H., Koo, Y., Kim, S., Hong, Y., and Hong, J.: A Study on Chemical Characteristics of Aerosol Composition at West Inflow Regions in the Korean Peninsula I. Characteristics of PM Concentration and Chemical Components, J.KOSAE., 32(5), 469-484, 2016

Gilardoni, S., Massoli, P., Giulianelli, L., Rinaldi, M., Paglione, M., Pollini, F., Lanconelli, C., Poluzzi, V., Carbone, S., Hilamo, R., Russell, L.M., Facchini, M.C., Fuzzi, S.: Fog scavenging of organic and inorganic aerosol in the Po Valley, Atmos. Chem. Phys., 14, 6967-6981, 2014

Hayes, P.L., Carlton, A.G., Baker, K.R., Ahmadov, R., Washenfelder, R.A., Alvarez, S., Rappenglück, Gilman, J.B., Kuster, W.C., de Gouw, J.A., Zotter, P., Prévôt, A.S.H., Szidat, S., Kleindienst, T.E., Offenber, J.H., Ma, P.K., Jimenez, J.L.: Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010, Atmos. Chem. Phys., 15, 5773-5801, 2015.

Hu, W.W., Hu, M., Yuan, B., Jimenez, J.L., Tang, Q., Peng, J.F., Hu, W., Shao, M., Wang, M., Zeng, L.M., Wu, Y.S., Gong, Z.H., Huang, X.F., and He, L.Y.: Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of central eastern China, Atmos. Chem. Phys., 13, 10095-10112, 2013.

Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E., and Worsnop, D.R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, Aerosol Science and Technology, 33, 49-70, 2000.

Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X., Smith, K.A., Morris, J.W., and Davidovits, P.: Ambient aerosol sampling using the aerodyne aerosol mass spectrometer, Journal of Geophysical Research Atmospheres, 108(D7), 8425, doi: 10.1029/2001JD001213, 2003.

DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R., Jimenez, J.L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. Anal. Chem. 78, 8281-8289. 2006.

Drewnick, F., Hings, S.S., Curtius, J., Eerdekens, G., Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany. Atmos. Environ. 40, 4316-4327, 2006.

DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R., Jimenez, J.L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. Anal. Chem. 78, 8281-

8289, 2006.

Drewnick, F., Hings, S.S., Curtius, J., Eerdekens, G., Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany. Atmos. Environ. 40, 4316-4327, 2006.

Feiner, P., Brune, W., Miller, D., Zhang, L., Cohen, R., Romer, P., Goldstein, A., Keutsch, F., Skog, K., Wennberg, P., Nguyen, T., Teng, A., DeGouw, J., Koss, A., Wild, R., Brown, S., Guenther, A., Edgerton, E., Baumann, K., Fry, J.: Testing Atmospheric Oxidation in an Alabama Forest. J. Atmos. Sci. 73(12), 4699-4710, 2016.

Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E., Worsnop, D.R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. Aerosol Sci. Technol. 33, 49-70, 2000.

Lee, J.D., Young, J.C., Read, K.A., Hamilton, J.F., Hopkins, J.R., Lewis, A.C., Bandy, B.J., James Davey, J., Edwards, P., Ingham, T., Self, D.E., Smith, S.C., Pilling, M.J., Heard, D.E.,: Measurement and calculation of OH reactivity at a United Kingdom coastal site. J. Atmos. Chem. 64, 53-76., 2009.

Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X., Smith, K.A., Morris, J.W., Davidovits, P.: Ambient aerosol sampling using the Aerodyne aerosol mass spectrometer. J. Geophys. Res. Atmos. 108, 10.1029/2001JD001213, 2003.

Mao, J., Ren, X., Chen, S., Brune, W.H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglueck, B., Flynn, J., Leuchner, M.,: Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies, Atmospheric Environment, 44, 4107–4115, 2010.

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

Song, M., Lee, M., Kim, J.H., Yum, S.S., Lee, G., Kim, K-R.: New particle formation and growth in relation to vertical mixing and chemical species during ABC-EAREX2005, Atmos. Res., 97, 359-370, 2010.

Underwood, G.M., Song, C.H., Phadnis, M., Carmichael, G.R., Grassian, V.H.: Heterogeneous reactions of NO_2 and HNO_3 on oxides and mineral dust: A combined laboratory and modeling study, J. Geophys. Res., 106(D16), 18055-18066, 2001.

Yoshino, A., Sadanaga, Y., Watanabe, K., Kato, S.Y., Miyakawa, Y., Matsumoto, J., Kajii, Y.: Measurements of total OH reactivity by laser-induced pump and probe technique - comprehensive observations in the urban atmosphere of Tokyo. Atmos. Environ. 40, 7869-7881, 2006.

Wang, Y. Q., Zhang, X. Y., and Draxler, R. R.,: TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environ. Modell. Softw. 24, 938-939, 2009.