

Authors response to Second round review of Kang et al. ACPD 2017

This paper describes results from an OFR - AMS/SMPS study at an island in Korea. The ACPD version had a large number of problems. The authors have addressed some of the problems in this revision, but have unfortunately ignored others. I would estimate that ½ of the major problems have been addressed in this revision. However new errors come to light with the added information. Before acceptance into a journal with high standards like ACP, the paper requires another round of major revision, followed by re-review.

We are grateful for your constructive in-depth review of our manuscript. While we find the review provides a number of constructive criticisms, we believe that we have been able to address major issues raised regarding the PAM experiment done under the limited field condition. If some responses were not satisfactory, however, it was not that we ignored them but that we have not been cautious enough to give an answer to every detail. In the second round review, we thoroughly read your comments and provide point-by-point responses.

The main concern is that the role of organic aerosol could be underestimated with a fixed high OH exposure. First of all, we would like to ask your full consideration for the unique environment of Northeast Asia where our experiment was conducted. As you already knew, sulfur is dominant in this region, which is different from other developed regions such as Europe and North America. It does not necessarily mean that sulfur is always most abundant through the year, though. Rather, the chemical characteristics of the atmosphere are largely dependent on meteorological condition that determines major sources and atmospheric processing such as the degree of oxidation. The chemical characteristics of aerosol are complex and significantly vary in time. It is well documented in previous studies conducted in Jeju Island (Lee et al., 2007; Song et al., 2010, Lim et al., 2012, 2014).

Although in the study region, the meteorological condition changes dynamically through the year, there was almost no information available on aerosol composition (PM_{1.0}) at Baengnyeong Island. Therefore, the modulation of OH exposure was not an option from the very beginning when we planned this study. In fact, a strong typhoon hit the island in the middle of the experiment and the station was evacuated.

Nevertheless, we agree with the basic sentiment of your review that the results of PAM experiment are by nature operationally-dependent and always require careful testing. Thus, all available information regarding PAM experiment was added to the revised manuscript, which was not fully provided in the submitted manuscript. Since this study is not a controlled lab experiment but a field experiment in a remote Island, however, there were limited resources for the experiment. Baengnyeong Island is right in front of North Korea and accessible only by ship (five hours). In the revised manuscript, therefore, we described the condition of the experiment and limitation of the results as clearly as we could.

- M. Lee, M.Song, K. J. Moon, J. S. Han, G.Lee, K.R. Kim, Origins and chemical characteristics of fine aerosols during the northeastern Asia regional experiment (Atmospheric Brown Cloud East Asia Regional Experiment 2005), *Journal of Geophysical Research*, 112, 2007.
- M. Song, M. Lee, J. H. Kim, S. S. Yum, G. Lee, New particle formation and growth in relation to vertical mixing and chemical species during ABC-EAREX2005, *Atmospheric Research*, 97, 359-370, 2010.
- S. Lim, M. Lee, G. Lee, S. Kim, S. Yoon, K. Kang, Ionic and carbonaceous compositions of PM10, PM2.5 and PM1.0 at Gosan ABC superstation and their ratios as source signature, *Atmospheric Chemistry and Physics*, 12, 1–18, 2012.
- S. Lim, M. Lee, S.-W. Kim, S.-C. Yoon, G. Lee, Y. Lee, Absorption and scattering properties of organic carbon vs. sulfate dominant aerosols at Gosan climate observatory in Northeast Asia, *Atmospheric Chemistry and Physics*, 14, 1-13, 2014.

Major Issues

(1) L156: a direct comparison (time series and scatter plot) of the AMS vs SMPS concentrations measured in this study is still not shown, despite being explicitly requested. This should be done for both the ambient measurements, and for the enhancements measured in PAM. This is a critical indicator of data quality, and in my opinion the paper should not be published without it.

[Response]

Since the aerosol characteristics were measured with SMPS and AMS in this study, a comparison of these two instrument results would be useful information to discuss and interpret the results of PAM reactor experiment. Thus we provide this additional information both to the revised manuscript and supplementary information.

L234, we added these sentences. “When the aerosol mass concentration measured by AMS and SMPS was compared each other, the SMPS mass was greater than AMS mass in sulfate-dominated episode compared to organic-dominated episode (Table 1 and Fig. 2(c)). It was possible that the particles not being detected in AMS such as EC (as shown in Fig. 4) or soil particles were included more in sulfate-dominated episode than in organic-dominated episode. “

Figures, the following figures were added as Figure 2(c).

“Figure 2(c). Time series of aerosol volume concentration measured by AMS and SMPS. Aerosol volume concentration from AMS was calculated with mass concentration and composition dependent

density.”

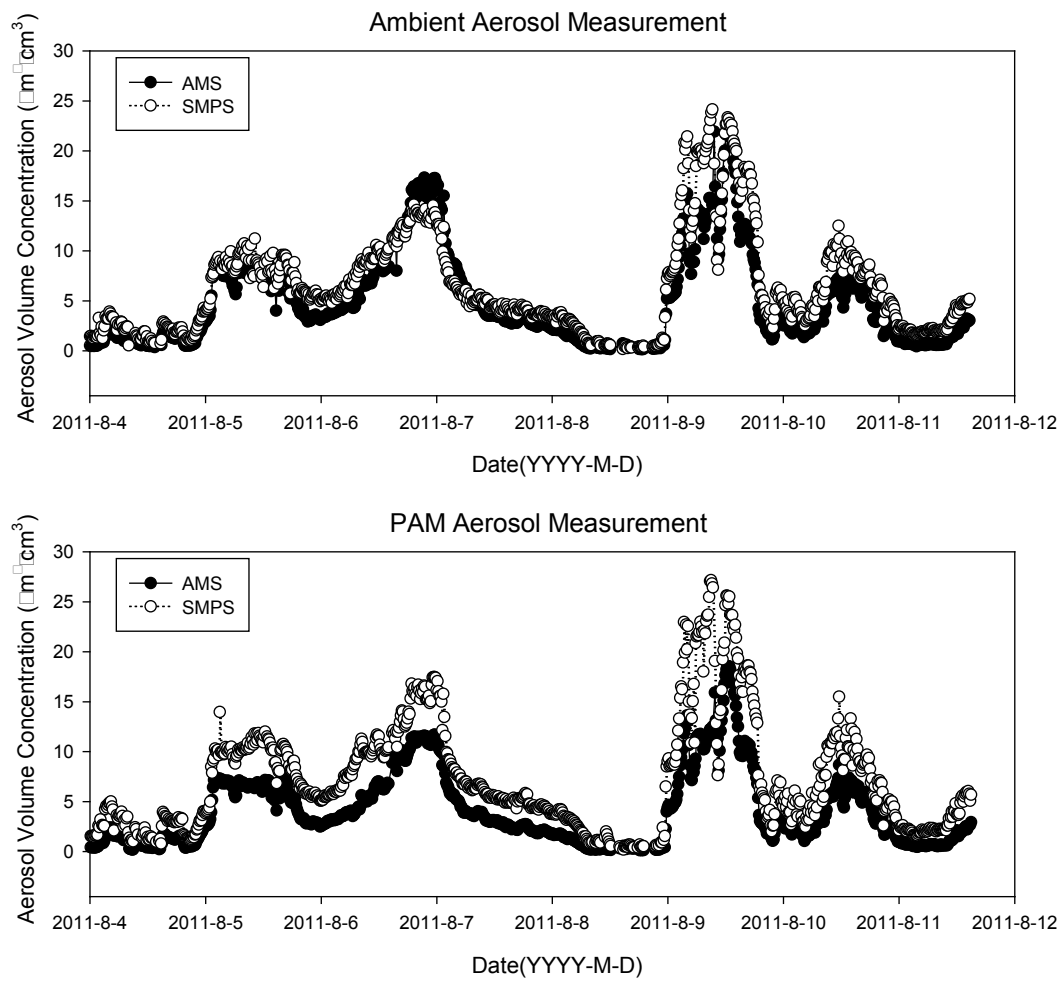
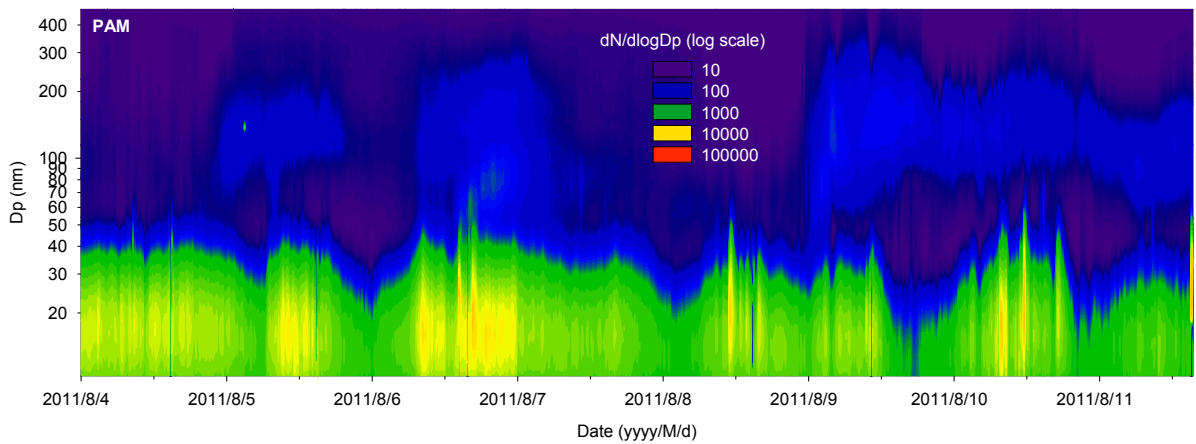
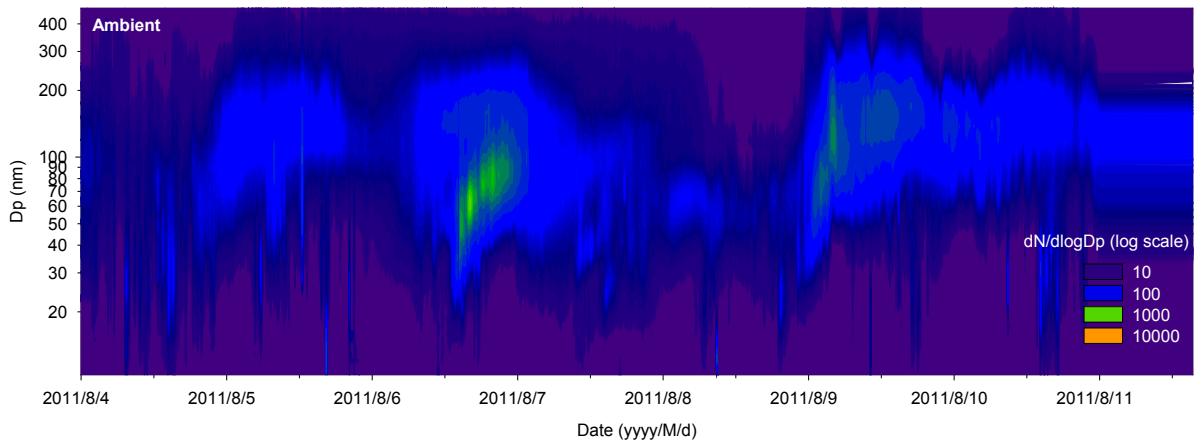


Figure 2(d), The size-separated number concentrations of ambient and PAM aerosols measured by SMPS.

[Figure 2(d)]

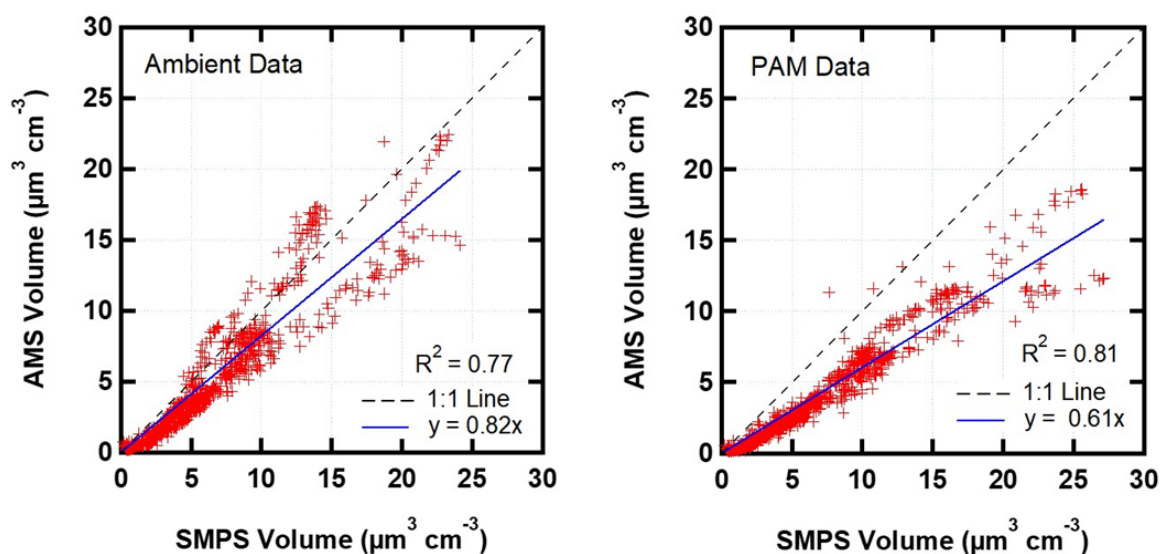


S7. A comparison of AMS vs SMPS

“Aerosol volume concentration obtained from AMS and SMPS was compared each other for ambient aerosol and PAM aerosol. Aerosol volume concentration from AMS was calculated from measured aerosol mass divided by composition-dependent density.

Figure 2(c) is a time series and figure S7 is a scatter plot of AMS and SMPS concentration. In ambient air, the agreement was generally good with SMPS mass concentrations being greater than those of AMS. While the AMS mass was slightly greater than or similar to SMPS mass in organics dominated episode, the AMS mass was smaller than SMPS mass in sulfate dominated episode. It is likely due to the contribution of EC (elemental carbon) and soil particles.

Figure S7. Scatter plots of SMPS aerosol volume concentration and AMS aerosol volume concentration. “



(2) L156: the statement is made in the responses (p8) that for the conditions of this study “CE would stay constant near 0.5.” However the next paragraph says “The composition dependent CE resulted in much better agreement between the mass measured by AMS and SMPS.” This makes no sense. First we are told that CE did not change, but then we are told that when applying a variable CE, the comparisons improved a lot? This makes the request for the direct comparison of SMPS and AMS mass (previous comment) even more important.

[Response]

First, we reduced AMS data with a constant CE. The AMS used for this study belongs to the government and we had a limited access to the AMS when the experiment was conducted. Later, T. Lee took a full responsibility for the AMS at Baengnyeong site for some period of time and was able to do several tests including the collection efficiency. As the other reviewer also recommended to use composition-dependent collection efficiency, we revised the AMS results using composition-dependent CE.

The first paragraph of the response in page 8 is to explain why we used a fixed CE of 0.5 in the original manuscript. In the next paragraph, we stated what we have done to comply with reviewers' comments regarding CE and what we got after applying composition-dependent CE to the AMS measurements.

(3) L203-204: this statement is erroneous. SVOCs have saturation concentrations (C^*) up to $1000 \mu\text{g m}^{-3}$, and IVOCs are in the range $10,000$ to $1\text{e}6 \mu\text{g m}^{-3}$. IVOCs will not partition significantly to the

particlephase under these conditions, and would require temperatures of -40C or so to start partitioning. Similarmuch of the SVOCs will be in the gas-phase, under the conditions of this study. Thus these statements are incorrect and should be revised. The implications of this revision should be propagated through the manuscript conclusions.

[Response]

While air mass is transported, VOCs will have gone through various atmospheric processing including partitioning, gaseous oxidation mainly initiated by OH, heterogeneous reaction on the surface, and deposit onto particle surface. The phrase "partitioned into the aerosol phase" means that I/SVOCs could have gone through these reactions and after all, transformed into particle. Not that it only indicates the process "partitioning between gas and aerosol phase" as a literal meaning. In Donahue et al. (AE), the chemical transformation of I/SVOCs were suggested as a missing source of SOA in the atmosphere.

L204, Modified from " thus it is likely that S/IVOCs were ..." to "thus it is likely that S/IVOCs were already transformed into particle phase, if existed ..."

N. M. Donahue, A. L. Robinson, S. N. Pandis, Atmospheric organic particulate matter: From smoke to secondary organic aerosol, *Atmospheric Environment*, 43, 94-106, 2009.

(4) L136: The difference between the outside and PAM temperature is not discussed clearly in the revised manuscript. The first two paragraphs on p35 of the responses document this issue, and should be included in the revised paper. The conclusion that evaporation (or condensation, as the authors rightly point out could be an issue for an air-conditioned trailer) is "insignificant" is not warranted. A more detailed discussion is needed.

[Response]

We added more details in the manuscript for the clarity.

L135, modified from "... inside the PAM reactor and its effect on evaporation of OA or nitrate was insignificant." To "... inside the PAM reactor. In a recent discussion, a 10 °C difference between PAM and ambient air caused the evaporation of NO₃ up to 34 % and OA up to 25 % (2016-10-17_PAM_Users_Mtg_Jimenez_Group_Final_v2.pdf). In this study, the ambient temperature varied in the range of 20~26°C and the temperature of air-conditioned laboratory remained around 20°C. Then, the difference in temperature between the PAM chamber and the ambient air was at most a few degrees. Therefore, the temperature-induced evaporation of OA or nitrate in the PAM reactor would

not be significant.”

(5) L137-144: was the calibration of OHexp used here and shown in p23 of the responses done on the same, or a different PAM reactor than the one used in this study. If a different reactor and lights were used for this study, the uncertainty on the OHexp increases considerably, being of at least a factor of 3. Whether the reactor was the same or different should be stated in the paper. If it was a different reactor, the increased uncertainty on the resulting OHexp should be discussed. (As an aside, if the Figure on p23 has not been previously published in the peer-reviewed literature, it should be included in the Supp. Info.).

[Response]

The calibration of OHexp was directly done with the PAM reactor in this study. We added this calibration curve in the supplements, although it was published in Kang et al., (2011a) (J. KOSAE Vol. 27, No. 5 (2011) pp. 534~544, Journal of Korean Society for Atmospheric Environment, DOI: <http://dx.doi.org/10.5572/KOSAE.2011.27.5.534>). This paper contains abstracts, figures and tables written in English, but the texts were written in Korean.

Supplements 3. Calibration of OH exposure in the PAM reactor

We used the OH exposure calibration which was done with a mixture of pure air and SO₂(g) in the laboratory by Kang et al. (2011a). The full manuscript can be found in J. KOSAE Vol. 27, No. 5 (2011) pp. 534~544, Journal of Korean Society for Atmospheric Environment, DOI: <http://dx.doi.org/10.5572/KOSAE.2011.27.5.534>.

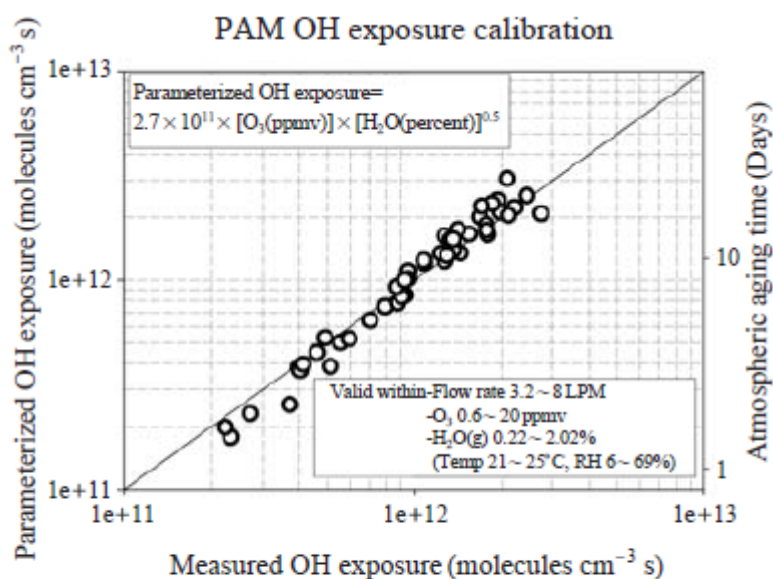


Fig. 2. OH exposure calibration curve and the empirical formula for the OH exposure. The absolute uncertainty in OH exposure is estimated to be $\pm 21\%$ at the 2σ confidence level.

[Figure S3-1. OH exposure calibration curve for the PAM reactor. From Kang et al., 2011a]

(6) The authors have calculated the condensation losses in the PAM. However they inexplicably use a single value for all their measurements, when e.g. their Figure 2 shows extremely large variations on PM concentrations, which will lead to dramatic changes in this correction. Since the authors have time-resolved SMPS measurements, implementing a time-dependent correction is easy and should be done here.

[Response]

The time dependent condensation losses were calculated and added to the supplement information. The manuscript was revised accordingly.

L193~199, we modified the sentences starting with “The condensable gases fate model for PAM reactors (Palm et al., 2016) predicts ...” and moved to the experimental method section like this.

L157 “Some of the condensable gases formed in the PAM reactor do not contribute to the observed particle mass concentration sampled by the SMPS and AMS at the exit of the PAM reactor. Some are deposited on the PAM reactor walls, and some do not condense before the particles are sampled. The calculation of the condensation sink (CS) indicates the fraction that are measured as particles. These calculations indicate that typically 60% to 70% of the condensable gases did condense on particles

before the particles were measured (Figure S5-1). The particle mass concentrations shown in the results have been corrected for this loss. The resulting mass concentrations sampled through the PAM chamber have an uncertainty of 20%, (2σ confidence).”

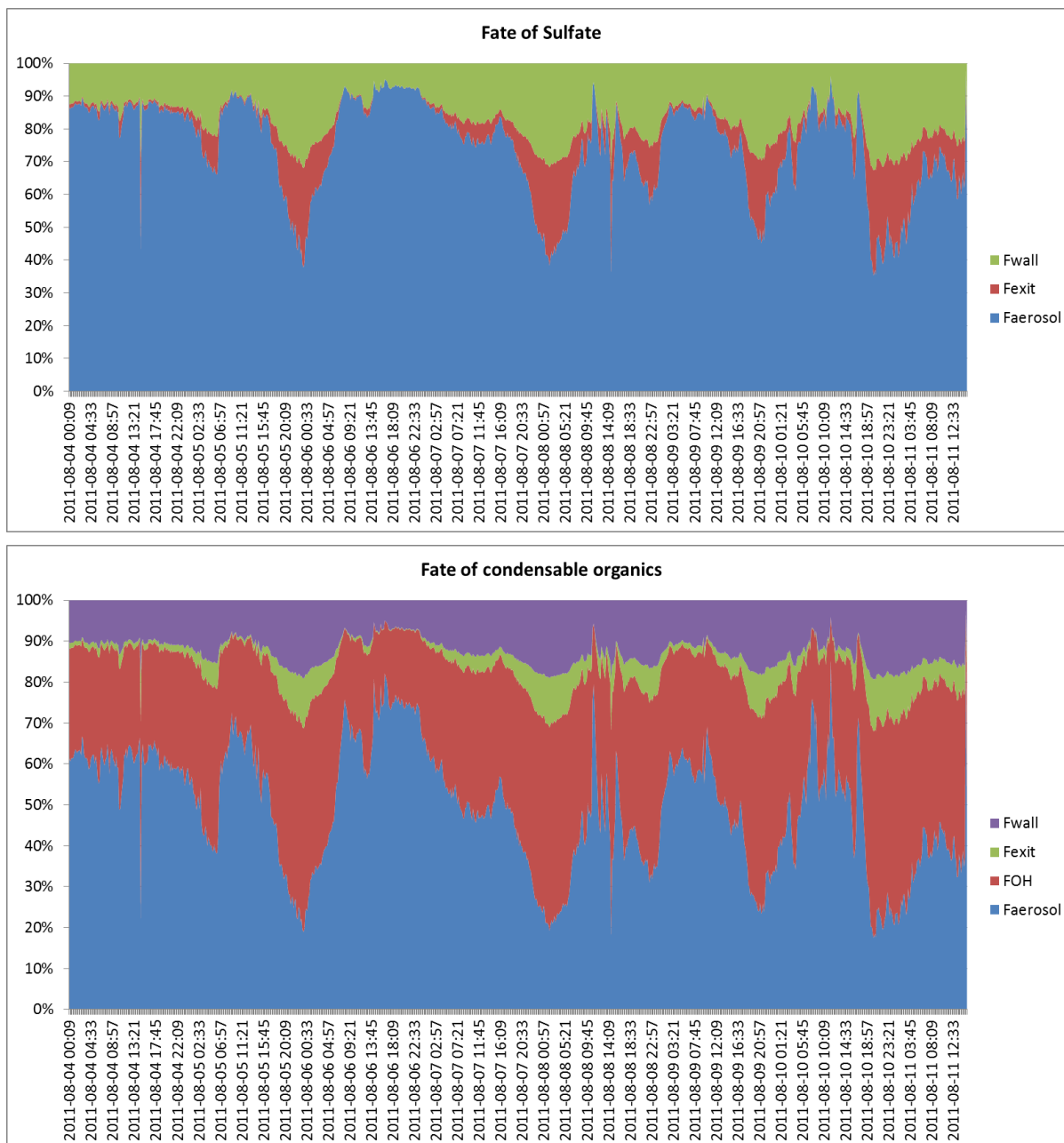
Supplements. We added the time-dependent loss test and AMS and SMPS mass concentration correction with the loss in the supplements as shown.

“**Supplements 5.** Estimating the condensation sink.

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), but for wall loss in our experiment, we used a measured loss of SO₂ of 11%. A proportion to condensing on the existing particles (Faerosol denoted in Figure S4-3) associates with the condensation sink (CS). The details of aerosol CS calculation were available in a previous paper (Salimi et al., 2015). Aerosol variation with respect to time was due to the existing particles concentration variation. About 20~70% 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 fraction of low-volatility gases that were not condensed in the PAM reactor was higher for organic-dominated case (~40%) than sulfate-dominated case (~30%) because of greater CS in latter than former.

For conversion of SO₂ to sulfate, the fraction of additional OH reaction-induced loss was set to 0 because of no more reactions between SO₂ and OH as described in Palm et al. (2016). The estimated fraction of sulfate condensation on existing particles was in the range of 40~90% and the rest were expected to be lost by walls and exit the reactor without being condensed.



[Figure S5-1. Fractional loss of SO₂ (upper) and condensable organics (down) in PAM reactor]

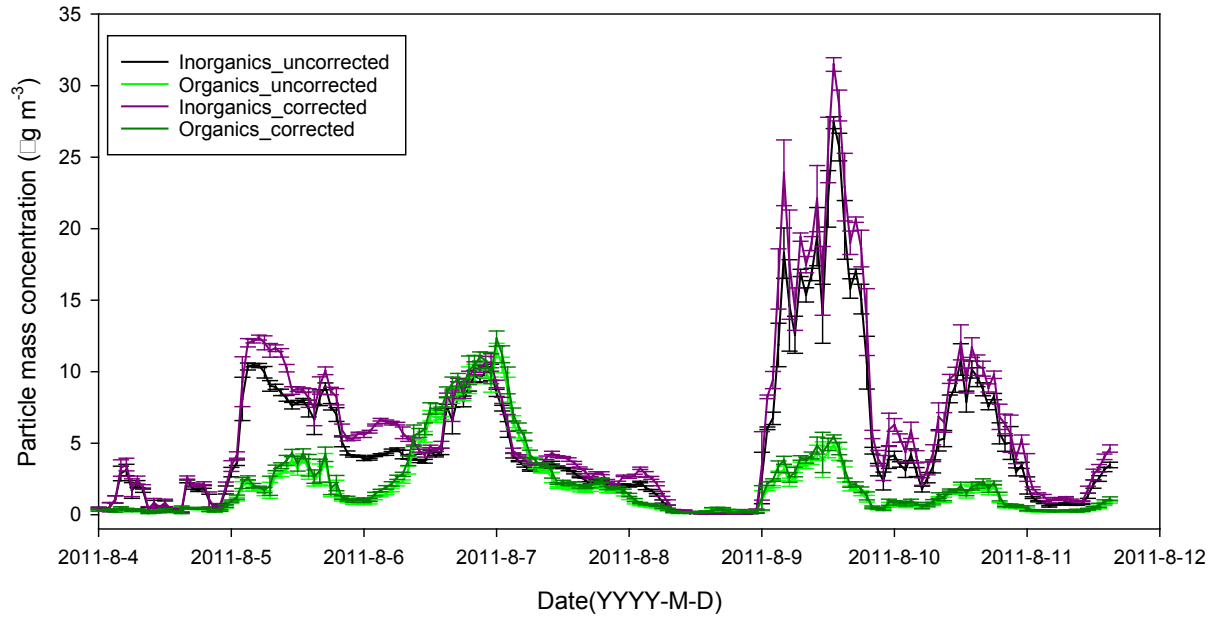
Supplements 6. Correction of the particle mass concentration in PAM reactor with condensation loss

We corrected the particle mass concentration measured in PAM reactor with condensation loss by the exiting the reactor and the wall. For AMS measurement, we used a loss of sulfate for sulfate, nitrate, ammonium and chlorine concentration and used a loss of organics for organics concentration. For SMPS measurement, we used a composition dependent loss,

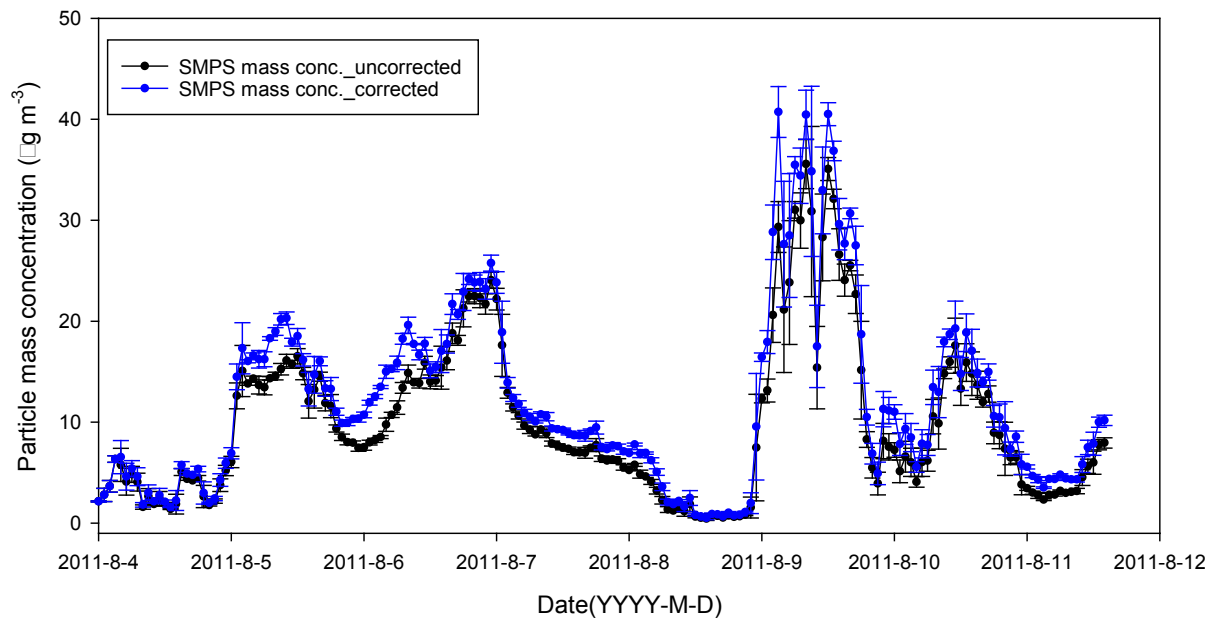
$$\left[\frac{\text{organics}}{\text{organics} + \text{inorganics}} \right] \times \text{organics loss} + \frac{\text{inorganics}}{\text{organics} + \text{inorganics}} \times \text{sulfate loss}$$
 for the total particle mass concentration. The figure S6 shows the uncorrected and corrected particle

mass concentration in PAM reactor. The errors are 2σ confidence. Note that the correction range of the particle mass concentrations was mostly overlapped with the error range.

AMS particle mass concentration loss correction



SMPS particle mass concentration loss correction



(7) *Supp. Info., P1: the statement “We calculated the predicted sulfate formation with measured SO₂ concentrations, assuming that all SO₂(g) was converted to sulfate(p) by reaction with OH inside the PAM reactor” indicates that this analysis was not performed correctly. At an OH_{exp} of 4.6 equivalent days, the fraction of SO₂ consumed should be $1 - \exp(-4.6/8.1) = 40\%$ of the SO₂, not 100% of the SO₂. This seems like a major error, which when corrected will result in a slope of ~3 in Figure S1 (before correcting the other error discussed below).*

[Response]

Thank you for the comment. We modified the supplements based on the 43% of SO₂ consumption (at 4.6 days of OH exposure days), inclusion of negative SO₄ enhancement to the scatter plot, and a new regression method of Total Least Squares Regression. We used the total least squares regressions (<http://www.real-statistics.com/regression/total-least-squares/>), which minimizes the sum of the squared Euclidean distances from the points to the regression line similar to orthogonal distance regressions.

We modified the S4 in the supplements as follows.

“Supplements 4. Comparison between calculated and measured sulfate formation in PAM reactor

We calculated the sulfate formation using SO₂ measurements from sampling through and bypassing the PAM chamber, assuming that SO₂(g) was converted to sulfate(p) by reaction with OH inside the PAM reactor. For this estimation, we adopted 2 ppbv offset for ambient SO₂ measurement, SO₂ gas loss of 11 % in the PAM reactor, and condensable sulfate loss by wall and exiting the reactor of about 38%. At 4.6 days of OH exposure, 43% of SO₂ will be consumed in the PAM reactor based on $k_{\text{SO}_2+\text{OH}} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$. The measured SO₄ enhancement was obtained by subtracting the ambient SO₄ concentration from the SO₄ concentration measured in PAM chamber. For this comparison, AMS measurements were averaged over an hour in accordance with the SO₂ measurement resolution. The figure below compares the measured and predicted SO₄ enhancement, showing that the measured explained well the expected (slope = 1.16 and an intercept = -0.137. We used the total least squares regressions (<http://www.real-statistics.com/regression/total-least-squares/>), which minimizes the sum of the squared Euclidean distances from the points to the regression line similar to orthogonal distance regression. The correlation between the measured and predicted was worsened by the very low measured SO₄ enhancement against a wide range of expected sulfate enhancement. Not to mention, uncertainty was involved in the measurement of SO₂ concentration, loss assessment of SO₂ and condensable sulfate, and the AMS measurement of particles smaller than 50 nm.

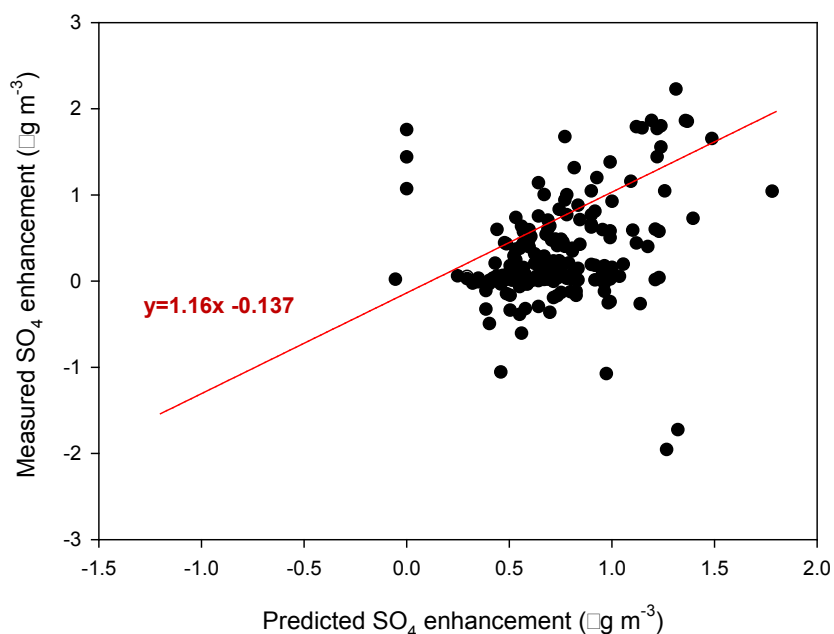


Figure S4-1. Measured SO₄ enhancement vs. calculated SO₄ enhancement.

(8) Fig S1: it is erroneous to remove the values with negative SO₄ enhancement. Seeing some negative values is normal due to measurement noise under low SO₂ concentrations. But removing these negative values will bias the regression analysis. Thus needs to be redone with those measurements included.

[Response]

Please see the responses of comment (7), (8) and (20).

(9) The figure shown on p20 shows that the mass distribution peaked at the upper limit of the SMPS measurement, which is close to the upper limit for the AMS measurement as well. This indicates a substantial limitation of the measurement size range. Some changes in particles before and after the reactor may actually be due to this effect, for example if particles grow out of the size of the SMPS / AMS, the enhancement in mass will not be counted. This effect needs to be described in the experimental section, and its effects assessed.

[Response]

In Figure 5, the mass peaks are shown at 200~300 nm. The SMPS counts particles at 10.4 nm ~ 469.8 nm, which is the size range we were able to observe the change in number and mass. Thus,

particles between 500-1000 nm were missing in SMPS. AMS ToF, however, measures the particles concentration up to 1 μm in diameter as shown in Figure 6. When analyzing the data, we compared SMPS and AMS results and extracted consistent results only. In Figure 6, the difference in composition between the PAM-processed and ambient air is similar in tendency for size range larger than 300 nm up to 1000 nm. Thus, the discussion focused on the particles in the range shown by SMPS.

L152, added the sentence. “Due to the size range of SMPS measurements, discussion of the enhancement or loss of aerosols is limited to particles smaller than 500 nm in diameter.”

(10) L113: the use of a PM1.0 cyclone upstream of an AMS/SMPS is very unusual. Both AMS and SMPS have approximate PM1 size cuts already, so normally a PM2.5 cyclone is used. Otherwise the PM1 cut is imposed twice, and results in PM0.75 transmission, and the concentrations will be lower than those measured without a PM1 cyclone. This should be mentioned in the revised manuscript. Referring to the AMS measurements as “PM1” is incorrect under these conditions.

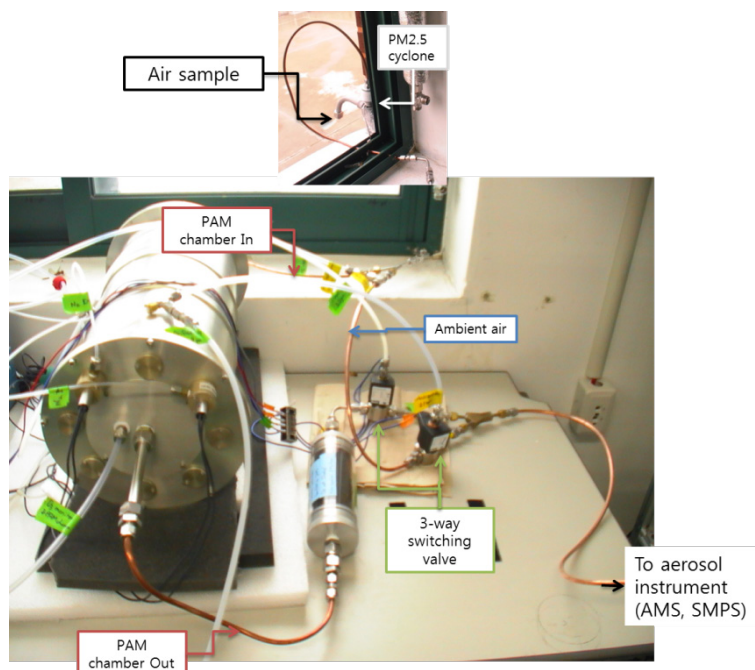
[Response]

We used a PM2.5 cyclone as shown the photo in the 1st response page 20 and “PM1.0 cyclone” was an error. Thank you for finding this error. So, we corrected it. We also added the sampling setup photo taken during the experimental period in the supplements.

L113, modified from “Ambient air sampled using a PM_{1.0} cyclone and was ...” to “Ambient air sampled using a PM_{2.5} cyclone and was ...”.

Supplements

“S1. The sampling setup of the PAM reactor



[Figure S1. The PAM reactor sampling setup]

In our experimental setup, the PAM reactor was installed beside the window in the laboratory and ambient air was pulled through a copper tubing (~ 30 cm) from PM2.5 cyclone outside the laboratory. The ambient air from the PM2.5 cyclone was introduced into the PAM reactor through an inlet plate and endcap and then rapidly dispersed before entering the reactor through a Silconert-coated (Silcotech, Inc.) stainless steel screen. Aerosol sampling tubes were 1/4 inch OD copper and stainless steel tubes and gas sampling tubes were 1/4 inch OD PTFE Teflon tubes. The ambient and PAM reactor through air samples were alternately switched to the aerosol measurement instruments by using a 3-way switching valve every 6 minute. When PAM aerosol was introduced in the measurement instruments, ambient aerosol was bypassed to outside and vice versa. The total flow rate to the PAM reactor and ambient sampling was set to 5 liters per minute. We tried to set up the PAM reactor as close as possible to the PM2.5 cyclone and the AMS/SMPS instruments as shown in the figure above.”

(11) The conclusion in the abstract that “... SO₂ is an unquestionably primary precursor of secondary aerosol in northeast Asia. In comparison, the contribution of organics to secondary aerosols is more variable during transport in the atmosphere” is still not justified. It is clear (from this study and many others) that SO₂ is an important secondary precursor of secondary aerosols in this region. But the present study has limitations, in particular the use of a single very high OH_{exp} and the use of inlets, that limit its ability to say much about the relative importance of SO₂ and organic precursors contributing to secondary aerosols in the real atmosphere. This needs to be clearly acknowledged, emphasizing the strong result (SO₂ is important) without stating a conclusion for which there is no

evidence from this study (SO₂ is more important than organic precursors).

[Response]

In the revised manuscript, we tried to clarify the conditions and limitation of the study and accordingly, modified the relevant parts enough not to mislead the audience. It is one time experiment on the ground and thus, the audience would know better than to generalize these results. The airborne experiment provides a unique chance to observe the whole atmosphere and its results are excellent materials to diagnose the current state of the atmosphere. In the study region, the meteorological condition varies dynamically recently with a tangible annual variation. Furthermore, the environmental change in China has been so rapid. For example, SO₂ concentration has been reduced since 2012, which was well presented in the last 2017 AGU fall meeting. Organics would play even more important role in SOA formation (e.g., Tröstl et al., 2016), compared to SO₂ in the study region. Therefore, it is virtually unlikely that someone generalizes the results of this study and disregards the importance of organic aerosols.

L32~47, we revised the abstract as follows. “. Conversely, during the organics-dominated episode, the m/z 44 component corresponding to further oxidized organics increased with a shift toward larger sizes, while during the sulfate-dominated episode, the m/z 44 component slightly decreased along with m/z 43. This difference suggests that oxidation in the PAM chamber was primarily by gas-phase oxidation and partitioning for re-equilibrium between the gas and particle phases in the organics-dominated episode and by heterogeneous oxidation in the sulfate dominated episode. It is not possible to quantify the maximum possible organic mass concentration for either episode because only one OH exposure of 4.6 days was used, but it is clear that SO₂ was a primary precursor of secondary aerosol in northeast Asia especially during the long range transport from China. In addition, nitrate evaporated in the PAM reactor as sulfate was added to the particles. These results suggest that the chemical composition of aerosols and their degree of photochemical aging particularly for organics, are also crucial in determining aerosol mass concentrations.”

L497~501, modified to the followings “In this study, it was not possible to estimate the potential contribution of organics in organic-dominated and sulfate-dominated case. However, the comparison of these two episodes indicates that organics and nitrate are likely to be relatively more important in near-source regions while sulfate is probably dominant in areas far from the source.”

Tröstl, et al., The role of low-volatility organic compounds in initial particle growth in the atmosphere, Nature, doi:10.1038/nature18271, 2016.

Other Important Comments

(12) *Experimental methods: the diameter, material, length, flow rate, and flow regime (laminar or turbulent) of all the inlet tubes is still not given in the manuscript. This should include the tube between the cyclone and PAM input, and the tube(s) between the PAM output and the AMS & SMPS measurements.*

[Response]

We added the details of experimental setup in the manuscript as follows and more details in the supplements as shown in the response (10).

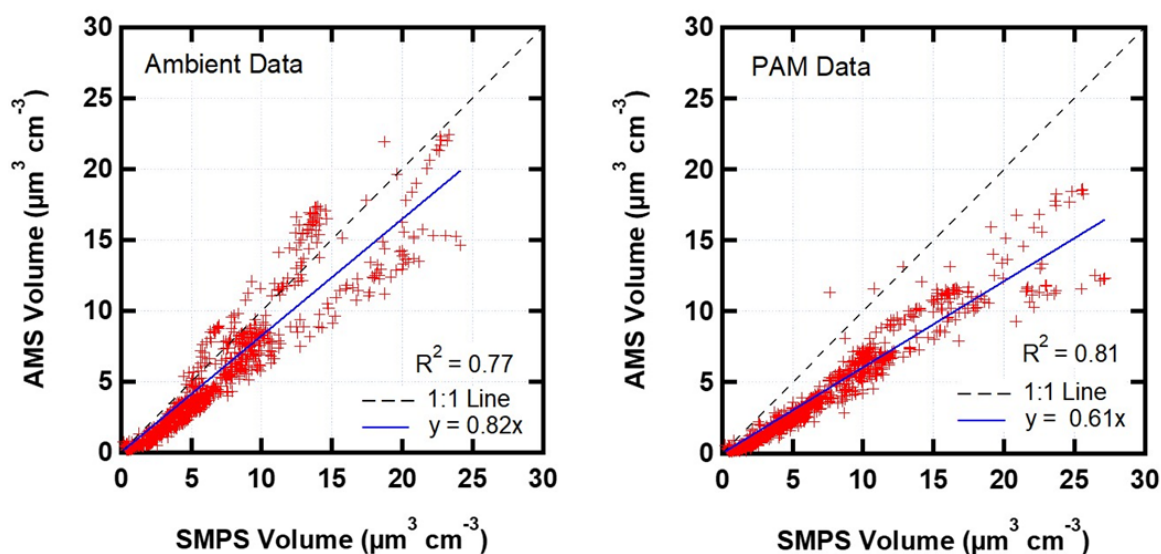
L123, modified from “For sampling, copper or stainless steel tubing was used ...” to “For aerosol sampling, copper or stainless steel 1/4 inch OD tubes were used ...”.

L124, added the sentences “The 1/4 inch PTFE Teflon tubes were used for the bypass flow. The total flow rate through the both ambient sampling and PAM reactor was 5 liters per minute. The flow in the PAM reactor was laminar (Reynolds number <50), and aerosols were sampled at the center line.”

L133, modified from “by nitrogen to prevent heat and ...” to “by nitrogen with a flow rate of ~50 sccm to prevent O₃ from building up inside the sleeves. This flow might be slightly low enough to prevent all heat being transferred from the lamps to the air stream in the chamber.”

(13) *P45 of the responses states “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.” This mixes apples and oranges. Internal mixing is indeed expected at remote sites like this one. But the density of the internally mixed particles will change substantially with composition. Estimating that density is literature one line of code, and given the limited time required, it does not seem acceptable to this reviewer to say that it is outside the scope of the manuscript.*

[Response]



With composition dependent density, the above figures are produced. But, SMPS mass is mostly greater than AMS mass concentration. The possible reasons can be the contribution of EC (elemental carbon) or soil particles. The difference between AMS measured particle mass concentration and SMPS measured particle mass concentration was greater in sulfate-dominated episode than in organic-dominated episode (as shown in Table 1 and Fig. 2(c)). It is possibly because that the particles not being detected in AMS such as EC (as shown in Fig. 4) were included relatively more in sulfate-dominated episode than in organic-dominated episode. For the additional explanation and manuscript revision, please see the response (1).

(14) Page 6: the reason why a single OHexp was used is still not stated in the revised paper. There is a long text in the responses, which seems to boil down to the fact that it was too difficult to do so experimentally at the time. This can just be stated in the paper, and serves to inform others that it is not that such variation was not considered important, but that it was not possible to implement it for this study.

[Response]

We modified the manuscript as follows.

L144, added the sentence. "Contrary to other studies (Ortega et al., 2016; Palm et al., 2016), we designed the experiment as simple as possible with a single OH exposure considering the dynamic change of meteorological conditions in the study region, a remote island."

(15) Supp. Info. p.1. The statement that attributes the high scatter in Fig. S1 to “mainly because the comparison was made for hourly averaged concentrations of AMS even though measurement was alternately made every 6 minutes between the ambient and PAM air” makes no sense. Averaging the AMS measurement to the same time resolution as the SO₂ measurement should reduce scatter, not increase it. It appears instead that the scatter is dominated by the low accuracy and precision of the available SO₂ measurement. The erroneous statement should be removed, and this section should be revised.

[Response]

We agree with you about the uncertainty does not come from the hourly averaged concentration because hourly average will smooth out the variation of every 6 minutes. We modified the relevant sentences as follows and the entire contexts regarding the calculated and measured SO₄ comparison were modified as seen in response (7).

Supplements,

L17, we removed the sentence “It is mainly because the comparison was made for hourly averaged concentrations of AMS even though measurement was alternately made every 6 minutes between the ambient and PAM air.”

(16) The figure shown on page 20 of the responses, showing the losses of particles through PAM when the lights were off, must be added to the Supp. Info., as it is an important characterization of the reactor that is needed in order to compare with other studies. At present the figure is shown in the responses, but is not included in the revised manuscript or Supp. Info. Figures that are left only in the responses are very difficult to find, as most readers will only look at the final published paper. Thus it is the responsibility of the authors to document all the important details on the paper itself, and not only in the responses.

[Response]

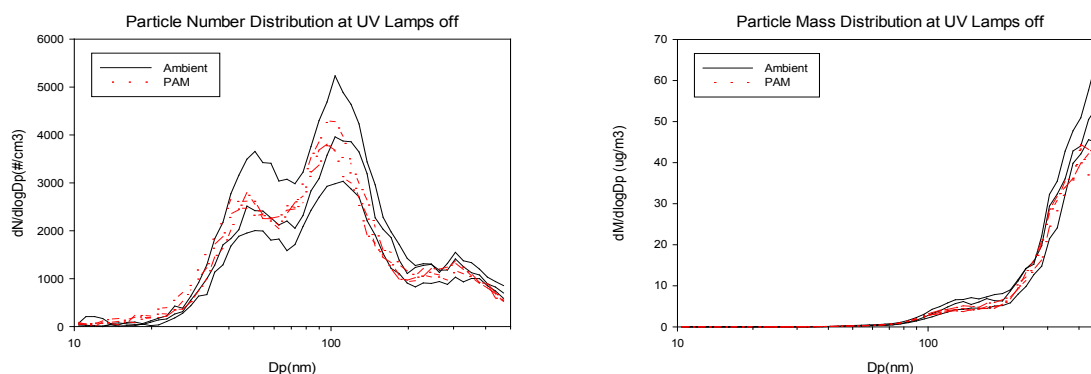
We provided more details and figures in the response to question (1) and added more detailed information to the supplement information as follows.

Supplements, added the wall loss test contexts.

S2. The wall loss test

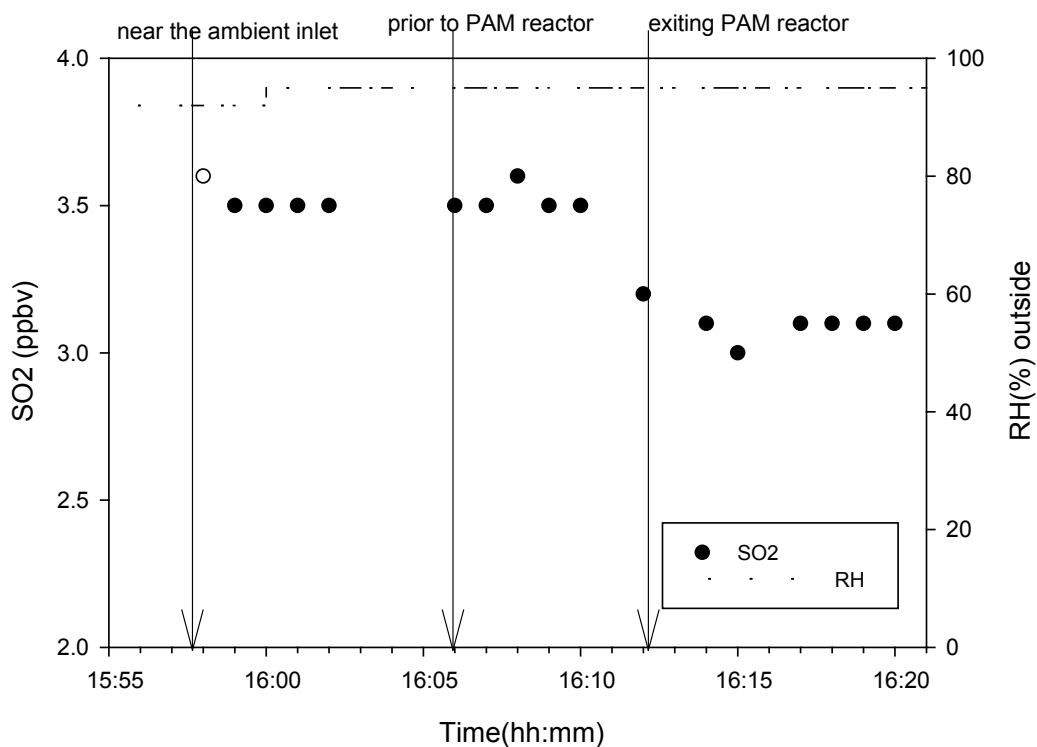
We conducted the loss test for 1) ambient aerosol and 2) SO₂ during the experiment in 2011. Its results are discussed below and the LVOCs fate is calculated using the method in Palm et al. (2016).

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 $13.1 \pm 2.06 \mu\text{g m}^{-3}$ and $11.6 \pm 0.46 \mu\text{g m}^{-3}$, 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 S2-1. 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 $11 \pm 7 \%$. There was loss in the sampling inlet line. The detailed information on SO_2 measurement is given below.



[Figure S2-2. SO₂ loss test results in PAM reactor]

(17) Similarly the figure about the SO₂ losses needs to be added to the Supp. Info. In addition, SO₂ losses in tubing and the PAM reactor are known to strongly depend on RH. So at a minimum the RH for the tests shown in the figure needs to be stated.

[Response]

We added the SO₂ loss test results with RH measured outside in supplements as shown in the response (16) above. Please see the response above.

(18) L133: The flow rate of N₂ through the sleeves needs to be given. The temperature increase may not be the same as in past studies, if a different N₂ flow rate was used.

[Response]

We used about 30~50 standard cc per minute (sccm) for nitrogen purging in the UV lamps housing. Thus, we modified the manuscript as follows.

L133, modified from “by nitrogen to prevent heat and ...” to “by nitrogen at ~50 sccm to prevent heat and ...”

(19) L142: no reference or description is given for the “chemistry model” (discussed as “oxidation chemistry model” in the text quoted in the responses, although the word “oxidation” is missing from the revised manuscript). The references at the end of the sentence appear to refer to OH reactivity. A description or reference for the model should be given (ideally after the word “model” in that sentence.

[Response]

We used an oxidation chemistry model that is the basis for the model used by Peng et al. (2016). We gave the model to the Jimenez group; they modified and improved some of the features, resulting in the model used by Peng et al. (2016) and sent it back to us; we added the improvements to our version; and then we compared the results from the two models and found that they were the same.

L142, modified from “... using the chemistry model with ...” to “... using the oxidation chemistry model (Peng et al., 2016) with ...”.

(20) Figure S1: it is unclear whether an appropriate regression method has been used for this figure. Since both the X and Y variables have errors, it is not appropriate to use standard regression, which assumes that only the Y variable has errors. A method such as orthogonal distance regression should be used, and this should be stated in the paper. By eye it seems to me that an ODR fit would be significantly steeper than the one shown. The uncertainties on the fitting parameters that the fitting function should provide should also be given. (But overall this is not a bad comparison, given how poor the available SO₂ data were).

[Response]

We used the total least squares regressions (<http://www.real-statistics.com/regression/total-least-squares/>), which is minimizing the sum of the squared Euclidean distances from the points to the regression line similar to orthogonal distance regressions We responded the comment (7), (8), (20) with the same contents because they are all linked together. Please see the response of comment (7).

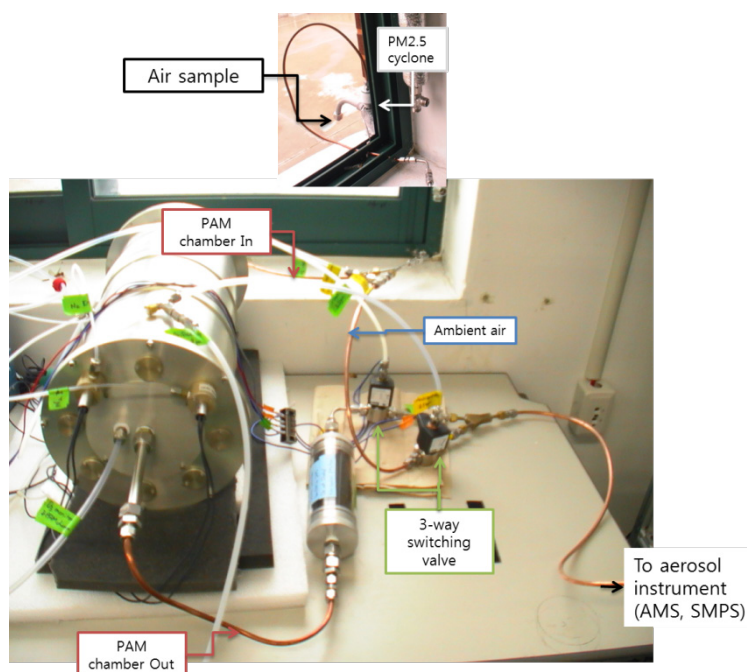
(21) The experimental setup shown on p36 of the responses should be added to the Supp. Info. This type of information is invaluable for future readers of the paper.

[Response]

We added a sampling setup in supplements as follows.

Supplements.

“S1. The sampling setup of PAM reactor



[Figure S1. The PAM reactor sampling setup]

In our experimental setup, the PAM reactor was installed beside the window in the laboratory and ambient air was pulled through a copper tubing (~ 30 cm) from PM_{2.5} cyclone outside the laboratory. The ambient air from the PM_{2.5} cyclone was introduced into the PAM reactor through an silconert—coated (Silcotech, Inc.) inlet plate and endcap and then rapidly dispersed before entering the reactor through a Silconert-coated stainless steel screen. Aerosol sampling tubes were 1/4 inch OD copper and stainless steel tubes and gas sampling tubes were 1/4 inch OD PTFE Teflon tubes. The ambient and PAM reactor through air samples were alternately switched to the aerosol measurement instruments by using a 3-way switching valve every 6 minute. When PAM aerosol was introduced in the measurement instruments, ambient aerosol was bypassed to outside and vice versa. The total flow rate to the PAM reactor and ambient sampling was set to 5 liters per minute. We tried to set up the PAM reactor as close as possible to the PM_{2.5} cyclone and the AMS/SMPS instruments as shown in the figure above.”

(22) L410: the underwood et al. reference reports results for mineral dust. There are chemical pathways available for dust that are not active for the sulfate-organic-nitrate aerosols of the submicron mode, that are studied here. I recommend that this text and reference are removed to avoid creating

confusion.

[Response]

We modified the words and removed the discussion about heterogeneous NO₂ reaction on the dust particles, because the heterogeneous reaction on the dust particles were mostly occurred in micrometer-size dusts such as Asian Dust event.

L408., modified from “A plausible source of HNO₃(p) in the PAM reactor is the deposition of gaseous HNO₃(g) or heterogeneous reaction of NO₂ on the particle surfaces (Underwood et al., 2001), even though the latter is not clearly understood.” To “A plausible source of HNO₃(p) in the PAM reactor is the formation of gaseous HNO₃(g) and deposition on the particles.”

L839, removed the reference “Underwood et al.,”.

Minor items and Typos

L94: possible typo on Lamb

[Response]

L94, corrected to “(Lamb et al., 2015; ...)”

L289, corrected to “(Lambe et al., 2012)”

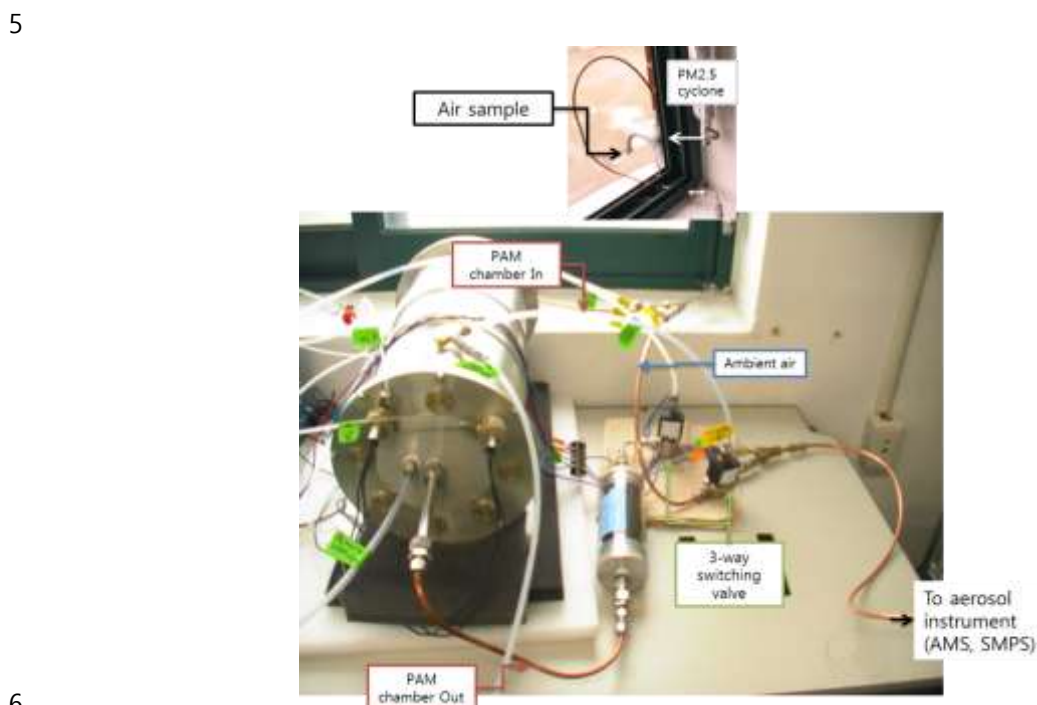
New Figure 6 has a typo on “organics” on the right side.

[Response]

Thank you. We corrected the typo.

1 Supplements for Kang et al., "Photochemical aging of organic and inorganic ambient
2 aerosol from the Potential Aerosol Mass (PAM) reactor experiment in East Asia"

3
4 S1. The sampling setup of the PAM reactor



[Figure S1. The PAM reactor sampling setup]

9 In our experimental setup, the PAM reactor was installed beside the window in the
10 laboratory and ambient air was pulled through a copper tubing (~ 30 cm) from PM2.5
11 cyclone outside the laboratory. The ambient air from the PM2.5 cyclone was introduced
12 into the PAM reactor through an inlet plate and endcap and then rapidly dispersed
13 before entering the reactor through a Silconert-coated (Silcotech, Inc.) stainless steel
14 screen. Aerosol sampling tubes were 1/4 inch OD copper and stainless steel tubes and
15 gas sampling tubes were 1/4 inch OD PTFE Teflon tubes. The ambient and PAM reactor
16 through air samples were alternately switched to the aerosol measurement instruments
17 by using a 3-way switching valve every 6 minute. When PAM aerosol was introduced in
18 the measurement instruments, ambient aerosol was bypassed to outside and vice versa.
19 The total flow rate to the PAM reactor and ambient sampling was set to 5 liters per
20 minute. We tried to set up the PAM reactor as close as possible to the PM2.5 cyclone and
21 the AMS/SMPS instruments as shown in the figure above.

22

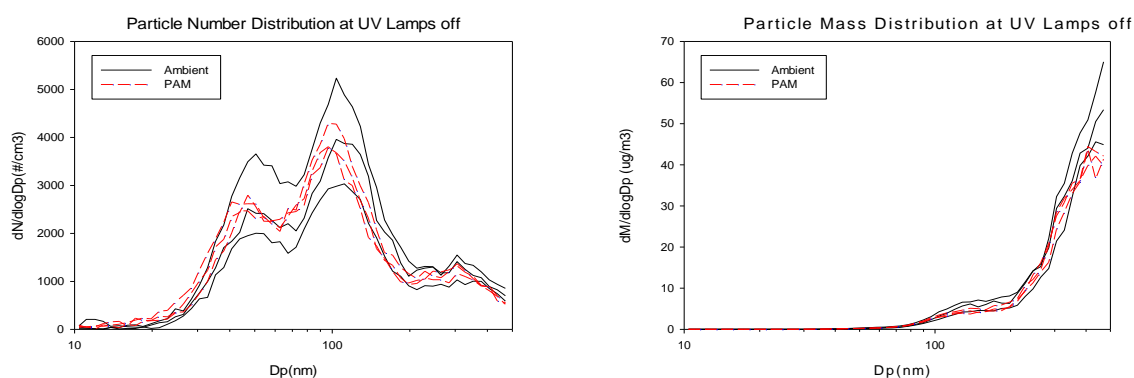
23 S2. The wall loss test

24 We conducted the loss test for 1) ambient aerosol and 2) SO₂ during the experiment in
25 2011. Its results are discussed below and the LVOCs fate is calculated using the method
26 in Palm et al. (2016).

27

28 First, PAM reactor was run for ambient air without lamp-on and the SMPS signals of air
29 entering and exiting the PAM reactor were compared to estimate the physical loss of
30 aerosol to the wall. In experimental setup, ambient air entering the PAM reactor was
31 introduced into SMPS alternately with air exiting the PAM reactor. For the test, this cycle
32 was repeated three times. Because entering and exiting air was not simultaneously
33 measured, there could be some error caused by the variation of ambient air. However,
34 there was no detectable variation in ambient air, judged from gaseous concentrations for
35 less than an hour of test period. The mass of ambient aerosol and aerosol exiting the
36 PAM reactor (without lamps on) was $13.1 \pm 2.06 \mu\text{g m}^{-3}$ and $11.6 \pm 0.46 \mu\text{g m}^{-3}$,
37 respectively, resulting in about 12 % of aerosol mass in the PAM reactor (Figure below).
38 However, the decrease in mass was due to the loss of pre-existing aerosols but not newly
39 formed secondary aerosols from condensable gases.

40



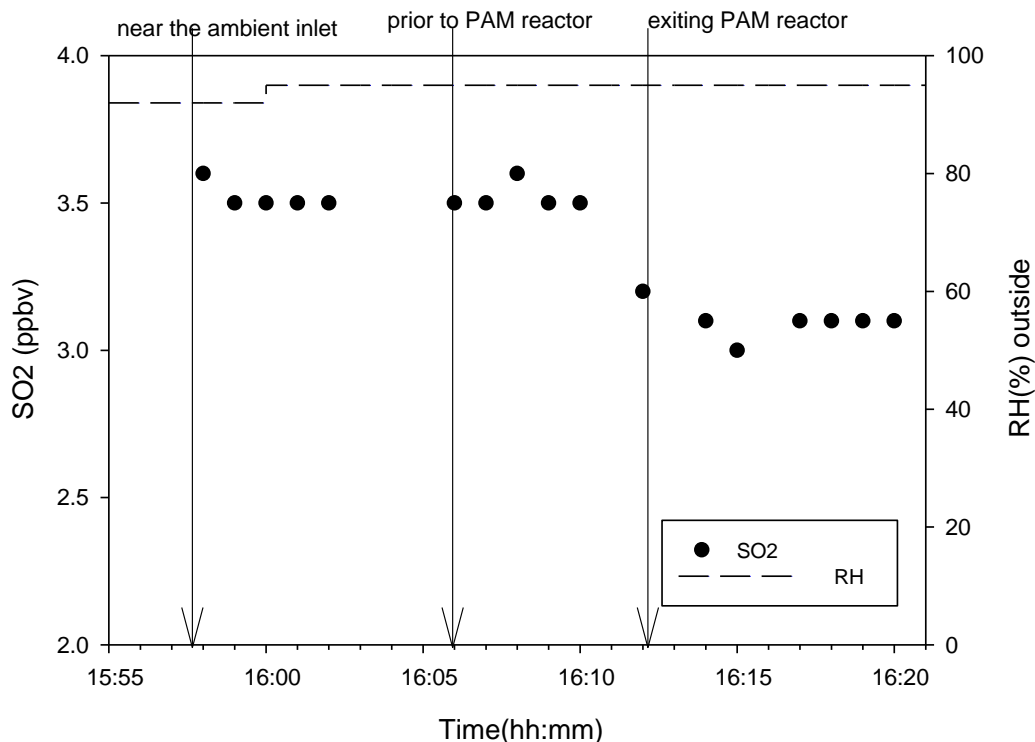
41

42 [Figure S2-1. SMPS particle number distribution (left) and mass distribution (right) for wall
43 loss test. Red and black color indicate air exiting and entering the PAM reactor.]

44

45 Second, we have tested SO₂ loss by the wall during the experiment. For this test, we used
46 ambient air instead of standard SO₂ mixtures in a wide range of concentrations. When air
47 was pulled through the PAM reactor inlet plate, SO₂ was measured first for ambient air in
48 front of the inlet, and then before it entered and after it exited the PAM reactor (Figure

49 below). SO₂ concentrations prior to and after the PAM reactor were 3.5 ppbv and 3.1
 50 ppbv, respectively, leading to SO₂ loss of 11 ± 7 %. There was loss in the sampling inlet
 51 line. The detailed information on SO₂ measurement is given below.



52
 53 [Figure S2-2. SO₂ loss test results in PAM reactor]

54

55 S3. Calibration of OH exposure in the PAM reactor

56 We used the OH exposure calibration which was done with a mixture of pure air and
 57 SO₂(g) in the laboratory by Kang et al. (2011a). The full manuscript can be found in J.
 58 KOSAE Vol. 27, No. 5 (2011) pp. 534~544, Journal of Korean Society for Atmospheric
 59 Environment, DOI: <http://dx.doi.org/10.5572/KOSAE.2011.27.5.534>.

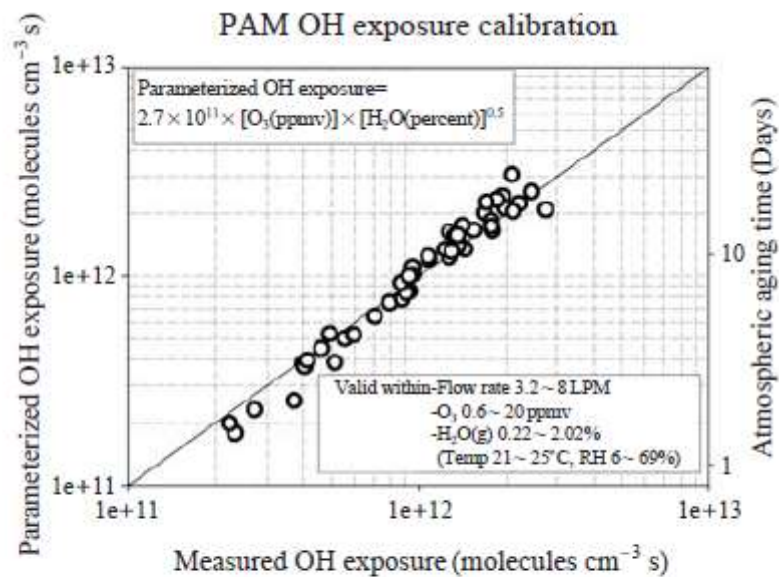


Fig. 2. OH exposure calibration curve and the empirical formula for the OH exposure. The absolute uncertainty in OH exposure is estimated to be $\pm 21\%$ at the 2σ confidence level.

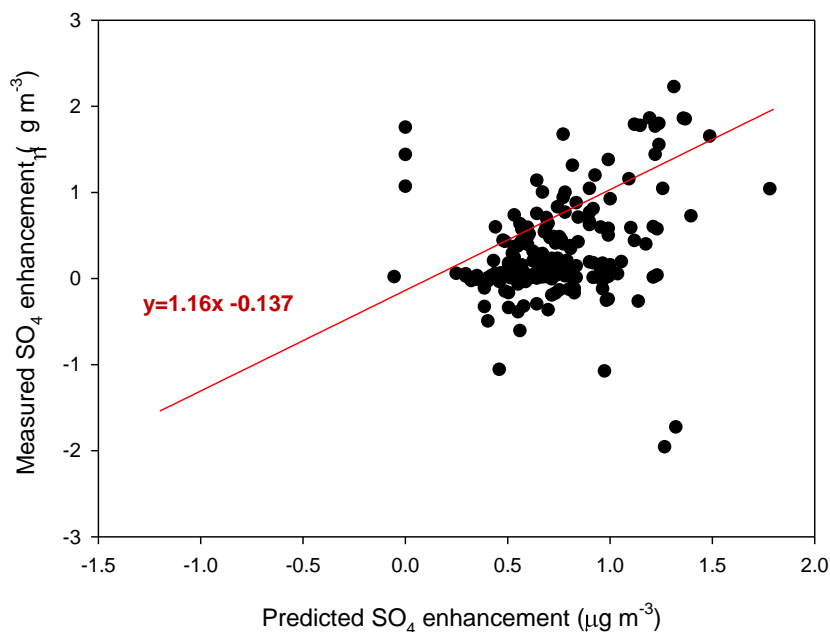
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63

[Figure S3-1. OH exposure calibration curve for this PAM reactor. (cited from Kang et al., (2011a)]

64 S4. Comparison between calculated and measured sulfate formation in PAM reactor
 65 We calculated the sulfate formation using SO_2 measurements from sampling through and
 66 bypassing the PAM chamber, assuming that $\text{SO}_2(\text{g})$ was converted to sulfate(p) by
 67 reaction with OH inside the PAM reactor. For this estimation, we adopted 2 ppbv offset
 68 for ambient SO_2 measurement, SO_2 gas loss of 11 % in the PAM reactor, and condensable
 69 sulfate loss by wall and exiting the reactor of about 38%. At 4.6 days of OH exposure, 43%
 70 of SO_2 will be consumed in the PAM reactor based on $k_{\text{SO}_2+\text{OH}} = 1 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.
 71 The measured SO_4 enhancement was obtained by subtracting the ambient SO_4
 72 concentration from the SO_4 concentration measured in PAM chamber. For this
 73 comparison, AMS measurements were averaged hourly to be consistent with the SO_2
 74 measurement. The figure below compares the measured and predicted SO_4 enhancement,
 75 showing that the measured explained well the expected (slope = 1.16 and an intercept =
 76 -0.137. We used the total least squares regressions (<http://www.real-statistics.com/regression/total-least-squares/>), which is minimizing the sum of the squared
 77 Euclidean distances from the points to the regression line similar to orthogonal distance
 78

79 regression. The correlation between the measured and predicted was deteriorated by the
80 very low measured SO₄ enhancement against a wide range of sulfate expected to be
81 enhanced. Not to mention, uncertainty was involved in the measurement of SO₂
82 concentration, loss assessment of SO₂ and condensable sulfate, and the AMS
83 measurement of particles smaller than 50 nm.

84
85



86
87 Figure S4-1. Measured SO₄ enhancement vs. calculated SO₄ enhancement.

88
89

90 S5. Estimating the condensation sink.

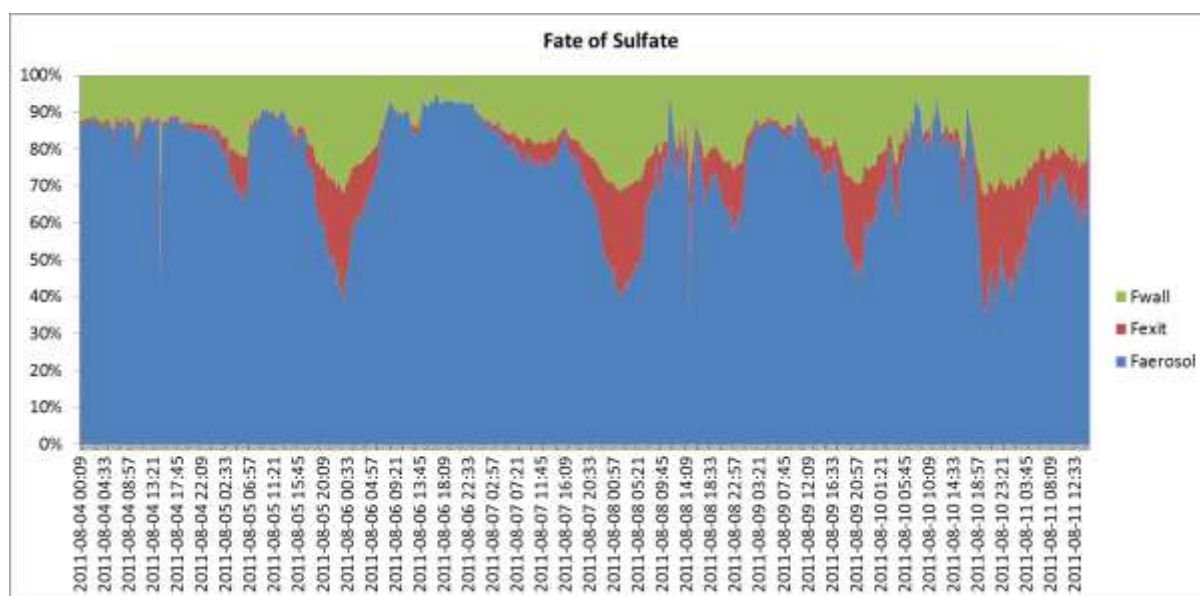
91 In addition, we estimated the loss of condensable gases by wall deposition, exiting the
92 reactor, and further OH reaction competing with condensation on existing particles,
93 based on Palm et al. (2016) and model posted in <https://sites.google.com/site/pamwiki/hardware/estimation-equations>. Although the model calculating the possible loss of
94 condensable gases was developed a couple of years after this experiment was performed,
95 the physical setup of our PAM reactor was very similar to the ones used in Palm et al.
96 (2016), Ortega et al. (2013), and (2016).

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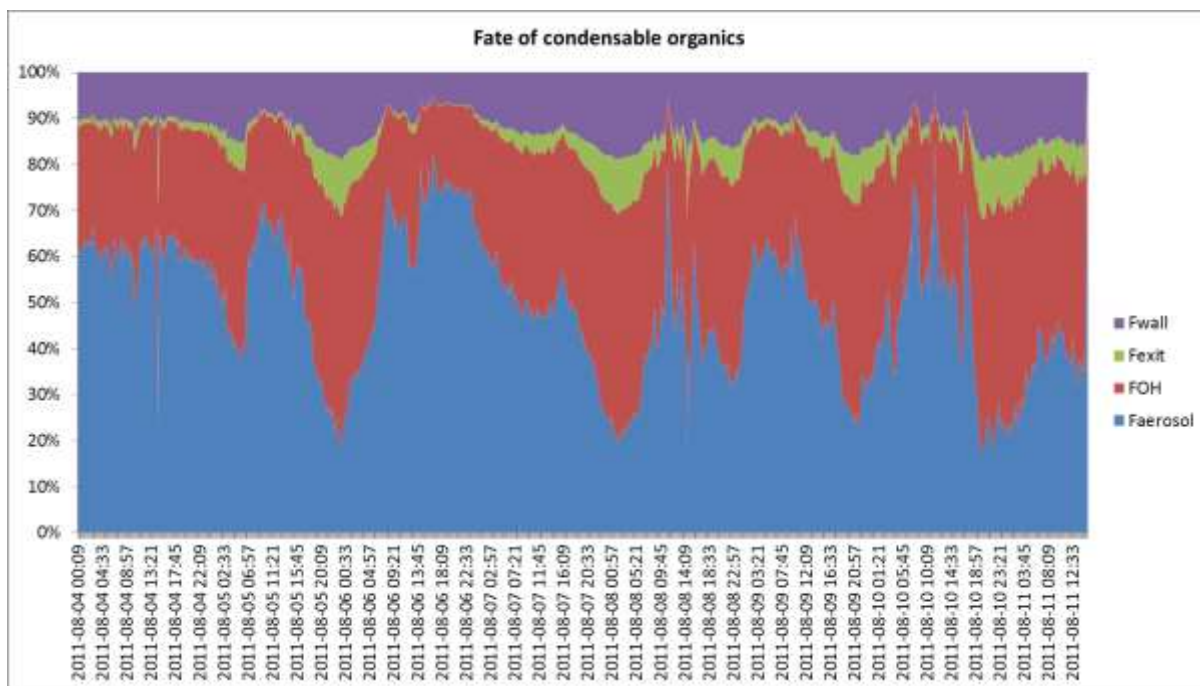
We used the same constants as those in Palm et al. (2016), but for wall loss in our

100 experiment, we used a measured loss percentage of SO₂ of 11%. A proportion to
101 condensing on the existing particles (Faerosol denoted in Figure S4-3) associates to the
102 condensation sink (CS). The details of aerosol CS calculation were available in a previous
103 paper (Salimi et al., 2015). Faerosol variation with respect to time was due to the existing
104 particles concentration variation. About 20~70% of condensable organic gases were
105 estimated to be condensed on existing particles, contributing to mass increase in PAM
106 reactor. It is similar to the case of high condensation sink (CS) shown in figure 5 of Palm
107 et al. (2016). In our study the fraction of low-volatility gases that were not condensed in
108 the PAM reactor was higher for organic-dominated case (~40%) than sulfate-dominated
109 case (~30%) because of greater CS in latter than former.
110 For conversion of SO₂ to sulfate, the fraction of additional OH reaction-induced loss was
111 set to 0 because of no more reactions between SO₂ and OH as described in Palm et al.
112 (2016). The estimated fraction of sulfate condensation on existing particles was in the
113 range of 40~90% and the rest were expected to be lost by walls and exit the reactor
114 without being condensed.

115



116

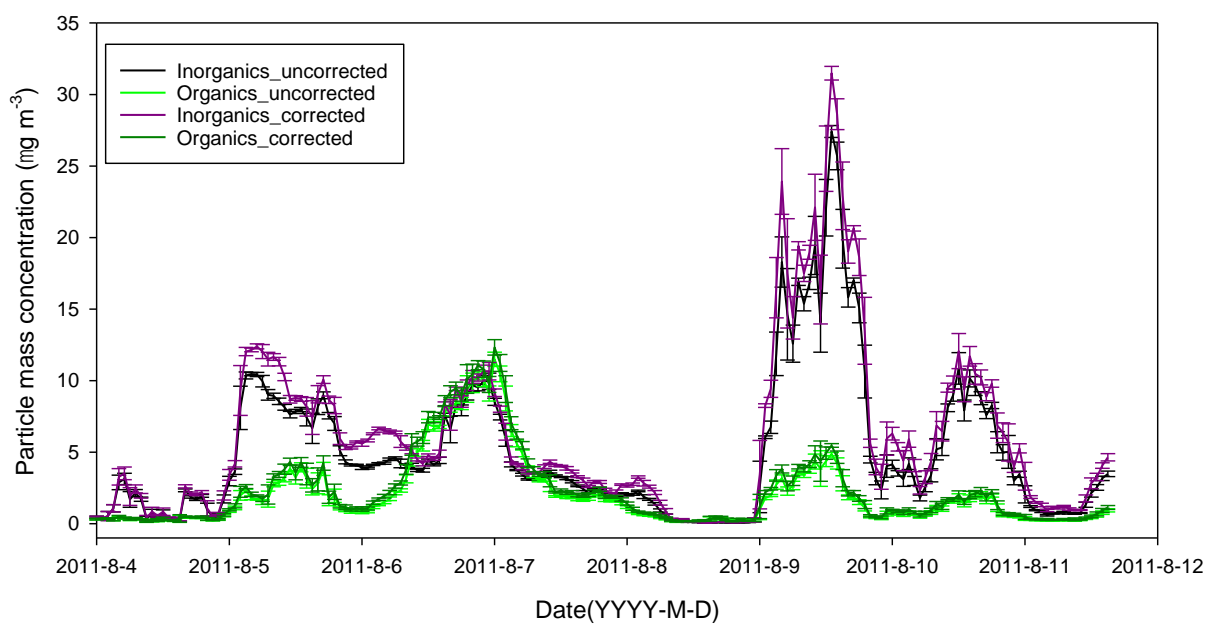


[Figure S5-1. Fractional loss of SO₂ (upper) and condensable organics (down) in PAM reactor]

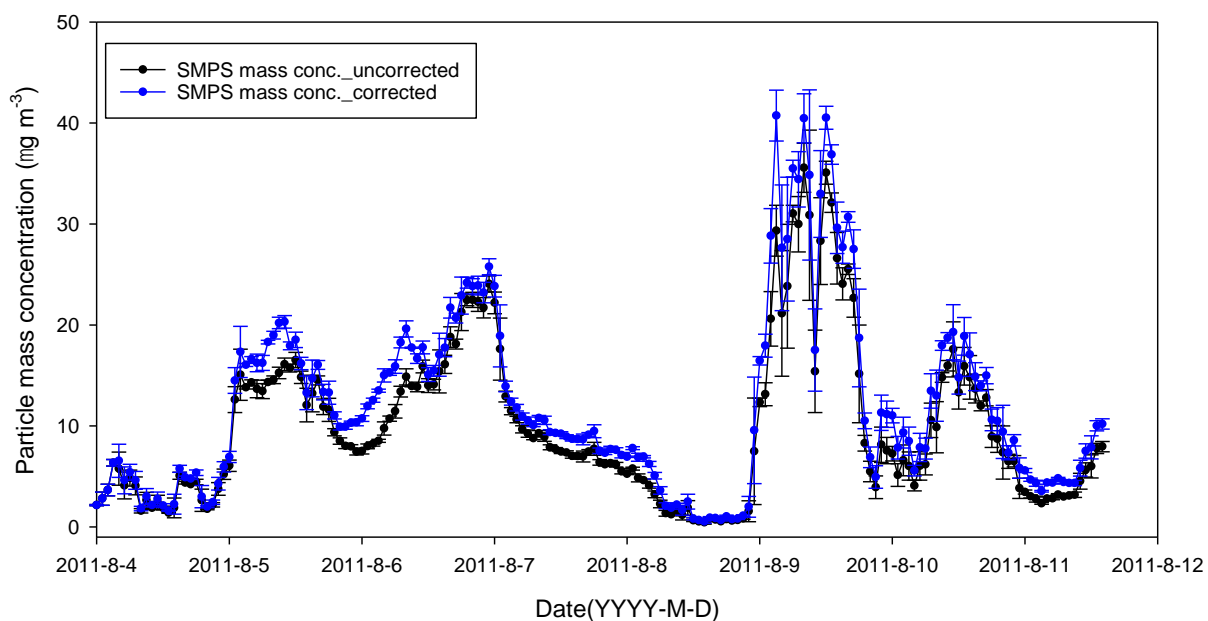
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S6. Correction of the particle mass concentration in PAM reactor with condensation loss
 We corrected the particle mass concentration measured in PAM reactor with condensation loss by the exiting the reactor and the wall. For AMS measurement, we used a loss of sulfate for sulfate, nitrate, ammonium and chlorine concentration and used a loss of organics for organics concentration. For SMPS measurement, we used a composition dependent loss $(\text{organics}/(\text{organics}+\text{inorganics}) \times \text{organics loss} + \text{inorganics}/(\text{organics}+\text{inorganics}) \times \text{sulfate loss})$ for the total particle mass concentration. The figure S6 shows the uncorrected and corrected particle mass concentration in PAM reactor. The errors are 2σ confidence. Note that the correction range of the particle mass concentrations were mostly overlapped with the error range.

AMS particle mass concentration loss correction



SMPS particle mass concentration loss correction



132
133 [Figure S6. Time series of uncorrected AMS and SMPS particle mass concentration
134 and corrected particle mass concentration with condensable gases loss. The errors are 2σ
135 confidence.

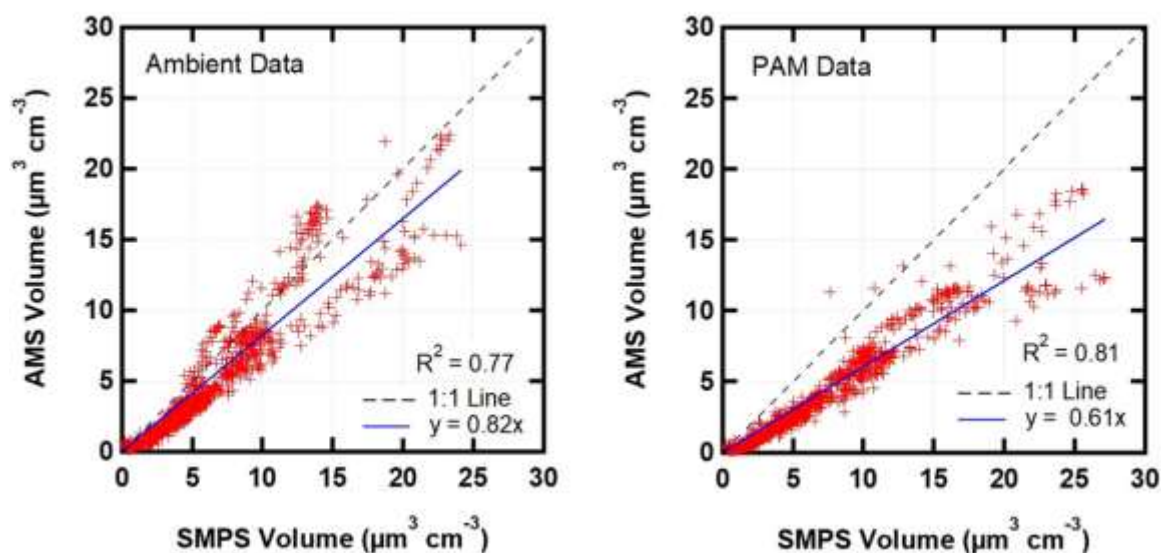
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138 **S7.** A comparison of AMS vs SMPS

139 Aerosol particles volume concentration obtained from AMS and SMPS was compared each other
140 for ambient and PAM aerosol particles. Particle volume concentration from SMPS was directly
141 obtained by the SMPS measurement, and particle volume concentration from AMS was extracted
142 by the measured particle mass concentration divide by composition dependent density.

143 Figure 2(c) in the manuscript is a time series of AMS and SMPS particle volume concentration and
144 the figure S7 here is a scatter plot of AMS and SMPS particle volume concentration. In ambient
145 aerosol particles, the data were generally agreed each other, but SMPS mass concentration was
146 greater than AMS mass concentration. The possible reasons can be the contribution of
147 EC(elemental carbon), sea salt and soil particles. In ambient aerosol particles data, in organics
148 dominated episode, the AMS was slightly greater than or similar to SMPS. But in sulfate
149 dominated episode, AMS was smaller than SMPS.

150



151
152 [Figure S7. Scatter plots of SMPS aerosol volume concentration and AMS aerosol volume
153 concentration.]

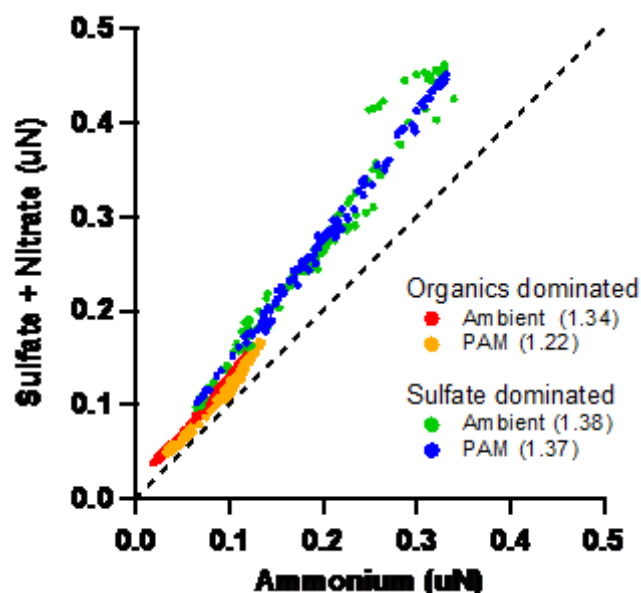
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155

156 **S8.** Ammonium balance with sulfate and nitrate

157 We plotted the ammonium balance with sulfate and nitrate for ambient and PAM
158 observation for each episode. The chloride concentration was under $0.4 \mu\text{g m}^{-3}$ which was
159 less than 1/10 of nitrate concentration, thus we only used sulfate and nitrate. The
160 inorganic aerosols were overall acidic, and the acidity in PAM aerosol was similar to

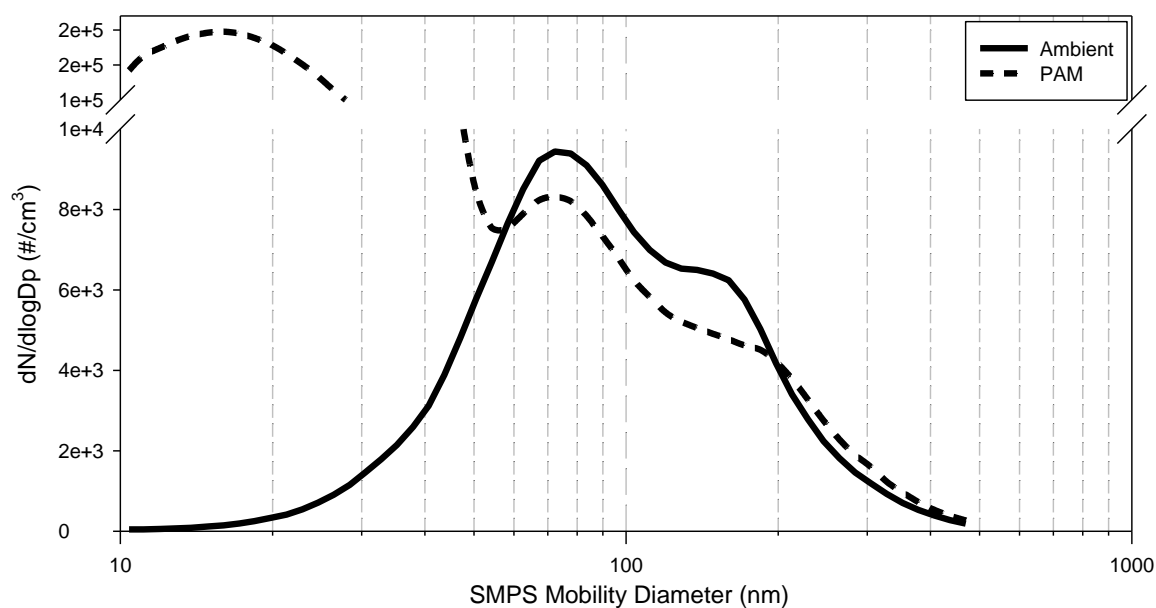
161 ambient aerosol in sulfate dominated episode. It is because of the sulfate enhancement
 162 in sulfate dominated episode while nitrate in PAM reactor was depleted a lot than
 163 ambient nitrate. In organics dominated episode, both of sulfate and ammonium was
 164 enhanced in PAM reactor while nitrate was depleted. Thus, the acidity was rather
 165 decreased in PAM reactor.



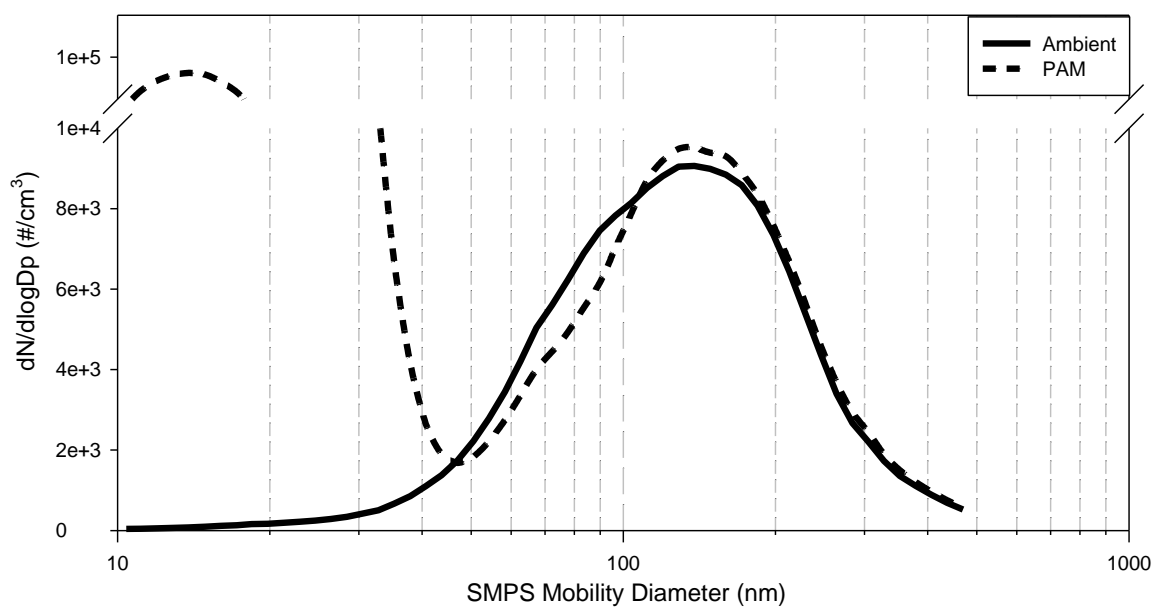
166
 167 [Figure S8. The normality balance of ammonium with sulfate and nitrate in ambient and
 168 PAM aerosol for organics dominated and sulfate dominated episodes. The numbers on
 169 the figure legend were the acidity of aerosols obtained from
 170 $[\text{sulfate} + \text{nitrate}](\mu\text{N}) / \text{ammonium}(\mu\text{N})$.]
 171
 172

173 **Figure S9.** Ambient and PAM particle size distribution for organic-dominated and sulfate-
 174 dominated episode. The $dN/d\log D_p$ ($\# \text{ cm}^{-3}$) of particles smaller than 50 nm in diameter
 175 for organic-dominated episode was about an order of magnitude greater than that for
 176 sulfate-dominated episode.

Organic-dominated episode



SO₄-dominated episode



177

178 Salimi, F., Crilley, L. R., Stevanovic, S., Ristovski, Z., Mazaheri, M., He, C., Johnson, G., Ayoko,
179 G., and Morawska, L.: Insights into the growth of newly formed particles in a subtropical
180 urban environment, *Atmos. Chem. Phys.*, 15, 13475-13485, [https://doi.org/10.5194/acp-](https://doi.org/10.5194/acp-15-13475-2015)
181 15-13475-2015, 2015.