Review of Kang et al.

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.

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

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.

(2) Line 119-122: More details are needed describing the OH exposure calculation. Was it done offline or online while sampling ambient air? What SO_2, 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 O_3, 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.

(3) **A very important comment.** Related to major problem #2, calculations comparing the measured SO_4 increase to that predicted based on OH_{exp} and ambient SO_2 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.

(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.

(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.

(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.

(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.

(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.

(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.

(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?

(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

sulfate acidity. This is important for quantification of the AMS data and needs to be thoroughly discussed.

(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).

(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.

(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.

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

precursors of SOA will depend strongly on inlet materials and residence times, and whether the flow was laminar or turbulent.

(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.

(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

(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.

(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.

(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?

(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.

(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.

(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.

(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.

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

Minor comments

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

Line 99. “Asian” not needed.

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

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

Line 169: air mass BACK-TRAJECTORIES

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

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.

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.

Fig. 3 caption: What is dWdlogDp?

References

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