Review of “Formation and characteristics of secondary aerosols in an industrialized environment during cold seasons” by Wu et al.

In this study, the authors utilized a soot-particle aerosol mass spectrometer (SP-AMS) to characterize the submicron aerosol composition in suburban Nanjing, China. To evaluate the formation mechanisms (aqueous phase reaction vs. gas phase reaction) of SO_4, NO_3, and organics, the authors analyzed the correlations between species concentration and relative humidity (RH) or O_x (O_3 + NO_2). Based on the correlations, the authors concluded that the aqueous-phase reactions enhance the production of SO_4, NO_3, and low-volatility oxygenated OA (LV-OOA). The formation of local SOA (LSOA) and semi-volatile oxygenated OA (SV-OOA) is driven by gas phase reactions. My major concern is that the correlation analysis between species concentration with RH or O_x cannot adequately reveal the formation mechanisms, because there are many confounding effects that influence the data interpretation. I will elaborate more below. Overall, I would not recommend this manuscript for publication in its current state.

Major comments

1. Possible confounding effects.

(1) One confounding effect that the authors should rule out is the diurnal variation. The RH is higher at night than the day, and the O_x shows the opposite diurnal trend. It is possible that the correlation between binned SVOOA and O_x is because both SVOOA and O_x have similar diurnal variation (i.e., both peak in the day). Similar case may be hold for the correlation between SO_4 and RH. In fact, the diurnal trend may explain many observations. Take the correlation between SOR (SO_4/SO_2 ratio) and RH in Figure 5b as an example. As the higher RH occurs at night, the lower SO_2 emissions but relatively constant SO_4 concentration at night will lead to higher SOR ratio. This offers an explanation to why SOR increases with RH. A more robust analysis would be plotting SO_4 vs RH while holding SO_2 and time of the day the same. The authors should show the diurnal trends of all the species and evaluate how the diurnal variation would affect the conclusions.

(2) The co-emission of SO_2 and NO_x is another confounding effect. In Figure 5d, the SOR has a negative correlation with O_x. The anti-correlation can be explained by the following. At high O_x period, the O_x is dominated by NO_2 (by eyeballing on Figure 2). As in many cases, high NO_2 is accompanied by high SO_2 (also according to Figure 2). The high SO_2 would lead to a low SOR ratio. In other words, to some extent, plotting SOR vs O_x is similar to plotting $1/SO_2$ vs NO_2 for

high O_x period. Does the SOR anti-correlate with O_3? It is also important to know if the high O_x periods occur in the daytime or nighttime.

(3) Particle liquid water content (LWC) is a better proxy for aqueous phase reaction than RH. It has been well-established that the particle LWC not only depends on RH, but also on particle composition. Also, particle LWC increases exponentially with RH when RH is high. The authors are encouraged to use thermodynamic models to estimate the particle LWC as well as particle acidity to better evaluate the role of aqueous phase reaction.

(4) The proxies used to evaluate aqueous-phase reaction (i.e., RH) and photochemical processing (i.e., O_x) are generally anti-correlated as shown in Figure 4a and 4b. This anti-correlation likely explains that in many circumstances, species concentration (such as LVOOA in Figure 8 and SOR in Figure 5) positively correlates with one proxy, but negatively correlates with the other proxy. The anti-correlation between RH and O_x could lead to some misleading conclusions. For example, in section 3.3.3, LVOOA is positively correlated with RH, but negatively correlated with O_x. Based on this observation, it is argued that aqueous-phase processing promotes LVOOA formation, but photochemical processing hinders the LVOOA formation.

The conclusions regarding LVOOA have other issues. For example, if the authors truly believe that the LVOOA is from aqueous phase reaction, then why would photochemical processing affect LVOOA?

2. Regarding the role of moisture on NO_3 formation, the authors concluded that a significant portion of nitrate is due to gas-to-particle conversion, and the photochemical production of nitrate is not significant. However, this conclusion is not well-supported. Firstly, in Figure 5a, NOR is slightly enhanced when RH increases from 60% to 70%. Out of this RH window (i.e., RH<60% or RH > 70%), the NOR does not change with RH. This figure likely suggests that RH has small effect on NOR. Even if RH has some effect on NOR, the window is only between 60-70% RH. Secondly, when the authors stated that “a significant portion of nitrate is due to gas-to-particle conversion” (Line 267-268), what is the “gas” the authors referred to, HNO_3 or NH_4NO_3? The production of both species are from photochemical reactions. Thus, it is inappropriate to conclude that the photochemical production of nitrate is not significant.

3. Questions regarding the conclusions on the effect of RH and O_x on SOA formation.

(1) The authors noted that the correlation between COA and O_x is likely a coincidence as the lunchtime was exactly noon/early afternoon with strong photochemical activities. To support this hypothesis, the authors should plot COA vs O_x while holding the time of day constant (i.e., plot COA vs O_x for noon data only), which rules out the confounding effect of diurnal variation. The same analysis should be done for SVOOA and LOA as well.

(2) In Figure S5a, HOA also has an increasing trend with RH. How to explain this trend?

(3) In Line 487, the conclusion that the OA pollution was not governed by RH effects is not supported. Even though the OA fraction in total PM_1 decreases with PM_1 concentration, the absolution OA concentration still increases with PM_1 concentration. What's the relationship between OA and RH?

4. In Figure 7d, the authors presented a graphical method to describe the OA evolution. Although the figure looks nice and potentially useful, it is not clear what new information can be drawn from the graph. The OA evolution (i.e., from less oxidized to more oxidized, aging with fragmentation) has already been well established.
5. As shown in Figure 10, the most dramatic change in the peak particle diameter of all species occurs below 50% RH. However, in previous figures (4,5, and 8), the RH has more pronounced effects on species concentrations when RH is above 50%. How do authors reconcile this difference? I also note that the species size distribution is very broad at the low RH. Thus, the calculated peak diameter is highly affected by the measurement uncertainties. Was a dryer applied upstream of SP-AMS?

Minor Comments

1. Line 83. Replace "isoprene" as "isoprene epoxide", as isoprene is not a direct aqSOA precursor.
2. Line 134. Please briefly describe how the dual-vaporizer works.
3. Line 270. Please explain why the aqueous-phase SO_2 oxidation may be stronger in Nanjing than Beijing.
4. Line 285-286. The sentence is not complete.

5. Line 290. As temperature generally has strong anti-correlation with RH, it is surprising that SOR has strong correlation with RH, but not with temperature. It would helpful to plot binned temperature vs. RH.

6. Line 541. Replace “whose emissions” with “emissions of which”