

## **Response to “Interactive comment on ‘Insights on organic aerosol aging and the influence of coal combustion at a regional receptor site of Central Eastern China’ by W. W. Hu et al.”**

The authors wish to thank the referees’ valuable comments and feedback on our manuscript. We have endeavored to address referee’s suggestion and comments. A detailed response to the comments is shown below. We welcome any further feedback that the editor and/or referees may have.

### **Response to Reviewer 2#**

#### **Specific comments**

1) There are many interesting results in the paper, but as a regional site the difference in aerosol chemistry needs to be stated more clearly.

**Response:** Sorry, we do not quite understand reviewer’s question.

2) Page 10811, line 16. Abstract section and the context, authors claimed several times that they reported CCOA for the first time. This is not true. Sun et al have already reported CCOA for Beijing winter aerosols using a similar online technique. (Sun et al ACP 2013, 13, 4577-4592)

**Response:** Yes, we agree with reviewer’s comment. CCOA was reported by Sun et al.[2013] before using the data from aerosol chemical species monitor (ACSM). Mass resolution of CCOA reported in Sun et al.(2013) are unit and the range of mass to charge ratio ( $m/z$ ) is limited to 100. But in our research, we found that the main characterization of CCOA is the high abundances of PAHs ion at the higher  $m/z$  (above  $m/z$  200, e.g.  $m/z$  128,  $m/z$  152,  $m/z$  165 etc.), which is consistent of the numerous studies before that PAHs contribute substantially to coal emitted OA [Shen et al., 2010; Wang et al., 2009; Y X Zhang et al., 2008]. With high resolution spectra of CCOA, specific PAHs ions ( $C_{10}H_8^+$ ,  $C_{12}H_8^+$  and  $C_{14}H_{10}^+$ ) and their contributions to CCOA are identified. This is the first that specific CCOA characterization in high resolution mass spectra reported. So, in our manuscript we will delete sentences “reported here for the first time” in the abstract, but explain

more in the main text of manuscript. Page 10820 line 18, Change to "...The CCOA in high resolution spectra is reported here for the first time in to our knowledge."

3) (1) In the paper, authors classified aerosols into four groups, HOA, SV-OOA, LV-OOA and CCOA. The former three groups are defined based on chemical composition and/or volatility, how about the last one, CCOA, i.e., coal combustion organic aerosols. What is the difference between CCOA and other three groups? In fact, coal combustion emissions also consist of HOA, SV-OOA and LV-OOA.

(2) Page 10812, line 16-23, here some statements need to be clarified. AMS usually takes HOA as a surrogate of anthropogenic primary organic aerosols and oxygenated organic aerosols as SOA, but the fact is that plants also emitted lots of HOA like n-alkanes and oxygenated OA like fatty acids.

(3) Moreover, biomass burning emissions also contain lots of SV-OOA and LV-OOA like carbonyls, polyols (e.g., glycerol) and carboxylic acids (malic acid), which are directly emitted rather than derived from secondary formation.

**Response:**

(1) Yes, it is usual to resolve HOA, LV-OOA and SV-OOA factors in an ambient AMS dataset. HOA, LV-OOA and SV-OOA are defined by the different oxidation state and volatility. The full name of HOA is hydrocarbon-like OA. Usually, HOA is full of alkyl fragments and shows the property of primary organic aerosol (POA), but it is hard to define what kinds of specific POA of HOA is, more like a total POA. SV-OOA and LV-OOA are all oxygenated organic aerosol, full of oxygenated ions. They are regarded as the surrogate of SOA. But during one campaign, if some specific sources have high contribution (e.g. >10%) to the total OA and their OA can show distinctive characterization in the spectra or time series, they also can be resolved in the PMF, like biomass burning OA in Mexico city [Aiken *et al.*, 2009], cooking OA in Beijing [Huang *et al.*, 2010]. Especially with high resolution mass spectra, the OA spectra from different sources are more distinguishing. The CCOA in Changdao campaign contribute 24% of total OA and are full alkyl fragments, which is similar to HOA. But unlike HOA, OA emitted by coal combustion has valid external tracer (naphthalene) and show specific characterization (high PAH abundance), which can be recognized clearly and

easily. We do not think CCOA are consist of HOA, SV-OOA and LV-OOA, but different. Actually, the CCOA should also be ascribed to POA. The total POA in Changdao campaign is the sum of HOA and CCOA.

(2) For the “plants also emitted lots of HOA like n-alkanes” we agree with referee’s suggestion. So we decided to delete the word “anthropogenic”. The sentences in the introduction were changed into “AMS usually takes HOA as a surrogate of primary organic aerosols and oxygenated organic aerosols as SOA”. But during Changdao campaign, the concentration of biogenic VOCs is very low [Yuan *et al.*, 2013], so the HOA in Changdao campaign should almost come from anthropogenic sources.

(3) The referee’s concern is reasonable. With the unit mass spectra of OA (e.g. detected by the Q-AMS or ACSM), it is hard to separate biomass burning OA (BBOA) and OOA for the similarity of their mass spectra. Sometimes there is biomass burning contributions to the OOA factors [Q Zhang *et al.*, 2007]. But with the higher resolution mass spectra of OA (e.g. detected by the HR-TOF-AMS), the elemental structure of fragment ions can be clear recognized. BBOA and OOA (no matter LV-OOA and SV-OOA) in the receptor model can be easily distinguished for their different characterization in mass spectra [Aiken *et al.*, 2009; He *et al.*, 2011]. Unless, the BBOA contribution to the total OA is very low (e.g. <5% in the PMF [Ulbrich *et al.*, 2009]). So, we believe the OOA resolved from high mass resolution OA matrix can be a surrogate of SOA. The BBOA resolved in different campaign indeed contain higher oxygenated ions compare to the other POA (e.g. CCOA, COA), which may come from carbonyls, polyols and carboxylic acids as reviewer suggested.

4) Page 10811, line 22, combustion,not combustion.

**Response:** corrected

5) Supporting information title is not consistent with the paper.

**Response:** sorry for the mistake, corrected

6) (1) Page 10815, line 5-10, Does it cause any particle loss when using such a 3-m long tube? (2) How about evaporation loss under the  $RH < 30\%$  condition, because the marine sampling site is humid.

**Response:** (1) During the campaign, 3/8" copper tube were used and wrapped with insulation tubes to protect the particle evaporation. The flow rate in the sampling line is 10 L/min. We use the particle loss calculator [von der Weiden *et al.*, 2009] to calculated the particle number losses in the tube. As figure 1 shows, particle number losses varied with different particle size. Most particle number losses happened under 100 nm and are even below 6%, if converting the particle number to particle masses, the particle mass losses in the sampling line is negligible. So it seems that there is no huge particle losses using 3-m long tube in this campaign.

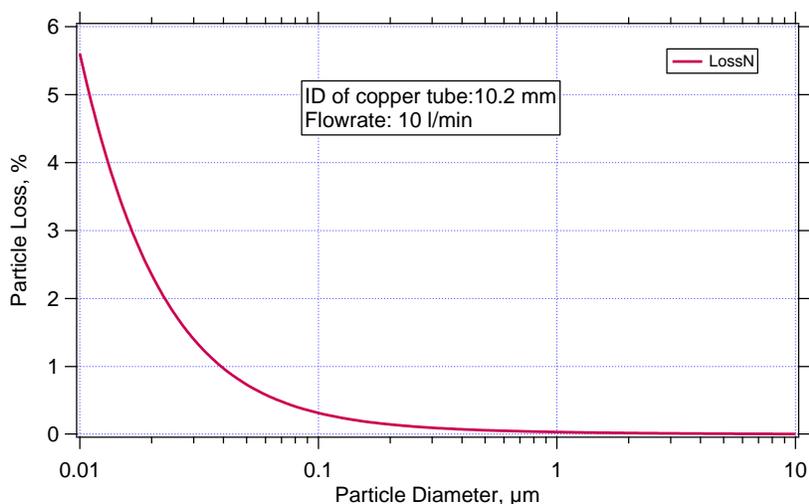


Figure 1 particle number losses varied with different particle diameter.

(2) The evaporation losses of particles from drying should be small. Because the residence time of particles between nafion and AMS instrument is within 1 min. But the evaporation time of particles are much higher ( $> 1$  hr) than this. E.g. For semi-volatile organic compounds, saturation concentration  $C^* = 1 \mu\text{g m}^{-3}$  in a 100 nm particle need 1 hour to evaporate [Donahue *et al.*, 2012]. Larger particle need longer evaporation time. The particle size in Changdao campaign is almost larger than 100 nm, as shown in the figure 2 of manuscript.

7) Page 10818, line 10-11, which should be “naphthalene and acetonitrile” not “acetonitrile and naphthalene”.

**Response:** Corrected

8) (1) Page 10819, line 14-19, as shown in Fig S-7, high fraction of  $\text{NO}_3^-$  was observed compared to other two downwind sites in China. What is the meaning on such an abundant nitrate? (2) The authors stated a positive correlation with higher RH, what is the correlation significance? (3) And how about  $\text{SO}_2$ ? If a significant conversion of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  was also observed under such a higher RH condition?

**Response:**

(1) The particle concentrations in Changdao ( $41 \mu\text{g}/\text{m}^3$ ), Backgarden ( $37 \mu\text{g}/\text{m}^3$ ), Kaiping ( $31 \mu\text{g}/\text{m}^3$ ) sites are similar. But comparing to the latter two sites (4% and 11%), the  $\text{NO}_3^-$  fractions of particle at Changdao site (28%) is higher. There may be 3 main reasons which could cause the huge different fractions of nitrate in similar concentration aerosols: Precursor  $\text{NO}_x$  concentration, neutralization of particle (determined by  $\text{NH}_3$  concentration) and Temperature. The average  $\text{NO}_x$  concentrations in Backgarden and Kaiping sites are  $21.1 \pm 14$  ppb [Xiao *et al.*, 2011] and  $15.5 \pm 7.3$  ppb [Huang *et al.*, 2011], which are similar to the average  $\text{NO}_x$  concentration ( $16.5 \pm 8$  ppb) in Changdao. And also all the ammonium balances in particles at 3 sites are neutral, so  $\text{NO}_x$  and ammonia concentrations should not be the main reasons causing the large differences among three sites. But it is noticeable that Backgarden and Kaiping sites are located in the south part of China, the temperature during two campaigns are  $20 \pm 6^\circ\text{C}$  and  $28.9 \pm 3.2^\circ\text{C}$ , which is much higher than the temperature ( $7.9 \pm 4.2^\circ\text{C}$ ) at Changdao site. The lower temperature facilitate the condensation of ammonium nitrate [Weimer *et al.*, 2006], which may be the main reason causing the higher  $\text{NO}_3^-$  fraction in the Changdao campaign.

(2) The scatter plots between RH and  $\text{NO}_3^-$  are shown in the figure 2. The results show that data points in high  $\text{NO}_3^-$  concentrations are corresponding to the high RH. But from the statistic calculation, the  $\text{NO}_3^-$  and RH show poor correlation coefficient, which is only around 0.22. That is because the high  $\text{NO}_3^-$  concentration are not only influenced by the higher RH ( $> 65\%$ ), but also air plumes direction (higher  $\text{NO}_3^-$  concentration from inland, and lower from sea area) at the same time. As the green period displayed in Figure 3, although the RH is higher, the air plumes during that period mostly come from the clean eastern sea, so the  $\text{NO}_3^-$  concentrations are still lower. So the high fractions of nitrate are found to be

positively correlated with higher RH (> 65 %) and abundant nitrate precursors (NO<sub>x</sub>) from inland at the same time.

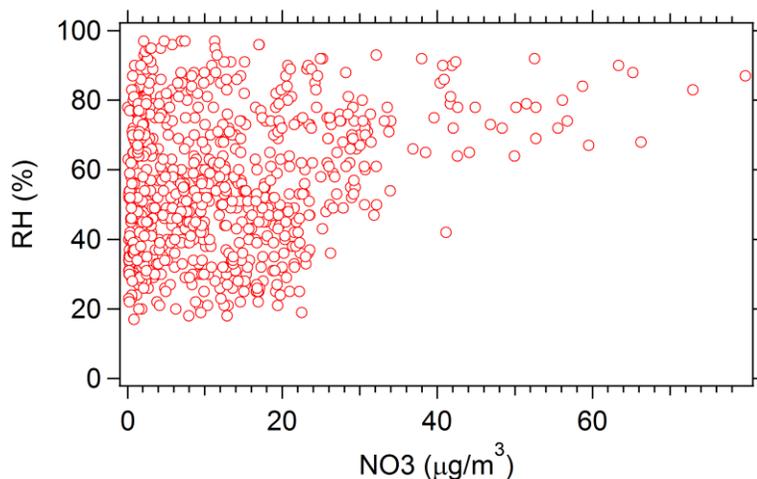


Figure 2 The scatter plots between RH and NO<sub>3</sub><sup>-</sup> in Changdao campaign.

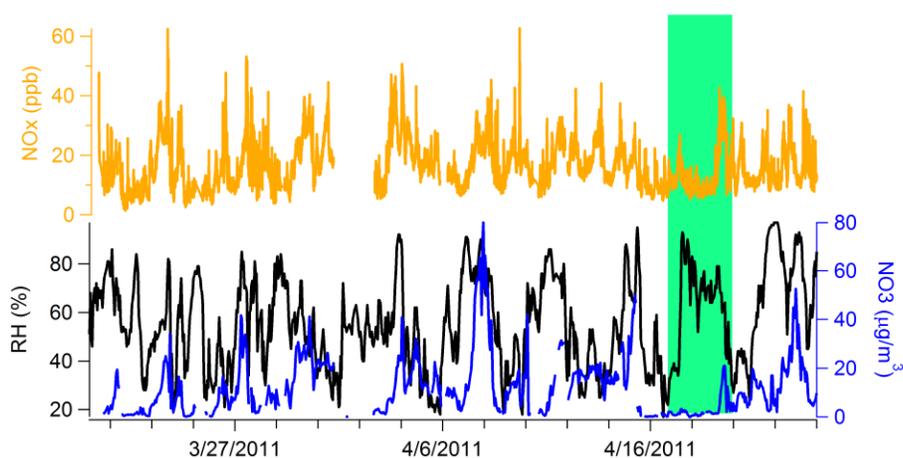


Figure 3 The time series of NO<sub>x</sub>, Nitrate and RH in Changdao Campaign.

(3) Yes, we indeed see the significant and strong dependence of SO<sub>4</sub><sup>2-</sup> formation on RH, as shown in the figure 4. When the RH is between 90%-100%, around 80% of the sulfur in SO<sub>x</sub> (SO<sub>2</sub>+Sulfate) are SO<sub>4</sub><sup>2-</sup>.

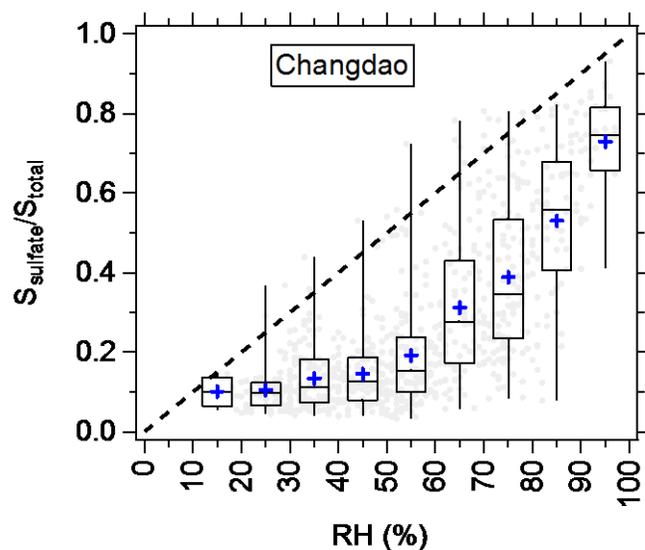


Figure 4 Box plots of sulfur concentrations between sulfate and total SO<sub>x</sub> (SO<sub>2</sub>+Sulfate) varied with RH.

9) Page 10820, line 18-19, the statement is not true, see the above.

**Response:** Please see the response of question 1.

10) Page 10820, line 15, it should be 0.35 (see Fig. 8), not 0.36. Page 10828, line 18, Yun et al (2013), not 2012.

**Response:** Corrected.

11) Page 10820, line 25-27, the regression slope is lower at the Changdao site in comparison with those in Mexico City and US, why? What does it imply?

**Response:** The lower regression slope indicated photochemical activities is low. The Changdao campaign was carried out during late winter and early spring. The campaign in Mexico and U.S. were conducted in the summer of the year. So it is reasonable that the photochemical activity in Changdao campaign is lower than that in Mexico and US.

12) Page 10829, line 12-15, if this means the aerosol phase oxidation is more significant?

**Response:** The LV-OOA indeed account for a larger percentage of OA during the aging process, however, it does not mean the aerosol phase oxidation is more significant. Because a lot of semi-volatile organic aerosol can evaporated from the

aerosol phase, oxidized and condense to particle again [*Presto et al.*, 2009; *Robinson et al.*, 2007]. So, it is hard to say whether aerosol phase oxidation or gas phase oxidation is more significant for the OA aging process.

13) Page 10830, line 5-10, this statement is wrong, because the  $K_{OH}$  for this study ( $5.2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ) is one order of magnitude lower than in previous studies ( $5-12.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ ).

**Response:** Sorry for the mistake. The  $K_{OH}$  reported in the literature (Hodzic and Jimenez, 2011; Spracklen et al., 2011) should be  $5-12.5 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , not  $5-12.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . So the statement in manuscript is still right. Apologize for the confusing mistake.

14) Page 10830, line 17-20, this seems unreasonable, because many field observations and chamber studies found that SOA production is enhanced under a higher temperature due to enhanced photochemical oxidation.

**Response:** In this study, we use scatter plots between O/C and photochemical age to explore the temperature influences on SOA formation. There are two advantage (1) O/C and photochemical are relative parameters, which can exclude the physical influences in atmosphere, such as boundary layer, wind speed etc. (2) the photochemical age can reflect the photochemical oxidation activity. What we see here is that higher temperature shows lower O/C that is lower SOA formations at different photochemical age, which already get rid of the photochemical activity influences. This result is more consistent of the traditional gas-particle participation principle and also most the chamber studies [*Pathak et al.*, 2007; *Svendby et al.*, 2008; *Takekawa et al.*, 2003]. And moreover, the temperature in Changdao range from  $-0.3$  to  $21$  °C. The chamber studies show that SOA yield are more sensitive to the temperature below  $15$  °C, and less sensitive to the higher temperature [*Pathak et al.*, 2007]. That may be another reason we can see clear temperature influences to the ambient SOA formation.

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