Response to interactive comments on “VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China” from referee #3

This study investigated VOC emissions and their contributions to SOA formation in Eastern China. It is found that the emission ratios of OVOCs are significantly lower than those from the emission inventory. Based on the measured VOCs, it is found that the modeled SOA is much lower than measured and the authors suggested that part of the missing SOA could be from the oxidation of SVOCs. While the paper is generally well-written, I think many parts of the manuscript require further clarification (please refer to specific comments below). The authors employed equations from de Gouw et al (2005). However, it is not clear if these equations can be applied to the Changdao data in the first place; the authors did not discuss the assumptions nor justify them in the manuscript. It is extremely important that the authors discuss these in details as they derived many of their conclusions based on results from these calculations. Further, the authors compared their results to a few other cities/locations (e.g., Beijing, Tokyo, Mexico City, NE US) and discussed the differences/similarities. However, they did not provide much context regarding why they chose to compare their results to these locations. (For example, do they expect the VOC emissions, photochemical processes, etc, to be similar in Changdao and these cities?) Hence, it is difficult to comprehend what conclusions they were trying to draw from such comparisons. Finally, the authors attempt to use the results from Changdao to infer SOA formation from anthropogenic emissions in China in the conclusions section. This section is weak and over-stretching without a detailed discussion on why the results from Changdao are representative of China as a whole. Overall, I think revision is needed to incorporate more detailed discussions and justifications of their methods/conclusions before the manuscript can be published in ACP.

Reply: We would like to thank the referee for his/her valuable comments. We considered thoroughly for the comments from the referee and the point-to-point responses to individual comments are listed below in this file.

Specific comments:

1. Page 6632, lines 19-22. I do not understand this sentence. The authors are comparing SOA formation from China in general to the measured SOA in Beijing and PRD?

Reply: We changed the sentence in the revised manuscript to “SOA formation potential of primary VOC emissions determined from field campaigns in Beijing and Pearl River Delta (PRD) are lower than the measured SOA levels reported in the two regions, indicating SOA formation is also beyond explainable by VOC oxidation in the two city clusters.” We use the literature reported emission ratios to compare the SOA formation potential with measured SOA enhancements in Beijing and PRD.

2. Page 6635, line 1. Why is this site a receptor site? Please explain further.

Reply: Thanks for the comments. Following the suggestions from referee #2, we added back trajectory analysis in the revised manuscript. The results from back trajectory show that Changdao mainly received air masses from the regions surrounding Bohai Sea, including
Shandong, Hebei, Tianjin, Beijing and Liaoning. The findings indicate that Changdao site can be viewed as a receptor site.

3. Page 6635, line 18. The authors stated that the introduction of internal standards led to interference from sampling lines or the canister. How does the interference affect their results? Are the results corrected for such interference? Please clarify.

Reply: The GC-MS/FID data from 20 March to 1 April are not used in the following data analysis. Only the data without any interference (2-25 April) is used in this study. We modified the sentence accordingly.

4. Page 6636, lines 29-30. Where are the T, RH, wind speed and direction measured exactly? If they are not measured exactly at the site or close to the site, how can the authors be sure that the data from the Bureau of Meteorology are representative of their site?

Reply: Meteorological parameters were measured by an automatic meteorological station, which is about 500 meters away from the Changdao site. This station is operated by Bureau of Meteorology of Changdao County. We modified the sentence in the revised manuscript to include this information.

5. Page 6637, lines 19-20. The authors wrote “The fractions of three main classes in the hydrocarbons are consistent with the results obtained at the suburban and rural sites around Beijing”. What is the basis of this statement? Do the authors expect the composition of hydrocarbons to be similar between Changdao and rural/suburban Beijing?

Reply: Thanks for the comments. We deleted the sentence in the revised manuscript.


Reply: We discussed the uncertainties in NO₃ concentration estimation in the supporting information in detail. The uncertainty of calculated NO₃ concentration come from measurement uncertainties of NO, NO₂, O₃, different VOCs species, NO₃ photolysis frequency and reaction rate coefficients used in Eq. S-9. Another important uncertainty source is the contribution of NO₃ and N₂O₅ heterogenic losses to NO₃ sink. The contributions vary significantly among different environments and different sites (25%-80% for polluted regions) (Brown et al., 2011). The calculation of NO₃ sinks from Eq. S-8 shows that reaction with NO is the most important pathway for NO₃ losses, due to high NO concentrations (0.9±1.2 ppb) in this study. Thus, NO₃ and N₂O₅ heterogenic losses to aerosol should only be important when NO is low at night (JNO₃ is also low). These calculated NO₃ data points may be overestimated by 33%-400% using the reported contributions of NO₃ and N₂O₅ heterogenic losses.

We include the discussion of NO₃ uncertainties in the supporting information, but not the main text, since the referee #2 suggest that section 3.2 should be shorten. We modified the statement in the revised manuscript to:
“The involved reactions, related parameters and uncertainties in the calculation of NO3 concentration are described in detail in the supplement. Note that NO3 loss due to N2O5 hydrolysis is not accounted in Eq. 3. Thus, NO3 concentration calculated from Eq. 3 are upper limits and the calculation of NO3 contributions to VOC losses is also overestimated.”

7. Page 6640. It is surprising that the reaction with NO3 is the dominant loss mechanism for isoprene and monoterpenes. The authors need to show the diurnal profiles of the calculated [OH] and [NO3], as well as that of isoprene and monoterpene to explain and justify this in more details.

Reply: Thanks for the suggestion. We show that reaction with NO3 is the dominant loss for monoterpene (63.2%) and also important for isoprene (25.7%). But we don’t think it is surprising. Geyer et al. (2003) showed that NO3 contributed to 31% to the 24-hour integer of the oxidation rate of alkenes at a site near Berlin, Germany. Warneke et al. (2004) also showed that the loss of biogenic species is dominated by NO3 oxidation, especially for α-pinene and β-pinene.

We added the diurnal profiles of calculated OH and NO3 concentration and measured isoprene and monoterpene concentrations in the supplement. The calculated NO3 concentrations are low in the day time and high in the evening. The estimated loss rates of isoprene and monoterpenes due to NO3 radical also show a peak in the evening.

But we admit that the NO3 contribution to the oxidations of VOCs species may be overestimated, due to the potential overestimation of NO3 concentration (see comments #7). We added a sentence after the discussion of NO3 contribution to biogenic VOCs to remind the readers about the uncertainty of NO3 estimation.

8. Page 6641, lines 1-5. What are the assumptions and why and how they general hold true for the Changdao data? Here and in many parts of the manuscript the authors used equations from de Gouw et al (2005) without much discussions. It is not clear how they can justify that the equations in de Gouw et al are applicable to the Changdao data. The authors need to provide more justifications.

Reply: Thanks for the comments. This comment is identical to the comment #7 from referee #2. We added several sentences in the beginning of Section 3.1 to fully assess the assumptions in the method. The inserted discussions are:

There are several underlying assumptions in the parameterization method to describe VOCs evolution at Changdao (de Gouw et al., 2005): (1) urban emissions are the dominant sources of VOCs sampled at Changdao site; (2) the speciation of VOC emissions were the same in different parts of the influencing regions and the magnitude of emissions is proportional to CO; (3) the removal of VOCs is mainly due to the reaction with OH; (4) The photochemical age can be described by the measured ratio between two VOC species (m+p-xylene and ethylbenzene in this study). Considering that concentrations of biogenic species were low during the campaign (Section 3.1) and the influences from biomass burning and local coal burning were filtered out (Section 2), the only dominant VOCs source is urban emissions (assumption 1). Note that urban emissions here include all of the activities that are considered as VOC emitters in/near urban
areas, e.g., vehicle exhausts, domestic usage of fossil fuel and industry emissions adjoin to urban areas. Measurement at several sites in Central Eastern China showed that VOCs concentration profiles are similar (Suthawaree et al., 2010; Suthawaree et al., 2012), suggesting that the first part of assumption (2) is reasonable. The analysis in Section 3.2 shows that assumption (3) holds true at Changdao site. The assumption (4) and the second part of assumption (2) will be investigated using alternative parameters in following analysis.

9. Page 6641, line 9. Why m-xylene and p-xylene are lumped together? Is this because they cannot separate these two compounds in their measurements? If so, can they choose another species to calculate the photochemical age?

Reply: Yes, our GC-MS/FID system cannot separate m-xylene to p-xylene. Actually, the sum concentrations of m-xylene and p-xylene are reported in the most of VOCs publications due to the difficulty to separate them.

We chose m+p-xylene/ethylbenzene ratio to calculate photochemical age, since this ratio has been widely used in the literature, including Sydney (Nelson et al., 1983), Southern Taiwan (Shiu et al., 2007), Beijing (Shao et al., 2011) and Pearl River Delta (Wang et al., 2008).

We also tried to use o-xylene/ethylbenzene ratio to calculate photochemical age and compare the calculated emission ratios of VOCs to CO using the two different ratios. The results is show in below and also Fig. S7 (D). The calculated emission ratios of VOCs to CO show good agreements for all of the VOCs species using the two different ratios. We added this comparison in the revised manuscript to show that m+p-xylene/ethylbenzene ratio works well in the calculation of photochemical age.

![Fig. R1. Comparison of emission ratios of NMHCs to CO using m+p-xyelne/ethylbenzene ratio and o-xylene /ethylbenzene ratio to calculate photochemical age. The black line indicates the 1:1 relationship, and the gray area shows agreements within a factor of two.](image)
10. Page 6641, lines 14-15. I do not understand what the authors mean by “these two terms...usually show up in pairs in the equation.” Please explain more clearly.

Reply: Since the two terms of [OH] and Δt show up together in the Eq. 5-6 in the revised manuscript, only the product of [OH] and Δt are required for the calculation. We modified the sentence to: “since the product of [OH] and Δt (usually called OH exposure) are only required for calculation in the equations.”

11. Page 6642, line 11. Please elaborate on the “traditional correlation method” and point out the main differences between this method and the parametrization method.

Reply: Sorry for the confusion. We changed the term of “traditional correlation method” to “directly linear regression method” for the clarification. Linear fits are used extensively in the literature to calculate the emission ratios or enhancement ratios for two different compounds, but the photochemistry in the atmosphere is not considered. Here we show that the calculated emission ratios to CO can be underestimated substantially for reactive species (Fig. S8 in the revised supplement).

12. Page 6643, line 11. Why unrealistic results are obtained from the fits if biogenic sources are included in Equation 7? What’s the physical reason behind?

Reply: The concentrations of isoprene and MVK+MACR were low during the campaign, thus it is reasonable to not include biogenic term in the Eq. 6 (Eq. 7 in the original manuscript). We did try to incorporate the biogenic term in Eq. 6, but unrealistic high emission ratios of OVOCs species to isoprene_{source} (see de Gouw et al., 2005) were obtained. The reason for this may be the biogenic term is smaller compared to the uncertainties in the fits of OVOCs. Thus, regression algorithm has to set large emission ratios of OVOC to isoprene_{source} to meet the least square criteria.

13. Page 6643, line 15. What do the authors mean by “calculated” OVOC concentrations? Did they fit the data and obtain values for the unknowns, then plug these values back to Equation 7 to get [OVOC]?

Reply: Thanks for pointing out this. Yes, the referee is correct. We modified the sentence to:

Table 3 shows the correlation coefficients between measured OVOC concentrations and calculated values using fitted unknown parameters in Eq. 6.

14. Page 6644. Why did the authors choose to compare results from Changdao to these other sites? Do the authors expect something in common (sources? Photochemical processes? Etc) between Changdao and these cities?

Reply: Thanks for the comments. Actually the datasets that are compared with the values obtained from Changdao, are all of the information we could find in the literature before Dec. 2012 when we submitted the manuscript to ACP. We revised the first paragraph to include the information that why we use values form these datasets.
15. Page 6647. Why are the values so unstable for an aerosol lifetime between 1-3 days?

**Reply:** The possible reason for the unstable results is the assumed low lifetimes (1-3 days) compared to the real conditions. It leads to very high L_{OA} values (0.014-0.042 h^{-1}) in Eq. 8 in the revise manuscript. We added this information in the revised manuscript: “The unstable values for aerosol lifetimes between 1-3 days may reflect these assumed aerosol lifetimes are too small compared to real conditions.”

16. Page 6651, glyoxal discussion. Do the authors have any evidence that the aerosols in Changdao are aqueous (or, have enough water) for glyoxal uptake? Can they infer this from their RH data? The authors stated that “Glyoxal could be a significant source of SOA formation...” But then later stated that “it should not be enough to explain the large discrepancies between measured and calculated SOA.” Without glyoxal measurements, how did the authors decide whether it is “enough” or not?

**Reply:** Fog events were encountered in the last few days of the campaign (e.g. 21-22 Apr.), as indicated by the high RH in Fig. S3. The fog events may favor the glyoxal uptake to aerosol. We added this information and delete the statement that “it should not be enough to explain the large discrepancies between measured and calculated SOA” in the revised manuscript.

17. Page 6653. I do not understand Equation 14. According to line 11, delMoi is the SOA formed from SVOC species i. But, SOAi is also the SOA formed from SVOC species i?

**Reply:** Thanks for the comments. We changed the HC_{i} term to EF_{i} to better represent emission factor. Now the equation is shown as:

\[ \Delta M_{0,i} = [EF_{i}] \times (1 - \exp(-k_{OH,i}[OH] \Delta t)) \times Y_{t} \]

In the equation, [EF_{i}] is the emission factor of species i from the specific source. [EF_{i}] has a unit of \( \mu g/km \) in diesel vehicle emissions, whereas [EF_{i}] has units of mg/kg fuel (e.g. coal or crop straw) in coal burning and biomass burning emissions. Thus, \( \Delta M_{0,i} \) is the amount of SOA formed from SVOC species i for 1 km running of a diesel vehicle or 1 kg burning of fuels. We modified this part accordingly in the revised manuscript.

SOAi in the Eq. 13 (Eq. 14 in the original manuscript) represent the amount of SOA formed from different SVOCs at Changdao. It is calculated from SOA amount of naphthalene at Changdao and the calculated \( \Delta M_{0,i} \) of naphthalene and other SVOC species. We modified the description of SOAi in the revise manuscript.

18. Page 6656, lines 4-21. Do the authors expect the Changdao data to be representative of all China? If not, this paragraph does not seem convincing and it appears that the authors are stating more than what they can conclude from their data.

**Reply:** We deleted this paragraph.

19. Page 6667. What are the monoterpene concentrations?
**Reply**: The average monoterpenes concentration measured by PTR-MS was 0.07±0.06 ppb. We added monoterpene into Table 1 in the revised manuscript.

20. **Page 6667. How are the uncertainties determined for each species?**

**Reply**: Values are expressed in the terms of “average±standard deviation”. Here the uncertainties for emission ratios are from the fits of Eq. 6 to various VOCs species. We added this in the caption of Table 1.

21. **Page 6670. Are low NOx data also calculated with Mo=15 and T=10?**

**Reply**: The dependence of SOA yields for aromatics (Ng et al., 2007) and alkanes (Lim and Ziemann, 2009) with organic aerosol loading and temperature under low-NOx conditions are not available in the literatures. Thus, the constant SOA yields for low-NOx conditions reported in the literatures are used in this study.

22. **Page 6671. Where do the VOC emissions data (color legend) come from?**

**Reply**: The VOCs emission data come from Zhang et al. (2009). We added this information in the caption of Fig. 1 in the revised manuscript.

23. **Page 6673. What is the shaded region? 30% uncertainty?**

**Reply**: The shaded areas show agreements of the emission ratios within a factor of two. We added this information in the revised captions of Fig. 3 and Fig. 5.

**Technical comments:**

1. **Page 6632, line 22. “This” should be “these”**.

**Reply**: Corrected.

2. **Page 6637, line 14. “significant” should be “significantly”**.

**Reply**: Corrected.

3. **Page 6642, line 14. Delete “but”**.

**Reply**: Corrected.

4. **Page 6646, line 13. “Poor-known” should be “poorly-known”**.

**Reply**: Corrected.

5. **Page 6649, line 28. Delete “Thus”**.
Reply: Corrected.

References:


