Response to interactive comments on "VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China" from referee #2

This paper presents analysis of an observational dataset of VOC composition from a site on an island, Changdao, in Eastern China. By applying a previously published empirical diagnostic method, the authors attempted to develop understanding of some important scientific questions, e.g., the accuracy of emissions inventories of VOCs, the sources and budget of organic aerosols in China. The paper is in general well written, with the analysis procedures described explicitly and the results presented clearly with high-quality graphs. Nevertheless, the conclusions are not well supported by the data and analysis, given the current inadequate discussions of the assumptions inherent in the method, and of the applicability of the method for the study region. I suggest a major revision to address the following issues before the paper could be considered for publication.

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 response to individual comments is listed below in this file. The comments are shown in italic black and the response is in blue.

Scientific comments

1. Page 6653 section 2 Measurements: The site is called a 'receptor' site in the paper but no reason for this is provided. Why is the site a 'receptor'? How was the site selected and what are the origins of air masses that the site sampled during the campaign? Has the authors done any meteorology modeling or back trajectory analysis for these? This information is especially important for applying the analysis method, as further discussed below.

Reply: Thanks for the comments. We added the back trajectory analysis in the revised manuscript, according to this comment and several other related comments. The back trajectory results show that Changdao site received air masses from the provinces surrounding the Bohai Sea, including Shandong, Hebei, Beijing, Tianjin and Liaoning provinces. The concentrations of primary pollutants (CO and benzene) are found to be associated with the origins of the air masses. Thus, it is reasonable to use Chandao site as a receptor site of the regions surrounding Bohai Sea.

2. Page 6637 last paragraph of Section 2: Additional information needs to be provided regarding the emission sources that influence the site.

Reply: We added sentences to discuss that data filtering is needed in this study, since we will focus on urban emissions. The discussion of the minor role from ocean emissions is also inserted to the paragraph. The emission sources influencing the Changdao site are also discussed in the assumptions in Section 3.3.

3. Page 6637 Section 3.1: Back-trajectory analysis would be more useful than the wind-direction dependence results.

Reply: Thanks for the comments. We added the back trajectory analysis in Section 3.1.

4. Page 6638 lines 1 – 12: These speculations for the reasons of the observed wind-direction dependence need to be investigated and discussed further. Since the paper actually attempts to do an in-depth quantitative analysis of emission sources, it looks odd that the reasons of the observed wind-direction dependence could not be fully explained.

Reply: Thanks for the comments. We rewrote the paragraph related to the original wind-direction dependence. The back trajectory results are added into the discussions to better characterize the regional influences.

5. Section 3.2: This section could be shortened or moved to the supplement. The different dominant loss pathways of different VOC species are not novel.

Reply: Thanks for the suggestion. We shorten this section by moving the description part of photolysis frequency of OVOCs into the supplement.

6. Page 6638 Equation 2: It was stated by Enhalt and Roher (2000) in the last paragraph of their Secion 3 that "the values of the coefficients derived here, however, are primarily applicable for the POPCORN campaign only, … and should only be used for air with similar composition". The estimated uncertainty from Zheng et al. (2011) by comparing their observed and calculated OH should not be cited here directly without any comparison of chemical compositions at these different places.

Reply: Thanks for the comments. The parameterization method in Enhalt and Roher (2000) is derived from the POPCORN campaign, which represents conditions at a continental rural site. Several studies obtained good agreements between calculated OH concentrations of the parameterization method and OH measurements or other estimation methods, including in Northeastern U.S. (Warneke et al., 2004, 2010) and at a suburban site (Yufa) near Beijing (Zheng et al., 2011). We agree that comparison of air compositions should be done before we cite Zheng's estimate of the uncertainty. Table below shows the average mixing ratios of several gases in Changdao and Yufa, indicating that concentrations of air pollutants expanded similar ranges at the two sites. We added this information in the revised manuscript and added a new table in the supplement to show mixing ratio of the gases and meteorological parameters at Changdao.

Table R1. Comparison of the air compositions at Changdao and Yufa.

Parameters (ppb)	Changdao	Yufa[a]	
		06:00-10:00	12:00-16:00
O3	43±15	15	76
NO	0.9±1.2	8.6	0.15
NO2	15.3±7.1	19.2	2.0
CO	563±428	920	650
Ethane	4.0±2.1	4.8	4.5
Ethene	1.8±1.5	4.0	3.1

a. data from Lu et al. (2013).

7. Page 6641 Equation (5): An important step before applying the tracer ratio method should be demonstrating the applicability of the method for the study data and region, especially considering the potentially different emission sources, chemistry and mixing in China than in the US, where emission sources are less uncertain and the behavior of the method have been characterized better. The authors simply state 'The assumptions in the method were fully discussed in the previous papers (de Gouw et al., 2005; Yuan et al., 2012) and generally hold true in the Changdao campaign.' But it is actually not clear to the reviewer that this is true. The authors do have demonstrated that OH removal is the dominant loss pathway of the majority of VOCs. Further, they probably also need to demonstrate that another assumption, i.e., the speciation of VOC emissions is the same for all the regions sampled, also holds true. At least, the assumptions need to be stated clearly here.

Reply: Thanks for the comments. 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.

8. Why did the authors choose to use m/p-xylene and ethyl benzene in equation (5)? It does not look like an optimal pair to use, as m/p-xylene includes two species with markedly different reactivities. Have the authors try experiments using different pairs? These experiments could provide insight into the behavior of the method.

Reply: Thanks for the suggestion. We chose m+p-xylene/ethylbenzene ratio to calculate photochemical age, since this ratio has been widely used in the literatures, 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-xyelne/ethylbenzene ratio to calculate photochemical age and compare the calculated emission ratios of VOCs to CO using the two different ratios. The results are shown 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.
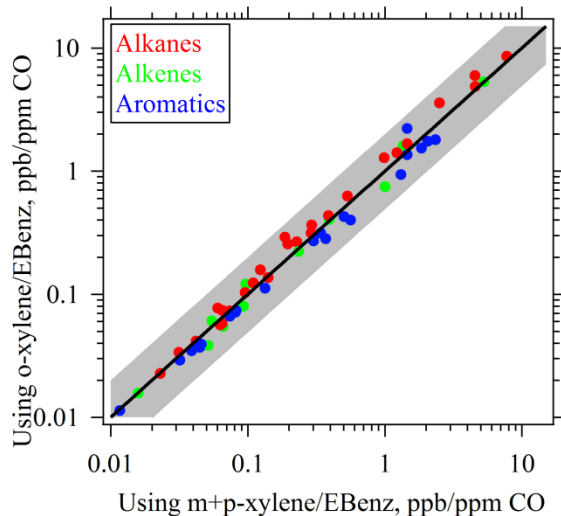

Fig. R1. Comparison of determined emission ratios of NMHCs to CO using m+p-xyelne/ethylbenzene ratio and o-xylene/ethylbenzene ratio to calculate photochemical age. The black line indicates the 1:1 relationship, and the gray area shows agreements within a factor of two.

9. Page 6642 Equation (6): de Gouw (2005) showed the derived kNMHC and laboratory k values. I suggest the authors do the same comparison here, at least shown in the supporting information, which will be a useful diagnostic of how the method behaves with the present dataset. It would also be interesting to see results using acetylene, instead of CO.

Reply: Thanks for the suggestion. We conducted the comparison of the derived k_{NMHC} with those from literatures (Fig. R2 and also Fig. S7). The results show that the derived k_{NMHC} agree well with the literature values for VOCs species with k_{NMHC} value lower than that of m+p-xylene, the more reactive species used to calculate photochemical age. This phenomenon is consistent with the observations in NEAQS and it could be mainly due to the removal time scales of more reactive species are of the same order of the uncertainty of photochemical age (de Gouw et al., 2005).

We also test the results of using acetylene as the urban tracer. Then Eq. 5 (Eq. 6 in the original manuscript) changes to (de Gouw et al., 2005):

$$[NMHC] = ER \times [Acetyelne] \times \exp[-(k_{NMHC} - k_{Acetylene})[OH]\Delta t]$$

The calculated emission ratios of various NMHC species to acetylene are compared with emission ratios to CO calculated from Eq. 5 in the manuscript. The result is shown in below (and also in the supplement). The estimated emission ratios to acetylene and to CO show excellent correlation and the regression slope of the data point is 4.87, which is close to the slope from linear fit of acetylene versus CO (4.30).

We modified the revised manuscript to include the two tests here and also add the graphs to the supplement.
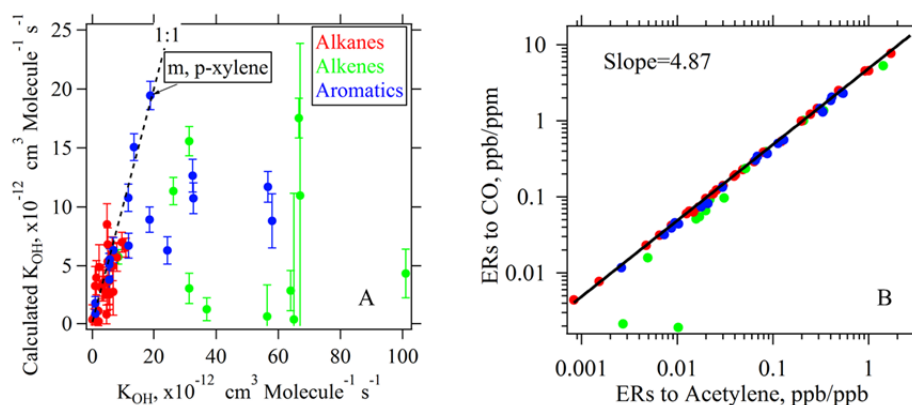

Fig. R2 (A) Comparison of the calculated k_{OH} from Eq. 5 with the values in the literature. The dashed line shows the 1:1 relationship. (B) Scatterplots of the calculated VOCs emission ratios calculated using CO as urban tracer with those calculated using acetylene as urban tracer. The black line is the linear fit to the data points.

10. Page 6642 line 9: How exactly did the authors do the fitting? For example, how are the uncertainties treated and weighted in the fitting? In general, there is a lack of discussion on the method/parameter uncertainties in the equations. How sensitive are the fitted ER to the assumed CO background concentration?

Reply: Thanks for the comments. We modified the description of the fitting in the manuscript: "Following the procedures in previous studies (de Gouw et al., 2005), all of the parameters in Eq. 5 are known except ER and k_{NMHC}, which are obtained from fits to Eq. 5 to each VOCs species."

Regarding of the uncertainties in various parameters (e.g. photochemical age, using a different urban tracer, CO background in Eq. 5), we conducted a series of tests to inspect the influences from uncertainties. Please refer to the reply to comments #8 for the test of calculating photochemical age using another VOCs pairs and reply to comments #9 for the test of using acetylene as urban tracer.

In Eq. 5, CO background concentration (CO_{bg}) is derived from the intercept of linear fit from correlation of CO with benzene. It is determined to be 104 ppb and 100 ppb was used throughout the manuscript. We conducted a test of using 70 ppb and 130 ppb (associating with 30% uncertainty) as CO background in Eq. 5, to account for the uncertainties in the calculation of CO_{bg}. The results are shown in the Fig. R3 and also Fig. S7 (C). The calculated emission ratios

of NMHCs decrease (increase) by about 5% if a 30% lower (higher) CO_{bg} is used. Thus, the uncertainties in CO_{bg} will not result in larger errors in this study.

We added a paragraph to combine the results from the tests we did (photochemical age, urban tracer and CO background) to reflect the uncertainties in the calculation of emission ratios. Our results show that the uncertainties in the calculated emission ratios are better than 50% for most of VOC species.
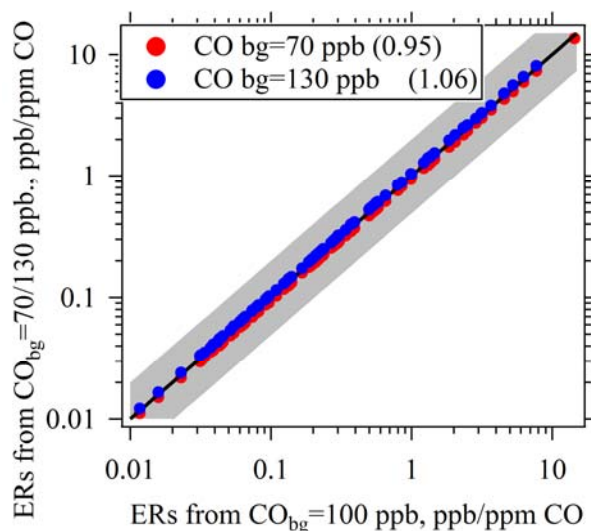

Fig. R3. Comparison of calculated emission ratios of NMHCs to CO using CO background concentrations of 100 ppb, 70 ppb and 130 ppb. The black line indicates the 1:1 relationship, and the gray area shows agreements within a factor of two.

11. Page 6644 Section 3.4: This section needs more work. It is potentially very interesting to show comparisons of the emission ratios in Changdao with other regions and the inventory data. But as mentioned earlier, the definition of emission sources sampled by the Changdao Campaign is missing in the paper. Changdao looks like a rural site sampling pollution transport from major sources in upwind locations. The emission ratios calculated here are essentially for these upwind emission sources. The meaning of the comparison between these sources with other places like Tokyo, Mexico city will be clear only if these sources are defined clearly. The current discussions sound like the authors are discussing sources in Changdao, or a very big but undefined region, such as the whole Eastern China. Without a characterization of the sampled air masses, it is not even clear weather the method work and the emission ratios derived here are truly emission ratios.

Reply: Thanks for the comments. We revised the first paragraph of Section 3.4 to include the discussions about the interpretation of the calculated emissions ratio at Changdao site. Thanking to the back trajectory analysis, this kind of discussions are possible in the revised manuscript. The reason that we compare Changdao results with the datasets in Beijing and other regions are also shown.

12. The authors compared their emission ratios of VOC/CO to INTEX-B emission inventory. How and where were the ratios for individual VOC species from the inventory obtained? The inventory is generally used as input data for chemical transport models and only has lumped VOC species (a number of VOC species lumped as one species) in the data downloaded from the website (http://www.cgrer.uiowa.edu/EMISSION_DATA_new/index_16.html). Please clarify.

Reply: Thank you for the comments. We obtained the emissions of individual VOC species from Prof. Qiang Zhang through personal communications. Prof. Qiang Zhang is the first author of the widely-cited paper about emission inventory for Asia (Zhang et al., 2009). It is true that only the emissions of lumped species for several chemistry mechanisms are available on the website. Emissions of individual VOCs in Zhang et al. (2009) are calculated by applying local profile databases to each source catalog and then lumped to species in different chemistry mechanisms.

13. Page 6646 lines 2-3: It is not obvious that from Figure 5 with log-scales that the agreement is 'unexpectedly good'. A Table showing ERs from the derivation and the inventory would show clearly. It also needs to be clarified what could be called 'compared well', e.g., within a factor of how many?

Reply: Thanks for the comments. Considering that the emission ratios of various VOCs species to CO span over several orders of magnitude, the log-scales in the axis of Fig. 5 (and also Fig. 3) are used. We also plot the agreement of a factor of 2 in gray areas and separate the species to three different groups to guide the readers' eyes. We decide not to use tables to display the results, since it would be hard to find the similar patterns for different species in tables.

We revised the sentences to show that the results agree with each other within a factor of 2. The stated uncertainties of emission inventory are also shown in the revised sentences.

14. Page 6646 Section 3.5: Likewise, this section suffers from the ambiguous definition of sampled sources and volume in which the carbon budget is calculated. It is not clear what conclusions about the budget could be drawn without a clear definition of the controlled volume where the organic carbon budget is examined. For example, in Page 6650 lines 2-3, the temperatures measured at Changdao are not necessarily the temperatures at which the SOA formed, which should occurred during the transport of air masses from the sources to the site.

Reply: Back trajectory analysis is added in Section 3.1 and the geographic domain where we are examined is well described now in the revised manuscript.

We agree with the referee that temperatures measured at Changdao are not necessarily equal to the temperatures at which SOA formed. Temperature change SOA formation by changing the vapor pressures of oxidation products formed from precursors. Low temperature will result in higher SOA yields. We tried to use minimum temperature (0 °C) during the campaign to calculate SOA yields, which represent the higher limits of SOA formation from various VOCs. We added the concern pointed out by the referee in the text to remind the readers.

15. Page 6651 Section 4: The authors basically discuss the reasons of the discrepancies by extensively citing almost all the possible pathways of SOA formation under discussion in current literature. It is not convincing that some of the issues discussed here, such as the total SOA budget in China, could be properly addressed with merely a VOC composition dataset from a single site. This might work, but at least much more discussions on how it works are needed. Otherwise, the conclusions will only be regarded as over-interpretations of the data.

Reply: We deleted the total SOA budget in China, due to the concerns about over-interpretations of the data.

16. Page 6653 Equation (13): The equation works well in the work by Chan et al. (2009) only because it is applied to their experimental data collected from a closed chamber, for which the air volume is fixed and known. In the atmosphere, a proper definition of the controlled volume is needed to calculate a budget of organic carbon.

Reply: The equation in the work by Chan et al. (2009) is used to compare the SOA masses formed by PAHs, higher alkanes and small aromatics from different emission sources (e.g. diesel vehicles, wood burning). In this study, we adopted this equation to infer the importance of SVOCs in SOA formations. The local source signatures available for China are used in this study, including biomass burning and coal burning, two important sources of PAHs in China. We don't intend to use Eq. 12 (original Eq. 13) to derive the absolute concentration or mass burden of SOA formed from these SVOCs. The relative masses from different SVOCs species to naphthalene calculated from the Eq. 12 are rather used. Then, the results are incorporated to Eq. 13 (originally Eq. 14) to determine the contributions of these species to SOA formation at Changdao.

The description of the equations and calculation method in Section 4.2 is revised in the newer version of manuscript, according to this comment and comments from referee #3.

Minor errors:

1. P6635 line 4 off from the coast -> off the coast

Reply: Corrected.

2. P6635 line 5 was on the top of a hill with a height about 30 m -> a height of about 30m above ground

Reply: Corrected.

3. P6635 line 13 'a flow of' -> a flow rate of

Reply: Corrected.

4. P6636 line 16 'time of flight' -> time-of-flight

5. P6638 line 7 'contrast to' -> in contrast to

6. P6638 line 9 'as' -> when

7. P6638 line 20 'with the execption of ozone' -> delete

8. P6640 line 4 'Due to' -> Since/because

9. P6640 line 7 'Contrast to' -> in contrast to

10. P6640 line 12 'Comparing to' -> Compared to

11. P6640 line 23 'photochemical aged' -> photochemical age

12. P6642 line 14 'but' -> delete

13. P6642 line 22 'suggest' -> suggests

14. P6643 line 14 'that describing' -> that describe

15. P6646 line 10 'The failure' -> failure of

Reply: Corrected.

16. P6647 line 10 'at a step' -> with a step

Reply: Corrected.

17. P6647 line 16 'as' -> with

Reply: Corrected.

18. P6650 line 27 'apping' -> applying

Reply: Corrected.

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