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Atmospheric Chemistry and Physics Discussions

Interactive comment on "VOC emissions, evolutions and contributions to SOA formation at a receptor site in Eastern China" *by* B. Yuan et al.

Anonymous Referee #2

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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.

Scientific comments

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.

Page 6637 last paragraph of Section 2

Additional information needs to be provided regarding the emission sources that influence the site.

Page 6637 Section 3.1

Back-trajectory analysis would be more useful than the wind-direction dependence results.

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.

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.

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.

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.

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.

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.

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?

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.

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.

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?

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.

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.

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.

Minor errors (might not be exhaustive):

6635 line 4 off from the coast -> off the coast

6635 line 5 was on the top of a hill with a height about 30 m -> a height of about 30m above ground

6635 line 13 'a flow of' -> a flow rate of

6636 line 16 'time of flight' -> time-of-flight

6638 line 7 'contrast to' -> in contrast to

6638 line 9 'as' -> when

6638 line 20 'with the execption of ozone' -> delete

6640 line 4 'Due to' -> Since/because

6640 line 7 'Contrast to' → in contrast to

6640 line 12 'Comparing to' → Compared to

6640 line 23 'photochemical aged' → photochemical age

6642 line 14 'but' → delete

6642 line 22 'suggest' → suggests

6643 line 14 'that describing' → that describe

6646 line 10 'The failure' → failure of

6647 line 10 'at a step' → with a step

6647 line 16 'as' → with

6650 line 27 'apping' → applying

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 6631, 2013.