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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China” *by* J. Zhang et al.

J. Zhang et al.

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Thanks Referee #3 for the comments and suggestions. Below are our changes to the manuscript and responses.

General remarks:
The manuscript of Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China by Zhang et al. performed a diagnostic analysis on VOCs sources during ozone episode in Hong Kong. The method, using the ratios of VOCs as well as other gas pollutants, is a useful one when reliable source inventory is not available. I personally think the use of C6H14-to-Toluene ratio is interesting. However, as the spatial distribution of VOCs sources is not addressed

in the manuscript, considering the complex of the emission sources in both Hong Kong and Pearl River Delta region, and also the roles of chemical processes and transportation, the conclusion from the preliminary diagnostic analysis seems not to be convincing enough. I will suggest more careful check is needed, before some very important points about VOCs sources, and also on the influence of Guangdong province to Hong Kong ozone problem, can be made.

Response:
This work is a part of the results of the Hong Kong and the Pearl River Delta Pilot Air Monitoring Study from October to December, 2002. And it is a succession of a previous study (Zhang, J., Wang, T., Chameides, W. L., Cardelino, C., Kwok, J., Blake, D. R., Ding, A., and So, K. L.: Ozone production and hydrocarbon reactivity in Hong Kong, Southern China, Atmos. Chem. Phys., 7, 557-573, 2007.) Therefore we did not repeat some methods used in that study but only gave a reference (for example, dCO/dNOy).

Here we use ratios of VOC to derive the source characteristics during ozone episode days in Hong Kong. It is only a preliminary analysis since only the total amounts of VOC and the emission inventory by sector are available, but not the spatial distribution. Chemical processes and transportation from mainland China are considered in the analyses of source of VOC (e.g. photochemical age as well as influence of mainland China).

Specific comments:
1.
Comment: The introduction
The current introduction section can be enhanced by adding more recent studies in Hong Kong and Pearl River Delta region on the measurements of ambient VOCs species, and VOCs sources including both inventories and source profiles. The

method and its constrain to use of VOCs ratios as a tool to explore the sources can also be discussed in this section.

Response:
Followed this comment, we added a paragraph in the introduction section stating more recent studies in Hong Kong and Pearl River Delta region on the measurements of ambient VOC species, and VOC sources including both inventories and source profiles. The method and its constrain to use of VOC ratios as a tool to explore the sources is added in Section 3.3 and Conclusion.

2.
Comment:
The comparison of VOCs ratios from ambient measurements with ratios derived from source inventories.

The whole section of 3.3 gave the readers an impression that the sources in both PRD and Hong Kong are not fully understood. Therefore, I would like to suggest that the ratios of the VOCs species in this manuscript derived from the published source inventories and relevant references are summarized before the ambient data is discussed. One needs to know how the ambient ratios comparing to the ratios of various sources. Of course, the reasons that may cause discrepancy will have to be mentioned, as the source inventories are annual average data, while the ambient data are only taken from October to December, and the local chemistry may play a role in changing the ratios from source to receptor site etc..

Response:
In Streets et al. (2003) for most VOC species only total amount of emissions were given, but not for different sources. A sentence is added in Section 3.2.2.1 (second paragraph) describing that the speciated version of emission inventory from CH2M

(2002) gives the ratio C6H14/toluene below 0.1 at Hong Kong and PRD region. Other ratios from the inventory are also described or illustrated in the text and figures. And a table is added for the ratios of the VOC species derived from the published source inventories and relevant references.

Some possible reasons that may cause discrepancy are mentioned in the text. For example, the source inventories are annual average data, while the ambient data are only taken from October to December. This point is mentioned in Section 3.3.3 and in the "Conclusion" that "the data on which our analyses are based are restricted spatially and temporally", and "more measurements would no doubt help characterize additional areas in more seasons and also check the accuracy of emission inventories more completely".

"Local chemistry" affects strongly the ratios of species with different photochemical age such as m,p-xylenes and ethylbenzene, but not much the ratios of species with same photochemical age such as hexanes and toluene. In our discussion, we used the ratios of species with different photochemical age to elucidate the impacts of chemistry (as well as a kind of indicator of distance from the sources), and the ratios of species with same photochemical age to illustrate the impacts of the sources (but not the chemistry or distance of transport). And in the ratios of alkanes in Section 3.3.2, we considered the impacts of dilution only and chemistry only (indicated by the two lines). Our measurements showed that with the impacts of both dilution and chemistry, the sources should be located in the upper right side of the intersection of the two lines (Fig. 9).

3.

Comment:

The interpretation of the sources of industrial, waterfront, and fuel storage activities

As stated in page 7 for the contribution of industrial, waterfront, and fuel storage

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sources, one has no idea how the ratios of C6H14-to-toluene are for these sources, so from the data present in figure 5a, it could be the excess of toluene comes from one or two of these 3 types of sources. The way to confirm which source could be more reasonable, is not explained adequately.

Response:
The sectors of sources in CH2M (2002) include energy, industry, transportation, VOC-containing products and other sources. Fuel storage is not specified in the report. Therefore we didn't get speciation of this source based on CH2M (2002) and we couldn't distinguish industrial, waterfront sources from fuel storage sources either. But we were able to infer some of the characteristics of industrial, waterfront sources and fuel storage sources from data collected at TP and TY (CH2M, 2002), two sites of which the first is located in a waterfront park where emission of industrial processes generated from Tai Po Industrial Estate could be monitored and the latter is located at the entrance portal of a tunnel. The characteristics of the two sites are added in the text.

4.
Comment:
The points on the influence of Guangdong by using the ratios of dCO/dNOy

I think more careful and detailed analysis were needed if the conclusion on the influence of Guangdong could be acceptable. Actually, the whole manuscript is more qualitative rather than quantitative, but in page 8, "over 30% of the variability was corrected with a factor associated with pollution from Guangdong province" was stated, the approach to obtain such an analysis was not provided. And this point was repeated even more strongly in summary of this part on page 10.

Actually, the anti-correlation between ratios of mp-xylene-to-ethylzenzene and ozone

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shown in figure 2a indicated that more likely the ozone formation at TO is a local chemical process.

Response:

Previous studies (Kok et al., 1997; Wang et al., 2001, 2003, cited in Zhang et al., 2007) show that dCO/dNOy can be used as a chemical tracer of influence of pollution from South Mainland China. Zhang et al. (2007) discussed the application of the ratio during the intensive campaign. To avoid repetition, this method is not described in this paper. Because the emission ratio of CO-to-NOx from Guangdong and Hong Kong are so different; i.e., $\sim$15 in Guangdong and $\sim$1 in Hong Kong (Streets et al, 2003), high ratios are generally indicative of air masses from Mainland China and low ratios of air masses impacted by local Hong Kong emissions.

On page 8, we used correlation analysis between the C6H14-to-toluene ratio and dCO/dNOy. The correlation coefficient R2 was 0.35, which means that 35% of the variability in the ratio C6H14/toluene was correlated with dCO/dNOy which could be regarded as a tracer of pollution from Guangdong Province or South Mainland China. And this is based on the statistical definition and significance of correlation coefficient.

Figure 2a showed that the ratio m,p-xylenes-to-ethylbenzene can be used as an indicator of photochemical age (of chemical process). Generally, an air mass from local sources has high ratio m,p-xylenes-to-ethylbenzene (shorter photochemical age), while an air mass from remote sources (i.e. transported from other places) is characterized by low ratio m,p-xylenes-to-ethylbenzene (longer photochemical age). Therefore from figure 2a only we cannot get enough support for that “the ozone formation at TO is a local chemical process.” Figure 2b showed the daily average ratio m,p-xylenes-to-ethylbenzene at TO is relatively low on 7 Nov., 2002, suggesting that this site is likely affected by upwind sources.

5.

Comment:

The discussion on the ratios of p-xylene-to-total xylenes is pretty strong in the manuscript. One would like very much to know the uncertainties of the ratios for both ambient data as well as the source data. And as the ambient data were obtained probably at different time of a day, the comparison of ambient level with ratios derived from sources needs to be very careful by put the error bars on.

Response:

In Figure 7 (ratio p-xylene/total xylenes), the data points were observed for hourly concentrations (data collected at Tai O) or 24-hr average (data collected at the four EPD sites). We did not put error bars on in the figure but added a sentence of statement in the text (due to too many points in the figure). The uncertainties for the concentrations of xylenes were below 10% (1%–10%, Colman et al., 2001). The ratio p-xylene-to-total xylenes has an uncertainty of below 10% for ambient data. The source emission by sector has an uncertainty of below 10% (CH2M, 2002). These uncertainties are now clarified in the text. Considering the use of source profiles of USEPA, the uncertainty of source inventory will increase.

6.

Comment:

The VOCs analysis done by UC Irvine gave different species at TO from that of EPD sites, and the author gave one detection limit for all species. I suggest this part on page 3 needs to be clarified though this is not the work of the authors. Response: The detection limits of VOCs analysis at TO and EPD sites were the same (5 pptv), as the samples were all analyzed by UC Irvine, though the VOC lists were a little different. This is clarified now in the text.

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7.
Comment:
As indicated by the authors, the source profiles from US EPA were used directly to make the speciated source inventories for Hong Kong and PRD. I can understand the reason when localized profiles are not as good as the one from US, however, the authors need to mention the possible problems by doing so.

Response:
Using source profiles from US EPA to speciate source inventories for Hong Kong and PRD may cause uncertainties in speciation. In the PRD region, fuels and other sources might probably have different profiles from those in the US. This difference might bring uncertainties in the speciation of source inventories in the region and thus cause uncertainties in VOC ratios of sources. However, fuels in Hong Kong are imported and supplied by companies such as Mobil, Shell. Therefore, the source profile in Hong Kong area should be similar to that in the US, and the using of US source profile will not probably cause large uncertainties in speciation of source inventories in Hong Kong. This is clarified now in the text about the speciation.

We thank Referee #3 again. The comments and suggestions will definitely improve our paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8847, 2008.