

Interactive comment on “Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory” by L. K. Xue et al.

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General comments:

- Does the paper address relevant scientific questions within the scope of ACP? Yes.
- Does the paper present novel concepts, ideas, tools, or data? The measurements are valuable.
- Are substantial conclusions reached? Fairly true generally.

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-Are the scientific methods and assumptions valid and clearly outlined? Overall good, but the authors still need to include details in method and results sections (see specific comments).

-Are the results sufficient to support the interpretations and conclusions? See specific comments.

-Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Fairly true.

-Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Many of the references cited are old.

Response: Some representative newer references have been cited in the revised manuscript (see response to the specific comments).

-Does the title clearly reflect the contents of the paper? Yes

-Does the abstract provide a concise and complete summary? Overall good.

-Is the overall presentation well structured and clear? Overall good.

-Is the language fluent and precise? Overall good.

-Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Overall good.

-Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? See specific comments.

-Are the number and quality of references appropriate? Need to cite newer studies.

Response: Some relevant newer studies have been cited in the revised paper (see response to the specific comments).

-Is the amount and quality of supplementary material appropriate? NA.

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This paper describes the VOCs seasonal (spring and summer) and diurnal variability (noon and midnight) at Mt Waliguan Observatory located in southwestern China in 2003, and discusses the VOC speciation in the air masses with five origins indicated by back trajectories. The authors then used the measurements to constrain a chemical box model to understand the photochemistry there. The objective is clear and important, the discussed science questions are within ACP's scope, and the measurements are valuable at an important location in Asia. Therefore, I recommend the paper to be published after the following concerns are dealt with.

Response: We thank the reviewer for the helpful comments. All the comments have been addressed and the manuscript has been revised accordingly. Below we give responses to the specific comments.

Specific comments:

1. Introduction

P11747, line 8-9: "In the lower troposphere, the photochemistry is more important than the stratospheric flux in controlling the ozone budget (Crutzen, 1995)." Recent studies have shown that the lower tropospheric ozone, especially at remote high-elevation regions may also be strongly affected by stratospheric intrusion during spring/summer. In page 11749, the authors cited a paper by Xue et al. 2011, showing the importance of stratospheric intrusion to ozone in the studied region in this paper.

Response: This sentence has been rephrased as "In the lower troposphere, the photochemistry plays a critical role in controlling the ozone budget".

P11747, list of reactions: I think they are somehow redundant for this paper. You did not describe all of them in the following text. Perhaps cite previous studies, and only the ones most relevant to WLG chemical regime should be kept.

Response: As these reactions are relevant to the description of calculation of the ozone production/destruction rates in Section 3.3.1 (Equations (1) and (2)), we choose to keep

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them in the manuscript.

P11748, the paragraph from line 7: "long-range transport" is a vague word in the context here. The authors should clearly define them using the terms of "hemispheric", "trans-Pacific", "transport from Europe to Asia", "import and export", etc. In addition, the references cited regarding the transport are relatively old. E.g., the sentence: "Moreover, there have been very few studies of the long-range transport of air pollution to East Asia from the upwind continents such as Europe (e.g., Wild et al., 2004)." is too strong. There are recent studies by the HTAP communities using multiple models regarding the impacts of transport of pollution from different source regions on east and south Asia pollution levels.

Response: We have adopted the more informative phrases suggested by the referee to define the "long-range transport" of different types. We have made a new literature review on the recent studies on hemispheric transport of air pollution, and cited some representative papers in the revised manuscript (see below).

Lin, M., Holloway, T., Carmichael, G. R., and Fiore, A. M.: Quantifying pollution inflow and outflow over East Asia in spring with regional and global models, *Atmos. Chem. Phys.*, 10, 4221-4239, 2010.

Lin, M., Fiore, A. M., Horowitz, W., Cooper, O. R., Naik, V., Holloway, J., Johnson, B. J., Middlebrook, A. M., Oltmans, S. J., Pollack, I. B., Ryerson, T. B., Warner, J. X., Wiedinmyer, C., Wilson, J., and Wyman, B: Transport of Asian ozone pollution into surface air over the western United States in spring, *J. Geophys. Res.-Atmosphere*, 117, D00V07, doi:10.1029/2011JD016961, 2012.

HTAP, Hemispheric transport of air pollution, Part A: ozone and particulate matter, New York and Geneva, 2010 (<http://www.htap.org/>).

The original statement concerned by the reviewer has been modified as "There are also relatively few studies on the transport from the upwind continents such as Europe

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to East Asia (e.g., Wild et al., 2004; HTAP, 2010; Lin et al., 2010)". We cite the HTAP report 2010 to refer the current efforts.

P11749, line 3: "Since then, ozone, greenhouse gases and aerosols have been measured continuously along with complete meteorological parameters (Tang et al., 1995; Ma et al., 2003; Zhou et al., 2003, 2004; Kivekas et al., 2009). These observations have yielded invaluable insight into the composition and chemistry of background atmosphere in the Asian continent" -Tropospheric ozone is an important greenhouse gas. -Why aren't they valuable? The authors described the findings based on ozone and meteorology measurements in the following paragraph. Maybe just remove this sentence.

Response: The original sentences have been changed to "Since then, greenhouse gases (including ozone) and aerosols have been measured continuously along with complete meteorological parameters (Tang et al., 1995; Ma et al., 2003; Zhou et al., 2003; Zhou et al., 2004; Kivekas et al., 2009). These observations have yielded valuable insight into the composition and chemistry of background atmosphere in the Asian continent."

P11750, line 3-9: maybe better to add the related section numbers when introducing the paper structure

Response: The section numbers have been added in the revised manuscript.

Fig. 1: Maybe better to add latitude/longitude. You have compared your measurements with those at other mid-latitude remote sites in Section 3.1.2, and TRACE-P data in Section 3.2.2. I'd be useful to include Mt. Tai and Haplo (which are also located within the big domain) in this figure. You should also denote the locations of TRACE-P samples in the figure.

Response: Figure 1 has been improved as suggested. Latitudes and longitudes are added, and the locations of Mt. Tai and Mt. Haplo are included in the big domain.

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As the comparison with the TRACE-P data is omitted from the revised manuscript (see response to the last comment), we don't denote the locations of the TRACE-P samples.

2. Method

P11751, line 2: "aimed to study: : "aimed at studying the impacts of non-local sources in spring/summer. You are going to discuss in specific the air mass source regions in Section 3.

Response: Changed.

P11751, line 18-22: please clearly define the sampling frequency. E.g., What do "continuously" and "routinely" mean?

Response: The trace gases including O₃, CO, NO and NO_y were measured in real-time at a time resolution of 1-minute, and the meteorological parameters were observed in real-time at a time resolution of 5-minute. We have added the time resolutions in the revised manuscript.

We used "routinely" to mean that the observations of meteorological parameters are a long-term routine work at WLG Observatory, within the framework of the WMO GAW programme, while the trace gas measurements were only performed during the present intensive campaigns.

P11751-11752, Section 2.2: I think the author should include more details regarding the trajectory analysis in this section:

- Back traj is not only useful for high-elevation sites. The authors could also add some references in which back traj were used for source attribution analysis. There are many of them.

Response: We modified the statement to "Backward trajectory analysis is a useful tool to track the transport history of air masses (Russo et al., 2003; Wang et al., 2006)". The following two references are added.

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Russo, R. S., Talbot, R. W., Dibb, J. E., Scheuer, E., Seid, G., Jordan, C. E., Fuelberg, H. E., Sachse, G. W., Avery, M. A., Vay, S. A., Blake, D. R., Blake, N. J., Atlas, E., Fried, A., Sandholm, S. T., Tan, D., Singh, H. B., Snow, J., and Heikes, B. G.: Chemical composition of Asian continental outflow over the western Pacific: results from Transport and Chemical Evolution over the Pacific (TRACE-P), *J. Geophys. Res.-Atmos.*, 108, 2003.

Wang, T., Wong, H. L. A., Tang, J., Ding, A., Wu, W. S., and Zhang, X. C.: On the origin of surface ozone and reactive nitrogen observed at a remote mountain site in the northeastern Qinghai-Tibetan Plateau, western China, *J. Geophys. Res.-Atmos.*, 111, 2006.

- How good are the FNL meteorological fields over these regions with complex topography? Citing some papers maybe helpful. What is the actual topography in the grid? Adding the spatial resolution and temporal frequency of FNL maybe useful.

Response: Waliguan is located in the northeastern part of the Qinghai-Tibetan plateau. The surrounding area is mountainous with an overall high elevation. The FNL meteorological fields should be suitable for investigating the large-scale transport as targeted in the present study. We have added the following references in the revised manuscript. The spatial and temporal resolutions (191 km × 191 km; 6 hour) are also added.

Gangoiti, G., Albizuri, A., Alonso, L., Navazo, M., Matabuena, M., Valdenebro, V., Garcia, J., and Millan M.: Sub-continental transport mechanisms and pathways during two ozone episodes in northern Spain, *Atmos. Chem. Phys.*, 6, 1469-1484, 2006.

Lin, M., Holloway, T., Streets, D., and Richter, A: Multi-scale model analysis of boundary layer ozone over East Asia, *Atmos. Chem. Phys.*, 9, 3277-3301, 2009.

- What is the method/criteria you used to define the five regions for your trajectory grouping?

Response: A total of 115 trajectories were computed corresponding to the VOC sam-

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ples. The trajectories were then grouped according to the directions (60° sectors; North, Northwest, Southeast, and Southwest) from which they came and the altitudes where they transported before reaching WLG (lower troposphere and middle troposphere). The results from this simple approach agreed very well with those determined from a cluster analysis for the whole campaigns (Wang et al., 2006). We have elaborated this in the revised manuscript.

Wang, T., Wong, H. L. A., Tang, J., Ding, A., Wu, W. S., and Zhang, X. C.: On the origin of surface ozone and reactive nitrogen observed at a remote mountain site in the northeastern Qinghai-Tibetan Plateau, western China, *J. Geophys. Res.-Atmos.*, 111, 2006.

P11753, paragraph from line 16: Since you only analyzed one day for each period, how representative are they for the spring and summer periods? Therefore, the conclusions based on such results indeed need to be further explored by extending the study period. Please also spell out the abbreviations before using them in this section.

Response: The original description may be misleading. We used the campaign-median diurnal measurement data in spring and summer to run the model, so we think the results may reflect the overall conditions of the measurement periods. We have elaborated this in the revised manuscript. The abbreviations are also spelt out.

3. Results

P11754-11756: I think this section could be better organized.

-Table 1: how big is the detection limit? Need to add in the notes. The VOC species in the table may be better ordered/grouped for us to read: e.g., based on the major sources lifetimes, or/and the order they are discussed in the text

Response: The detection limit is 3 pptv, and has been added in the notes. Table 1 has been updated as follows: the VOC species are grouped into "Alkanes", "Alkenes", "Alkynes", "Aromatics" and "Halocarbons"; within each group the species are ordered

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by the carbon numbers.

-Emissions and concentrations of VOC species from biosphere such as isoprene are not only sensitive to temperature, but also others such as radiation, etc, which can cause the strong seasonal variability.

Response: We have corrected this by mentioning the influence of radiation on the biogenic VOC emissions.

-Table 2: in the notes, Cimone. . .m.asl. messed up (typesetting issue)

Response: We have rechecked and made the format of the table notes consistent, and will contact the editorial office on the typesetting issues if accepted.

P11757-11758: - Please consider rewording the title of "influence of long-range transport"

Response: The section title has been changed to "Air mass transport and VOC speciation".

-The authors included the VOC emissions in Fig. 3 together with the trajectories but did not discuss them in detail. The emissions plotted did not reflect the biomass burning emissions. Also, the anthropogenic VOC emissions along the "North" trajectory are low, but the VOC measurements (Table 3) in these air masses are higher than "NW" and "NW-MT", close to the highly-polluted "NE" and "SW", may be useful to add some explanations on this.

Response: The VOC emissions are shown in Figure 3 to provide readers an overall picture of anthropogenic VOC emissions over the study region. Here the point is that anthropogenic VOC emissions are concentrated in eastern/central China and India but very low in central Asia. We have added a sentence to elaborate this in the revised manuscript. To avoid making the figure too busy, the biomass burning emissions are not included here.

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Although the anthropogenic VOC emissions along the "North" trajectory are low from the figure (maybe due to the relatively low resolution (50 km × 50 km) of the emission data), several large cities, such as Yinchuan (2 million people) and Xining (2 million people; close to WLG), are located along the trajectory. The high VOC levels in these air masses should be due to the influence of anthropogenic emissions in northern China, mostly likely these large cities. We have added discussion on this in the revised manuscript.

P11758-11759: I am not very convinced by the idea of direct comparing the TRACE-P data in 2001 with the WLG measurements in 2003 in this study, to represent the inflow/outflows of "China sub-Continent". I am also not convinced by the conclusions in this section. Specifically,

1) The emissions (anthropogenic, biomass burning, etc) and the meteorological conditions may vary significantly for these two periods. You have mentioned that CO measurements during TRACE-P were higher than measurements in this study. However, previous study (e.g., Tang et al., 2003) has shown biomass burning could have a big impact during TRACE-P. At least the authors should discuss these differences between these two years.

2) TRACE-P data you used covered a larger area in E. Asia, rather than measurements at a single location (this study).

3) I doubt whether WLG measurements are representative of the inflows (transported from Europe). The Fig.7 (screenshot below) in a study by Lin et al. (2010) indicated that the impacts of European emissions on E. Asia air quality were spatial varying during TRACE-P period, and the strongest impact did not appear to be at WLG based on their conclusions.

4) The Lin et al. (2010) paper also showed that outflows of CO, O₃, PAN can be extended to 6-9 km during TRACE-P, indicated by observations and models. It'd be useful to compare your conclusion of "Emissions in China may not have significant

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influence on the free tropospheric outflow” with theirs.

5) The authors should be careful about using the words of “airmass(es) from Europe” and “European pollution”.

References

Lin, M., Holloway, T., Carmichael, G. R., and Fiore, A. M.: Quantifying pollution inflow and outflow over East Asia in spring with regional and global models, *Atmos. Chem. Phys.*, 10, 4221-4239, doi: 10.5194/acp-10-4221-2010, 2010.

Tang, Y., et al. (2003), Influences of biomass burning during the Transport and Chemical Evolution Over the Pacific (TRACE-P) experiment identified by the regional chemical transport model, *J. Geophys. Res.*, 108, 8824, doi: 10.1029/2002JD003110, D21.

Response: The discussion about the inflow/outflow comparison has been removed from the revised manuscript.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 11745, 2013.