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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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The Waliguan Observatory (WLG) is an WMO global atmosphere baseline station, located in the northwestern part of the Tibetan Plateau. Observed levels and variations of O3, CO and relatively long-lived VOCs at WLG generally reflect the chemical and transport processes of these species on a large (Eurasian or Northern Hemisphere) scale. This paper by Xue et al. reports VOCs measurements made in the late spring and summer of 2003 at WLG. The authors also investigate the chemical budget of O3

and radicals with a chemical (Master Chemical Mechanism) box model, constrained by measured VOCs and other species including NO and O3. This kind of study is very import for understanding the chemistry of the remote atmosphere as well as the perturbations from human activities.

The VOC data reported in this study is valuable, and the modeling method they applied appears to be fine, although some parameters and simulation results need to be introduced in detail. In contrast to previous modeling work, the authors show net production of ozone at WLG in summer. This finding is very interesting and needs investigating further. On the other hand, I do have a doubt about their method used to access the pollution inflow and outflow of the China sub-continent. I am also too conservative to accept their conclusion in that transport of anthropogenic pollution from central and eastern China can SIGNIFICANTLY perturb the chemistry of the background atmosphere over the Tibetan Plateau. I think that VOCs measurements and modeling work presented in this study may still have a big gap to attain this conclusion. In my opinion, the paper can be considered as accepted after major revisions having been made in response to my comments and questions below.

Response: We thank the reviewer for the helpful suggestion and comments. The manuscript has been revised accordingly. Below are the responses to the specific comments.

1. The method used to access the inflow and outflow of the sub-continent of China does not sound. What geographic domain does "the sub-continent of China" refer to in this study, the eastern China or the entire China area? In either case, measurements at a ground station like WLG cannot be used directly to infer an inflow, especially considering that the air masses tend to undergo substantial aging and mixing processes while being transported. Moreover, the authors did not provide a strong evidence to demonstrate that the air masses encountered during TRACE-P had originally come from (or passed by) WLG, partially mixed with emissions from eastern China, and then transported to the west Pacific. A simple arithmetic operation as performed in this study

seems not sufficient to obtain such a conclusion as “the surface emission in China may not have significant influence on the free tropospheric outflow”. Therefore, I would recommend Sect. 3.2.2 and Table 4 (as well as related conclusions in the abstract and Sect. 5) being skipped.

Response: The discussion on the inflow/outflow comparison (including Section 3.2.2, Table 4, and related conclusions in the abstract and summary) has been omitted from the revised manuscript.

2. In contrast to previous work, this study has derived a net ozone production from in-situ photochemistry at WLG. In addition to the NO level, which appears to be the most important factor in determining the net ozone production at WLG, the authors may want to have a discussion on the effect of the differences in the concentrations of other chemical species. While NO being constrained by measurements, how was NO2 treaded in their box model simulations, and how about its mixing ratio value(s)? What are the levels of intermediate products such as HCHO and H2O2 predicted by the model? Are the mixing ratios of NOy simulated by the model comparable to its measured values?

Response: We examined the parameters used in the previous modeling work (Ma et al., 2003) and in the present study, and found three major differences. (1) The concentrations of NMHCs, in particular alkenes and alkanes (except ethane), were much higher in the previous study. For example, very high level of ethene (2.23 ppbv versus 0.10 ppbv in the present study) was determined in that study. However, the difference in NMHC concentrations is not believed as the reason for the contrary conclusions on in-situ ozone production, as our sensitivity studies showed that the in-situ ozone production was not sensitive to NMHCs at WLG. And higher NMHCs in the previous study would lead to more ozone production by facilitating radical cycling, rather than the net ozone destruction. (2) The level of H2O2 measured in the previous study was also high (daily average = 1.6 ppbv) and was attributed to the long-range transport. In the present study, H2O2 was not measured but predicted by the model. As the model

did not take transport into account, the model-simulated H2O2 should be considered as the locally produced, and was much lower than the previous measurements (daily average = 0.38 ppbv). This difference is also not the cause of different conclusions between two studies, because higher H2O2 would promote ozone production by providing more radicals. Our sensitivity model run with higher H2O2 level (daily average = 1.6 ppbv) indeed show higher rate of net ozone production at WLG. (3) The NOx levels were much lower in the previous study (NO = 13-18 pptv; NO2 = 48 pptv) than ours (daytime average: NO = 47 pptv; NO2 = 100 pptv). We think this should be the key factor resulting in different conclusions between the two studies, as the NOx levels can lead to different ozone photochemical regimes, i.e. production or destruction, at remote locations. We performed a sensitivity model run with lower NO (18 pptv) and indeed found a net ozone destruction (net rate = -0.03 ppb/h) in summer at WLG. A paragraph has been added in the revised manuscript to discuss the above differences.

NO2 was simulated by the model with constraints of the measured NO. The daily average NO2 mixing ratios were 0.17 ppbv in spring and 0.11 ppbv in summer. We have added this information in the revised manuscript.

The model-simulated H2O2 and HCHO (and other intermediates) should be only of local photochemical origin. The modeled daily average H2O2 levels were 0.18 ppbv in spring and 0.38 ppbv in summer. As mentioned above, the summertime level was much lower than that measured in the previous work (1.6 ppbv; Ma et al., 2003). We have conducted sensitivity model run with that higher H2O2 concentrations and found that the main conclusions of the present study (1. net ozone production in summer and 2. predominant role of O3 in primary radical sources) did not change (the daytime-average net ozone production rate in summer increased from 0.26 ppb/h in the base run to 0.28 ppb/h; the daytime-average OH production rate increased from 13 ppt/h to 53 ppt/h, which was still lower than 274 ppt/h from ozone photolysis).

The model-simulated daily average concentrations of HCHO were 0.29 ppbv in spring and 0.53 ppbv in summer. Previous measurements of HCHO were very scarce at

WLG, and the only available data from a 10-days campaign in August-September 2005 showed very high levels of HCHO (average of 4.16 ppbv; and also CH3CHO) at WLG (Mu et al., 2007). Such high levels of HCHO were usually observed in polluted suburban or rural environments, but were rarely measured at remote sites. If this was also the case in the present study, HCHO would be the predominant radical source (620 ppt/h of HO2 production rate at 4.16 ppb of HCHO) and stronger net in-situ ozone production (daytime average = 0.35 ppb/h) would be expected, as indicated by our sensitivity model run. Further accurate measurements of HCHO and other OVOCs are needed. We have added a discussion in the revised manuscript.

The NOy measurements in the present study may be subject to positive interferences, so we made a comparison between the modeling results and the measurements of individual NOy components made in summer 2006 (Xue et al., 2011). The model-simulated daily average concentrations of NO2, PAN and HNO3 in summer 2003 were 0.11, 0.25 and 0.03 pptv, compared to the measured levels of 0.32, 0.44 and 0.26 ppbv in summer 2006. Note that formation of aerosol nitrate was not included in the MCM, so the concentration of aerosol NO3- was not available (and the simulated HNO3 may be also underestimated). The modeling results were lower than the measurements because (1) more pollution transport from eastern China resulted in higher pollution at WLG in summer 2006 (e.g., CO = 149 ppbv; NO = 71 pptv) than in summer 2003 (e.g., CO = 125 ppbv; NO = 47 pptv) (Xue et al., 2011) and (2) the model did not consider transport that is important for the long-lived NOy species. We have stated this limitation (i.e., without consideration of transport) of our results in the revised manuscript.

References:

Xue, L. K., Wang, T., Zhang, J. M., Zhang, X. C., Deliger, Poon, C. N., Ding, A. J., Zhou, X. H., Wu, W. S., Tang, J., Zhang, Q. Z., and Wang, W. X.: Source of surface ozone and reactive nitrogen speciation at Mount Waliguan in western China: new insights from the 2006 summer study, J. Geophys. Res.-Atmos., 116, 2011.

Ma, J. Z., Tang, J., Zhou, X. J., and Zhang, X. S.: Estimates of the chemical budget for ozone at Waliguan Observatory, J. Atmos. Chem., 41, 21-48, 2002.

Mu, Y., Pang, X., Quan, J., and Zhang, X.: Atmospheric carbonyl compounds in Chinese background area: a remote mountain of the Qinghai-Tibetan Plateau, J. Geophys. Res.-Atmosphere, 112, D22302, doi:10.1029/2006JD008211, 2007.

3. One of the important conclusions of this study is “the transport of anthropogenic pollution from central and eastern China can significantly perturb the chemistry of the background atmosphere over the Plateau”. The authors might want to consider making this argument weaker and narrower according to the following aspects. First, being located in the northwest corner of the Tibet Plateau, WLG cannot represent the main body of the plateau, which is rarely influenced by air masses from central and eastern China during summertime. Second, the authors do not provide any evidence to show increasing NMHCs at WLG with increasing pollution in central and eastern China. They should make a comparison of the levels of NMHCs at WLG measured in this study with those made in previous years, instead of listing the results from Mt. Tai experiment in Table 2. Nevertheless, while this study focuses on photochemistry of volatile organic compounds, the authors have shown by their model tests that the ozone production at WLG is insensitive to CH4 and NMHCs. Third, the authors observed much higher levels of NO in this study than from previous work. However, they could not make it clear whether such discrepancy was due to an increasing influence of pollution or the difference in the experimental method. Even if an increasing trend of NO was found, the cause from local emission sources (within the plateau) should be excluded before reaching such a conclusion.

Response: We agree the points of the reviewer. But actually we make this argument not based on the results of VOCs or NO, but according to the radical budget analysis together with our previous study on ozone transport. Specifically, the present study indicates that ozone is a predominant radical source at Waliguan; our previous study has suggested the dominant contribution of pollution transport from central and eastern

China to the summertime ozone at Waliguan (Xue at al., 2011). As the ROx radicals are the principle oxidants in atmospheric chemistry, we make the point that pollution transport can perturb the background atmosphere over the Plateau, not only in composition (O3) but also in chemistry (ROx).

The statements in the original manuscript may be misleading, and we have clarified this in the revised manuscript. We have also weakened this conclusion by removing it in the abstract and rephrasing it in the summary as follows. "...transport of anthropogenic pollution from central and eastern China MAY perturb the chemistry of the background atmosphere over the Plateau."

Reference:

Xue, L. K., Wang, T., Zhang, J. M., Zhang, X. C., Deliger, Poon, C. N., Ding, A. J., Zhou, X. H., Wu, W. S., Tang, J., Zhang, Q. Z., and Wang, W. X.: Source of surface ozone and reactive nitrogen speciation at Mount Waliguan in western China: new insights from the 2006 summer study, J. Geophys. Res.-Atmos., 116, 2011.

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