

Interactive comment on “Low-level isoprene observed during summertime at a forested mountaintop site in southern China: Implications for strong regional atmospheric oxidative capacity” by Daocheng Gong et al.

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Dear Referee#2,

We greatly appreciate the time and effort that you spent in reviewing our manuscript. The comments are really thoughtful and helpful to improve the quality of our paper. Most of the modifications were made in the manuscript (attached) and below are point-by-point response to these comments. There follows a list of referee comments (**in black**), together with our response (**in blue**) and details of corrections/improvements to the manuscript (**in red**).

The authors present field measurements of isoprene, MACR and MVK at a forested mountain site in southern China. Relatively lower concentration levels of isoprene and higher ratios of (MVK+MACR)/isoprene than other forest sites were observed. The authors argued that the low isoprene levels were ascribed to the strong atmospheric oxidative capacity in the region, and a chemical box model constrained with observations further confirmed this argument. Overall, this paper presents new data of isoprene and its first-stage degradation intermediates in a unique environment with interactions of both biogenic and anthropogenic emissions. It is well organized and written. Therefore, this

manuscript can be considered for publication after the following specific comments being properly addressed.

Response: We thank the referee for this overview. We have made changes to the manuscript based on the referee's helpful comments.

Major comments:

The authors used an MCM chemical box model to predict the concentrations of OH and NO₃ radicals. This model has been applied in several previous studies. However, there are still several issues that need to be clarified, and some additional modeling runs are needed to check the sensitivity of modelling results to these issues.

-1. Some previous studies have suggested that the MCM model may not work well for reproducing the HO_x concentrations at high-BVOCs and low-NO_x conditions, which seems to be the case of the study area in the present study. The authors may need to check the applicability of the MCM to the environmental condition at this forested mountain site.

Response: Many thanks and we agree with the referee that MCM needs to be improved and further optimized at pristine forest environments. And also as the OH mixing ratios modelled by PBM-MCM can only represent the levels at the site. Therefore, a parameterization method using measured aromatic hydrocarbons has been applied to estimate the regional mixing ratios of daytime OH radicals (Fig.1 and Fig.2) (Shiu et al., 2007). We think that this additional approach provides a good complement to the current model for evaluating the atmospheric oxidative capacity in the present forest regions. We have therefore added this point in the Section 2.3 and 3.3.1.

In the Section 2.3:" Several issues should be noted in applying PBM-MCM to the present study. The first is that some previous studies have suggested that MCM may not work well for reproducing the OH concentrations in pristine forest environments (Kim et al., 2015). And also as the OH mixing ratios modelled by PBM-MCM can only represent the levels at the site. To provide a complement to the PBM-MCM model, a parameterization method using measured aromatic hydrocarbons was applied to

estimate the regional mixing ratios of daytime OH radicals (Shiu et al., 2007). Details about the parameterization method are given in the Text S1.”

In the Section 3.3.1: “...The regional mixing ratios of OH ($19.7 \pm 2.3 \times 10^6$ molecules cm^{-3}) were even higher than the modelled site-level OH ($11.7 \pm 0.4 \times 10^6$ molecules cm^{-3}) during 09:00 – 15:00 LST (Fig. S1), though the results at 11:00 LST estimated by the two methods were comparable (13.2 ± 0.7 and $13.9 \pm 4.3 \times 10^6$ molecules cm^{-3}) (Fig. S2). Overall,...”.

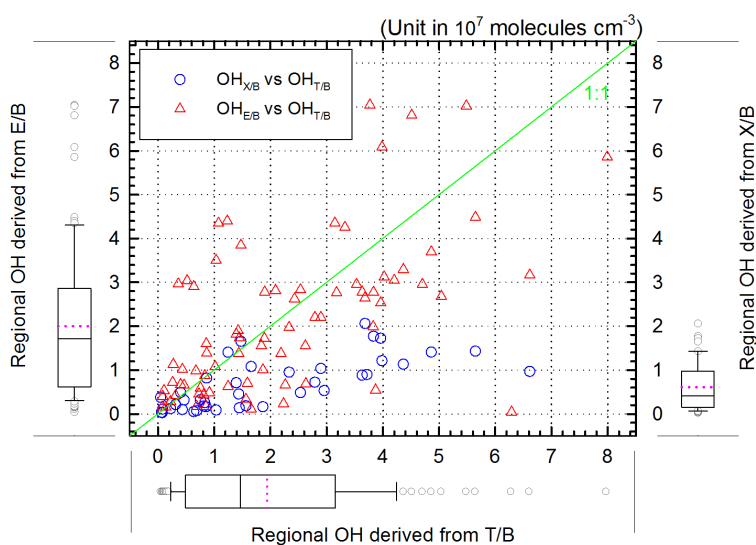


Fig.1. Scatterplots of the regional mixing ratios of OH during 09:00 – 15:00 LST derived from the toluene/benzene ($\text{OH}_{\text{T/B}}$), ethylbenzene/benzene ($\text{OH}_{\text{E/B}}$) and m,p-xylene/benzene ($\text{OH}_{\text{X/B}}$) ratios. The green line denotes a 1:1 relationship. Next to axes are the box and whisker plots of each result, and the pink dotted lines denote the mean values.

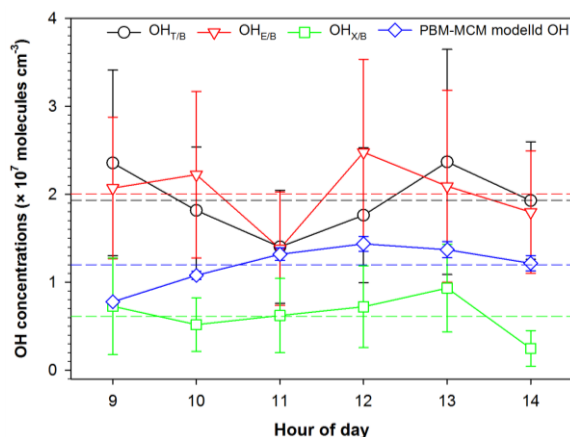


Fig.2. Hourly variations of OH concentrations derived from the toluene/benzene ratio ($\text{OH}_{\text{T/B}}$), ethylbenzene/benzene ratio ($\text{OH}_{\text{E/B}}$), m,p-xylene/benzene ratio ($\text{OH}_{\text{X/B}}$) and PBM-MCM during 09:00 – 15:00 LST. Short-dashed lines denote the mean values of each method. Error bars indicate the 95% confidence interval.

References:

Shiu, C. J., Liu, S. C., Chang, C. C., Chen, J. P., Chou, C. C. K., Lin, C. Y., and Young, C. Y.: Photochemical production of ozone and control strategy for Southern Taiwan, *Atmos Environ*, 41, 9324-9340, 10.1016/j.atmosenv.2007.09.014, 2007.

Kim, S., Kim, S. Y., Lee, M., Shim, H., Wolfe, G. M., Guenther, A. B., He, A., Hong, Y., and Han, J.: Impact of isoprene and HONO chemistry on ozone and OVOC formation in a semirural South Korean forest, *Atmos Chem Phys*, 15, 4357-4371, 10.5194/acp-15-4357-2015, 2015.

-2. The NO₂ measurement analyzer used in this study may significantly overestimate for NO₂ at rural and remote sites. The authors are suggested to conduct more modeling analyses with artificially reduced NO₂ concentrations to examine the sensitivity of predicted OH and NO₃ to the input NO₂ data.

Response: Many thanks for spotting this, we have therefore conducted sensitivity analyses of modelled daytime OH and nighttime NO₃ with cutting NO₂ concentrations. The OH and NO₃ concentrations showed decreasing trends with the NO₂ reducing (Fig.3). Assuming the average concentrations of daytime and nighttime NO₂ have been overestimated by $64.4 \pm 2.9\%$ and $62.4 \pm 3.0\%$ (Fig. 4), respectively, according to the results at a high-altitude mountain site in China (Xu et al., 2013), the mean daytime OH concentration at the present site would decrease from $7.3 \pm 0.5 \times 10^6$ molecules cm⁻³ to $5.5 \pm 0.4 \times 10^6$ molecules cm⁻³, with a reduction rate of $23.8 \pm 6.2\%$. And for nighttime NO₃, the decreasing rate was $41.5 \pm 5.2\%$ (from $6.0 \pm 0.5 \times 10^8$ molecules cm⁻³ to $3.5 \pm 0.3 \times 10^8$ molecules cm⁻³). We have therefore added discussions about this point in the Section 2.3 and 3.3.3.

In the Section 2.3: "...Second, the NO₂ concentrations, an important input into PBM-MCM, may be significantly overestimated at this remote mountaintop site that receives a considerable amount of photochemically aged air (Xu et al., 2013). To examine the sensitivity of predicted OH and NO₃ to the input NO₂ data, we have therefore conducted several modelling analyses with artificially reduced NO₂ concentrations. More details are discussed in Section 3.3.3...."

In the Section 3.3.3: "As mentioned in Section 2.3, the overestimated NO₂ and unmeasured HONO were the two main uncertainties in applying the PBM-MCM to evaluate the atmospheric oxidative capacity in the present study. As for the first issue, we conducted sensitivity analysis of modelled OH and NO₃ with artificially reduced NO₂ concentrations for the period Aug. 11 – Aug. 15 2016. The OH and NO₃ concentrations showed decreasing trends with the NO₂ cutting (Fig. S9). Assuming the average

concentrations of daytime and nighttime NO_2 have been overestimated by $64.4 \pm 2.9\%$ and $62.4 \pm 3.0\%$, respectively, according to the results at a high-altitude mountain site in China (Xu et al., 2013), the mean daytime OH concentration would decrease from $7.3 \pm 0.5 \times 10^6$ molecules cm^{-3} to $5.5 \pm 0.4 \times 10^6$ molecules cm^{-3} , with a reduction rate of $23.8 \pm 6.2\%$. And for nighttime NO_3 , the decreasing rate was $41.5 \pm 5.2\%$ (from $6.0 \pm 0.5 \times 10^8$ molecules cm^{-3} to $3.5 \pm 0.3 \times 10^8$ molecules cm^{-3})....”.

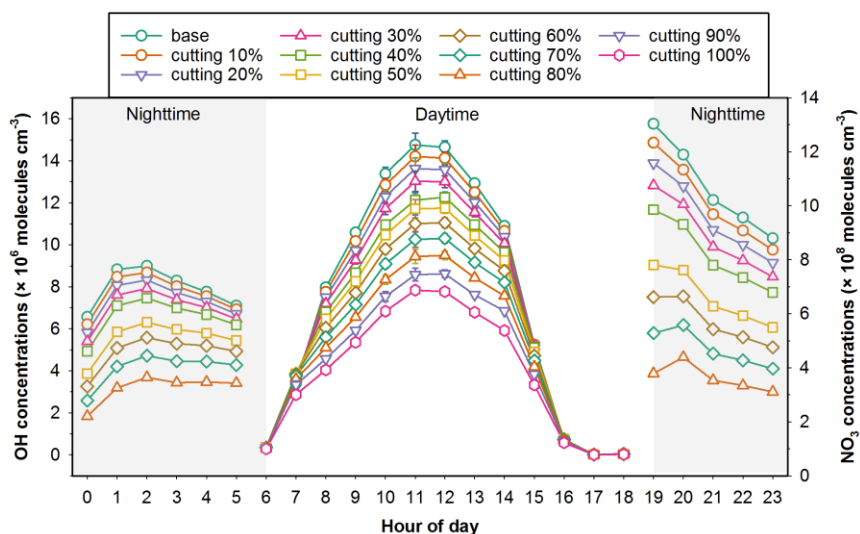


Fig.3. Sensitivity analysis of PBM-MCM modelled daytime OH and nighttime NO_3 with reduced NO_2 concentrations for the period Aug.11 – Aug.15 2016.

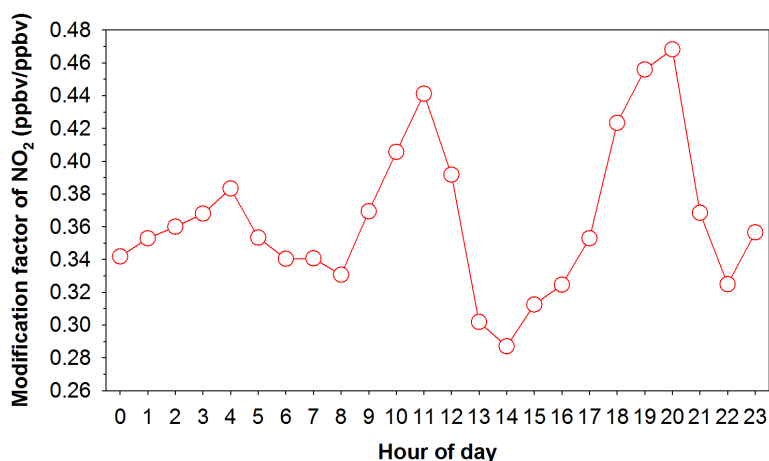


Fig.4. Hourly modification factor of NO_2 during July 15–August 17 2016 at the Nanling site. The data in the figure are reproduced from the study conducted at a high-altitude mountain site (Mt. Tai) in central China by Xu et al. (2013).

References:

Xu, Z., Wang, T., Xue, L. K., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S. L., Chai, F. H., and Wang, W. X.: *Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China*, *Atmos Environ*, 76, 221-226, 10.1016/j.atmosenv.2012.09.043, 2013.

-3. The heterogeneous reactions of N₂O₅ play an important role in the nocturnal NO₃ chemistry. How does the PBM-MCM model present the N₂O₅ chemistry? What uptake coefficients of N₂O₅ onto particles were adopted in the model? Previous MCM modelling studies with addition of heterogeneous N₂O₅ chemistry have indicated the significant effect of this process on the simulation of photochemical processes (Xue *et al.*, 2014). Additional modelling analyses are needed to examine the sensitivity of NO₃ to the N₂O₅ heterogeneous chemistry.

Response: We appreciate the referee's question and we agree that taking N₂O₅ heterogeneous chemistry into consideration would be very meaningful. Unfortunately, we were not able to quantitatively take into account this important mechanism. We have admitted this limitation in the manuscript.

In the Section 2.3: "...Finally, some recent studies have reported that the heterogeneous process of N₂O₅ is a considerable uncertainty in the current understanding of nocturnal NO₃ chemistry in certain polluted regions (Xue *et al.*, 2014b). Unfortunately, we were not able to quantitatively take into account this potential important mechanism in this study....".

In the Section 3.3.3: "...In addition, the absence of N₂O₅ heterogeneous chemistry in current modelling may also overestimate the nighttime NO₃ concentrations to a certain extent, and further studies are needed to make up this limitation."

References:

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: *Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes*, *Atmos. Chem. Phys.*, 14, 13175-13188, 10.5194/acp-14-13175-2014, 2014b.

4. Similarly, the HONO chemistry was also not well represented in the MCM model, but plays an important role in the OH simulation (Xue *et al.*, 2014). Did the PBM-MCM model take this chemistry into account? If not, the authors may need to conduct some sensitivity analyses or at least mention the potential uncertainty of modeling results.

Xue *et al.*, *Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes*, *Atmos. Chem. Phys.*, 14, 13175- 13188, 2014.

Response: Many thanks for spotting this. Since we did not measure the concentrations of HONO in the sampling periods, the average diurnal profiles of HONO observed at a background site (Hok Tsui) in Hong Kong in autumn 2012 (Zha, 2015) were applied to conduct sensitivity analyses. The results showed that daytime OH concentrations with HONO taken into account was $22 \pm 19\%$ higher than that without HONO (Fig.5). Nonetheless, the results are not representative due to the lack of HONO measurements at the present site. Thus, certain uncertainties remain and we have therefore added discussions about this point in the Section 2.3 and Section 3.3.3.

In the Section 2.3: "...And thirdly, a number of studies have shown that HONO plays an important role in daytime OH formation (Xue *et al.*, 2014b); but regrettably, we did not measure the concentrations of HONO in the sampling periods. We have therefore conducted sensitivity analyses of modelled daytime OH with average diurnal profiles of HONO observed at a background site (Hok Tsui) in Hong Kong in autumn 2012 (Zha, 2015). The results are discussed in Section 3.3.3....".

In the Section 3.3.3: "...Another issue was the lack of HONO measurements, we have therefore conducted two days' sensitivity analyses (Aug. 13 and Aug. 15 2016) by using the average diurnal profiles of HONO observed at a background site (Hok Tsui) in Hong Kong in autumn 2012 (Zha, 2015). The results showed that daytime OH concentrations with HONO taken into account was $22 \pm 19\%$ higher than that without HONO (Fig. S10). Nonetheless, the results are not representative since the HONO mixing ratios were not observed in the present study. Thus, certain uncertainties remain in the present modelling for HONO chemistry....Overall, we made an attempt to took these uncertainties into account by assuming the modification factor based on the above sensitivity analyses (Fig. 4). On average, current PBM-MCM may have $19 \pm 9\%$ and $73 \pm 16\%$ overestimation of the daytime OH and nighttime NO₃ concentrations, respectively."

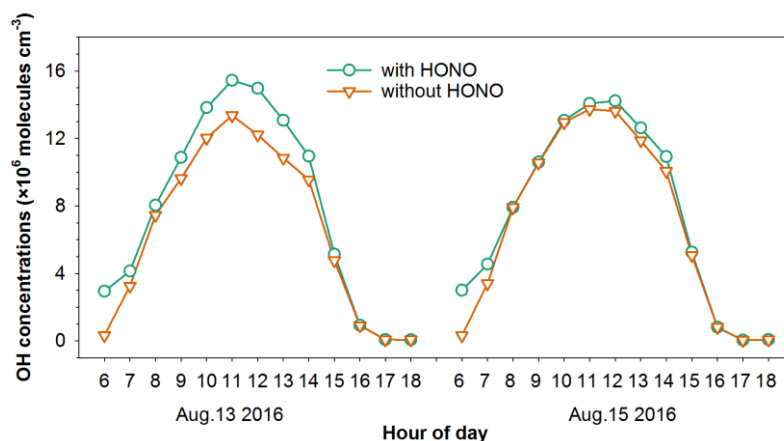


Fig.5. Sensitivity analysis of PBM-MCM modelled daytime OH with and without HONO for the period Aug.13 and Aug.15 2016. The HONO data was obtained from the study conducted at a background site (Hok Tsui) in Hong Kong in autumn 2012 by Zha (2015).

References:

Zha, Q.: *Measurement of nitrous acid (HONO) and the implications to photochemical pollution*, MPhil dissertation, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 2015.

Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: *Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes*, *Atmos. Chem. Phys.*, 14, 13175-13188, 10.5194/acp-14-13175-2014, 2014b.

-5. Sections 2.4 and 2.5: additional information about the calculation methods of the isoprene reaction time and air mass age, including principles and uncertainties, are required for readers to better understand and reproduce the results. The authors may also need to comment on the difference between reaction time and air mass age.

Response: Many thanks for spotting this. We have supplied more information about the principles and uncertainties of the calculation methods in the Section 2.4 and Section 2.5, respectively.

In the Section 2.4, principles added: “In this “back-of-the-envelope” approach, we have assumed that the rates of turbulent mixing and horizontal convection are similar for all three compounds, *i.e.*, the difference in the rate does not play a significant role during the time of transport from the nearby forest canopy to the altitude of the observation (Kuhn et al., 2007).”

In the Section 2.4, uncertainties added: “Two potential uncertainties arise when applying this approach to the low-NO atmosphere in the present study (Wolfe et al., 2016). First, the yields of MVK and MACR from OH-initiated isoprene oxidation are a nonlinear function of NO. Previous applications of this method (de Gouw, 2005; Roberts et al., 2006; Stroud et al., 2001; Karl et al., 2007; Kuhn et al., 2007) have assumed lab-derived constant yields for MVK and MACR, respectively (Atkinson and Arey, 2003), which may not be appropriate in the present case. In this study, we chose the results in Master Chemical Mechanism (MCM) v3.3.1 (Jenkin et al., 2015). Second, the reaction time implied by any observed daughter/parent ratio depends on the concentration of radical (*i.e.*, OH and NO₃), which was not measured and varies as an air mass ages. Rather than assume a single “typical” value for radical, we express reaction time in terms of “exposure”, defined here as the product of radical concentration and reaction time. Also, the atmospheric reaction time of isoprene can be calculated based on the modeled OH and NO₃ concentrations in this study.”

In the Section 2.5, principles and uncertainties added: “The limitations of using aromatic ratios to calculate photochemical age are addressed by previous studies (Parrish et al., 2007). Three issues should be noted when applying this method to present study. The first is the mixing of fresh emissions with aged air masses caused by the transport processes in the atmosphere. Second, the modelled OH at this site can’t represent the regional value in the air parcel. And third, the effect of horizontal and vertical mixing are similar for two compounds of BTEX ratio. Here we assume that there were no fresh emissions of those aromatics along the paths travelled and the OH concentrations were constant during hourly modelling duration throughout the pristine forest atmosphere. Regardless of those uncertainties, this air mass age estimation method still provides useful indicators of the degree of photochemical processing in the atmosphere.”

As for the differences between reaction time and air mass age, we have added an explanation of reaction time and a description of air mass age in the Section 2.4 and Section 2.5, respectively.

In the Section 2.4: “...the time of isoprene in the atmosphere between emission and detection,...”

In the Section 2.5: “The estimation of isoprene reaction time in an air parcel provides useful information on the isoprene oxidation rates. In addition, measurements of certain anthropogenic VOCs provided us a chance to evaluate the aging degree of the air mass via the determination of photochemical age which

can be calculated by the ratios of two VOC species that share common emission sources but with large different reactivities with OH (Parrish et al., 2007). It is well known that BTEX (benzene, toluene, ethylbenzene, and xylenes) provide particularly promising VOC ratios for following photochemical processing on timescales of hours to days (de Gouw, 2005;Shiu et al., 2007;Yuan et al., 2012;Yang et al., 2017).”

References:

- Kuhn, U., Andreae, M. O., Ammann, C., Araujo, A. C., Brancaleoni, E., Ciccioli, P., Dindorf, T., Frattoni, M., Gatti, L. V., Ganzeveld, L., Kruijt, B., Lelieveld, J., Lloyd, J., Meixner, F. X., Nobre, A. D., Poschl, U., Spirig, C., Stefani, P., Thielmann, A., Valentini, R., and Kesselmeier, J.: Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on the atmospheric chemistry and the local carbon budget, *Atmos Chem Phys*, 7, 2855-2879, 10.5194/acp-7-2855-2007, 2007.
- Wolfe, G. M., Kaiser, J., Hanisco, T. F., Keutsch, F. N., de Gouw, J. A., Gilman, J. B., Graus, M., Hatch, C. D., Holloway, J., Horowitz, L. W., Lee, B. H., Lerner, B. M., Lopez-Hilifiker, F., Mao, J., Marvin, M. R., Peischl, J., Pollack, I. B., Roberts, J. M., Ryerson, T. B., Thornton, J. A., Veres, P. R., and Warneke, C.: Formaldehyde production from isoprene oxidation across NO_x regimes, *Atmos Chem Phys*, 16, 2597-2610, 10.5194/acp-16-2597-2016, 2016.
- de Gouw, J. A.: Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *Journal of Geophysical Research*, 110, 22, 10.1029/2004jd005623, 2005.
- Roberts, J. M., Marchewka, M., Bertman, S. B., Goldan, P., Kuster, W., de Gouw, J., Warneke, C., Williams, E., Lerner, B., Murphy, P., Apel, E., and Fehsenfeld, F. C.: Analysis of the isoprene chemistry observed during the New England Air Quality Study (NEAQS) 2002 intensive experiment, *Journal of Geophysical Research-Atmospheres*, 111, 10.1029/2006jd007570, 2006.
- Stroud, C. A., Roberts, J. M., Goldan, P. D., Kuster, W. C., Murphy, P. C., Williams, E. J., Hereid, D., Parrish, D., Sueper, D., Trainer, M., Fehsenfeld, F. C., Apel, E. C., Riemer, D., Wert, B., Henry, B., Fried, A., Martinez-Harder, M., Harder, H., Brune, W. H., Li, G., Xie, H., and Young, V. L.: Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study, *Journal of Geophysical Research-Atmospheres*, 106, 8035-8046, Doi 10.1029/2000jd900628, 2001.
- Karl, T., Guenther, A., Yokelson, R. J., Greenberg, J., Potosnak, M., Blake, D. R., and Artaxo, P.: The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, *Journal of Geophysical Research-Atmospheres*, 112, 17, 10.1029/2007jd008539, 2007.
- Atkinson, R., and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos Environ*, 37, S197-S219, 10.1016/S1352-2310(03)00391-1, 2003.
- Parrish, D. D., Stohl, A., Forster, C., Atlas, E. L., Blake, D. R., Goldan, P. D., Kuster, W. C., and de Gouw, J. A.: Effects of mixing on evolution of hydrocarbon ratios in the troposphere, *Journal of Geophysical Research-Atmospheres*, 112, 10.1029/2006jd007583, 2007.
- Shiu, C. J., Liu, S. C., Chang, C. C., Chen, J. P., Chou, C. C. K., Lin, C. Y., and Young, C. Y.: Photochemical production of ozone and control strategy for Southern Taiwan, *Atmos Environ*, 41, 9324-9340, 10.1016/j.atmosenv.2007.09.014, 2007.

Yuan, B., Shao, M., de Gouw, J., Parrish, D. D., Lu, S. H., Wang, M., Zeng, L. M., Zhang, Q., Song, Y., Zhang, J. B., and Hu, M.: Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis, *Journal of Geophysical Research-Atmospheres*, 117, 10.1029/2012jd018236, 2012.

Yang, Y. D., Shao, M., Kessel, S., Li, Y., Lu, K. D., Lu, S. H., Williams, J., Zhang, Y. H., Zeng, L. M., Noelscher, A. C., Wu, Y. S., Wang, X. M., and Zheng, J. Y.: How the OH reactivity affects the ozone production efficiency: case studies in Beijing and Heshan, China, *Atmos Chem Phys*, 17, 7127-7142, 10.5194/acp-17-7127-2017, 2017.

-6. The major conclusion of this study is the strong regional atmospheric oxidative capacity leads to fast oxidation of isoprene in southern China. Some recent long-term observational studies have indicated the increasing trends of ozone concentrations in this region (Wang *et al.*, 2009; Xue *et al.*, 2014). As ozone is usually regarded as an indicator of the regional atmospheric oxidation capacity, these studies confirmed the increasing trend of atmospheric oxidizing capacity in southern China. It would be useful if the authors could discuss the trends of ozone and atmospheric oxidative capacity and comment on the projected trend in the future.

Wang *et al.*, *Increasing surface ozone concentrations in the background atmosphere of southern China, 1994-2007*. *Atmos. Chem. Phys.*, 9, 6217-6227, 2009.

Xue *et al.*, *Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities*, *Environ. Sci. Tech.*, 48, 10769-10775, 2014.

Response: Many thanks for spotting this. We have therefore added the following text to the revised manuscript in the Section 2.1 and Section 4, respectively.

In the Section 2.1: “Ground-level O₃, another indicator of the regional atmospheric oxidative capacity, was found to increase at a rate of 0.27 to 0.86 ppbv/year from recent long-term observational studies in this region (Wang *et al.*, 2009;Xue *et al.*, 2014a;Wang *et al.*, 2017b;Wang *et al.*, 2017a). Given these trends in OH and O₃ suggest generally a strong atmospheric oxidative capacity in the PRD region, we hypothesized that the atmospheric chemistry of surrounding forests is susceptible to the influence from PRD.”

In the Section 4: “Furthermore, recent long-term observational studies in the PRD region (Wang *et al.*, 2009;Xue *et al.*, 2014a;Wang *et al.*, 2017b;Wang *et al.*, 2017a) have indicated the increasing trends of surface O₃, another indicator of the regional atmospheric oxidation capacity, thus, ...”

References:

Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background atmosphere of Southern China, 1994-2007, *Atmos Chem Phys*, 9, 6217-6227, 2009.

Xue, L., Wang, T., Louie, P. K., Luk, C. W., Blake, D. R., and Xu, Z.: Increasing external effects negate local efforts to control ozone air pollution: a case study of Hong Kong and implications for other Chinese cities, *Environ Sci Technol*, 48, 10769-10775, 10.1021/es503278g, 2014a.

Wang, T., Xue, L., Brimblecombe, P., Lam, Y. F., Li, L., and Zhang, L.: Ozone pollution in China: A review of concentrations, meteorological influences, chemical precursors, and effects, *The Science of the total environment*, 575, 1582-1596, 10.1016/j.scitotenv.2016.10.081, 2017a.

Wang, Y., Wang, H., Guo, H., Lyu, X., Cheng, H., Ling, Z., Louie, P. K. K., Simpson, I. J., Meinardi, S., and Blake, D. R.: Long term O₃-precursor relationships in Hong Kong: Field observation and model simulation, *Atmospheric Chemistry and Physics Discussions*, 1-29, 10.5194/acp-2017-235, 2017b.

Minor comments:

-7. Page 1, Lines 22-23: this sentence is incomplete. Rephrase this sentence.

Response: Many thanks for spotting this, correction have been made to read “To investigate the atmospheric oxidizing capacity in forested high mountain areas adjacent to the photochemistry-active Pearl River Delta (PRD) region in southern China, one-month online observations of isoprene and its first-stage oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) were conducted at a national background station in summer 2016.”.

-8. Page 2, Lines 27-31: the oxidation of isoprene by OH radicals is very complex. MACR and MVK can be further oxidized to form MGLY and other secondary compounds. Here it would be helpful to add several sentences to briefly summarize the thorough oxidation chemistry of isoprene as well as the major knowledge gaps in understanding this chemistry.

Response: Many thanks, we have therefore added brief descriptions and major gaps in this paragraph: “...In the real atmosphere, the NO-channel and HO₂-channel reactions are the major competing reaction pathways which dominate in polluted and pristine atmospheres, respectively (Paulot et al., 2009; Su et al., 2016). The relative importance of the NO and HO₂ pathways varies with NO_x mixing ratios. Methyl

vinyl ketone (MVK) and methacrolein (MACR) are the major first-stage products which can be further oxidized to produce methylglyoxal and other secondary compounds (Jenkin et al., 2015). Recent studies in pristine Amazon forest have reported the disturbance of anthropogenic influence to the oxidation of isoprene and the amplification of atmospheric oxidation capacity (Santos et al., 2017;Liu et al., 2018). However, studies on this kind of disturbance and amplification in certain polluted isoprene-rich environments such as the remote forests surrounding megacities remains scarce. Thus, it is vital to understand the isoprene photochemistry under polluted forest atmospheric conditions that with high isoprene emissions and a broad range of NO_x concentrations.”

References:

Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kurten, A., St Clair, J. M., Seinfeld, J. H., and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, Science, 325, 730-733, 10.1126/science.1172910, 2009.

Su, L. P., Patton, E. G., de Arellano, J. V. G., Guenther, A. B., Kaser, L., Yuan, B., Xiong, F. L. Z., Shepson, P. B., Zhang, L., Miller, D. O., Brune, W. H., Baumann, K., Edgerton, E., Weinheimer, A., Misztal, P. K., Park, J. H., Goldstein, A. H., Skog, K. M., Keutsch, F. N., and Mak, J. E.: Understanding isoprene photooxidation using observations and modeling over a subtropical forest in the southeastern US, Atmos Chem Phys, 16, 7725-7741, 10.5194/acp-16-7725-2016, 2016.

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-9. Page 3, Lines 1-4: at nighttime, NO₃ is generally in a thermal equilibrium with N₂O₅, which can be also taken up onto aerosols. Such heterogeneous reaction of N₂O₅ is an important sink of NO_x at nighttime, and can compete with the reactions of NO₃ with BVOCs. The authors are suggested to add several sentences to mention this process and provide a thorough picture of the nocturnal chemistry.

Response: Many thanks and we have amended this paragraph to read “The dominant night-time oxidant for isoprene is the NO₃ radical (Sobanski et al., 2016;Schulze et al., 2017;Edwards et al., 2017). NO₃ formed through the O₃ and NO₂ reaction is short lived during daytime due to its rapid photolysis and

reaction with NO. The NO₃ can be abundant at night, together with the concentration increasing of dinitrogen pentoxide (N₂O₅). N₂O₅ is generally in a thermal equilibrium with NO₃ via the reaction of NO₃ with NO₂ (Brown et al., 2016; Millet et al., 2016). It should be noted that N₂O₅ can also be taken up onto aerosols via heterogeneous reactions, which is an important sink of NO₂ and O₃ at night and can compete with the reactions of NO₃ with isoprene (Xue et al., 2014b; Brown et al., 2016). Overall, the abundance of NO₃ during nighttime directly depends on the mixing ratios of both O₃ and NO₂. Therefore, in polluted atmospheres with high levels of O₃ and NO₂, isoprene oxidation with NO₃ is especially important at night.”

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-10. Page 3, Lines 20-21: rephrase this sentence.

Response: Many thanks for spotting this, corrections have been made to read “This paper is structured as follows. Firstl_y, an overview of the measured concentrations and diurnal variations of isoprene and

its oxidation products were given. Then the calculated levels of daytime OH and nighttime NO₃ were presented and discussed. And furthermore, we describe in detail the atmospheric reaction time of isoprene, along with brief estimations of initial isoprene and the air mass age. Finally, concluding remarks including a synthesis of current findings and some implications are presented.”

-11. Page 4, Line 19: Southeast Asia

Response: Many thanks for spotting this – correction made.

-12. Change “atmospheric boundary layer (ABL)” to “planetary boundary layer (PBL)” throughout the manuscript.

Response: Many thanks, correction made.

-13. Page 5, Lines 18-19: it has been confirmed that this commercial NO_x analyzer with a default molybdenum oxide converter can significantly overestimate for NO₂, especially in rural and remote areas such as the forested mountaintop in the present study. The authors may need clarify the detailed configuration of this NO_x analyzer (e.g., the converters for converting NO₂ to NO) and state the uncertainty of NO₂ measurements if the MoO converter was used.

Xu et al., Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China, Atmos. Environ., 76, 221-226, 2013.

Response: We agree with the referee on the impact of molybdenum oxide converter may have on the measured NO₂ concentrations and we have added a discussion accordingly in the Section 2.2.2 and Section 3.1, respectively.

In the Section 2.2.2: “Oxides of nitrogen (NO-NO₂-NO_x) were measured at 1 min resolution using chemiluminescence analyser (Model 42i-TL, Thermo Scientific, Inc.), which has a detection limit of 50 pptv. NO₂ is converted to NO by a heated molybdenum converter before it can be measured by the

chemiluminescence detection of NO. Studies have shown that the converter may overestimate NO₂ as the measured NO₂ may have included other oxidized nitrogen compounds (Xu et al., 2013), and thus, the NO₂ concentrations given below are considered the upper limits of their actual values.”

In the Section 3.1: “It should be noted that the measured NO₂ concentrations are in fact upper limits, because the NO₂ probably includes some oxidized reactive nitrogen that was converted by the molybdenum. It has been confirmed that the NO₂ concentrations measured by analyzer with internal molybdenum oxide converter can be significantly overestimated in areas far away from fresh NO_x emission sources such as the remote mountaintop in the present study (Xu et al., 2013). Therefore, we made a modifying to the observed NO₂ by adopting the modification factors (Fig. S8) obtained at Mountain Tai, a high-altitude site (1533 m a.s.l.) in central-eastern China (Xu et al., 2013). The modified NO₂ (889 ± 27 pptv) was 1.1–2.5 times (1.8 ± 0.3) lower than that observed.”

-14. Page 7, Lines 7-9: it is a little bit strange that the observed concentrations of benzene (and also toluene) are very low. The lifetime of benzene is rather long and thus its ambient abundances are usually not so low.

Response: Thanks for your good question. We are also surprised by the low-level benzene and toluene, and the possible reasons may include:

(1) Long distance of the site away from city centers. The site is located in the free troposphere (FT) or upper planetary boundary layer (PBL) of southern China. Therefore, the low observed values suggest that the diffusion of benzene and toluene from ground source emissions within the PBL to the FT is strong, and thus they might have reached a steady state in this remote and high-elevation atmosphere.

(2) The strong oxidizing power of the troposphere in PRD region. Intensive studies have pointed to worsening photochemical pollution and strong atmospheric oxidative capacity throughout this region. Thus the chemical removal of benzene and toluene by radicals (e.g., OH) occurs rapidly and thoroughly along the paths air parcels traveled in the absence of mixing with fresh emissions in this pristine forest region.

(3) The high relative humidity ($92.2 \pm 8.3\%$) and cloudy conditions are favorable to the removal of benzene and toluene at this site, which may also lower the levels to a certain extent.

We have therefore added a discussion accordingly in the Section 3.1: "...Aromatic compounds showed very low mixing ratios, among which, toluene is the most abundant (154 ± 20 pptv, average $\pm 95\%$ confidence interval, the same below), followed by benzene (51 ± 8 pptv), ethylbenzene (47 ± 6 pptv) and m,p-xylene (38 ± 4 pptv). Being remote from major anthropogenic emission sources, the ambient aromatics levels at this site were significantly low compared to the abundances that measured at a regional background site in the PRD region, while they were comparable with other remote mountain sites. The low-level aromatics provide additional evidences showing that the site is remote and suffering from minor influence of local anthropogenic emissions."

-15. Page 7, Lines 9-11: provide standard deviations for the averages.

Response: Many thanks, done.

-16. Page 8, Lines 13-14: rephrase this sentence "Although ..."

Response: Many thanks for spotting this, correction made.

-17. Page 8, Line 20: on the source of MVK and MACR at this site, I wonder if regional transport could also contribute to the observed MVK and MACR. What are the lifetimes of MVK and MACR?

Response: We appreciate the referee's question and the possible regional transport of MVK and MACR are explained in the following.

The lifetimes of MVK and MACR by reaction with OH are 1.9 and 1.0 hours, respectively, assuming 12-h daytime $\text{OH} = 8.0 \times 10^6$ molecules cm^{-3} . The average daytime wind speed during the sampling periods was 3.9 ± 0.2 m s^{-1} at the site, and the distance between the sampling site and the nearest urban

center is 38 km (Fig. 6), the air parcel from upwind locations would spend about 2.7 hours to arrive at the sampling site. This is enough time for the depletion of MVK and MACR along the traveling path during the daytime.

However, the nighttime chemical oxidation of MVK and MACR was slow, with lifetimes of MVK and MACR by NO_3 oxidation of 0.5 years and 72 hours, respectively, assuming 12-h nighttime $\text{NO}_3 = 5.0 \times 10^8 \text{ molecules cm}^{-3}$. Apart from biogenic sources, the anthropogenic sources of MVK and MACR, e.g., motor vehicles, biomass burning and industrial sources, have been reported by many studies (Borbon et al., 2001; Wagner and Kuttler, 2014; Hsieh et al., 2016; Diao et al., 2016). Therefore, the regional transport of MVK- or MACR- laden air could affect the observed nighttime levels at the site.

The “polarPlot” technique was therefore used for source identification (Fig. 7). The red dotted sectorial domains in the figure are interpreted as the regional transport interference as the concentrations of species increase with increasing wind speed. The high levels of species at high wind speeds most likely came from the nearby urban centers. Therefore, measurements that are deemed to be affected by regional transport are all excluded from the dataset in the analysis.

We have therefore added a discussion accordingly in Section 3.2: “...Moreover, MVK and MACR could be also transported from anthropogenic sources in neighbour cities to the sampling site at night (More detailed discussion is given in Text S5)...”

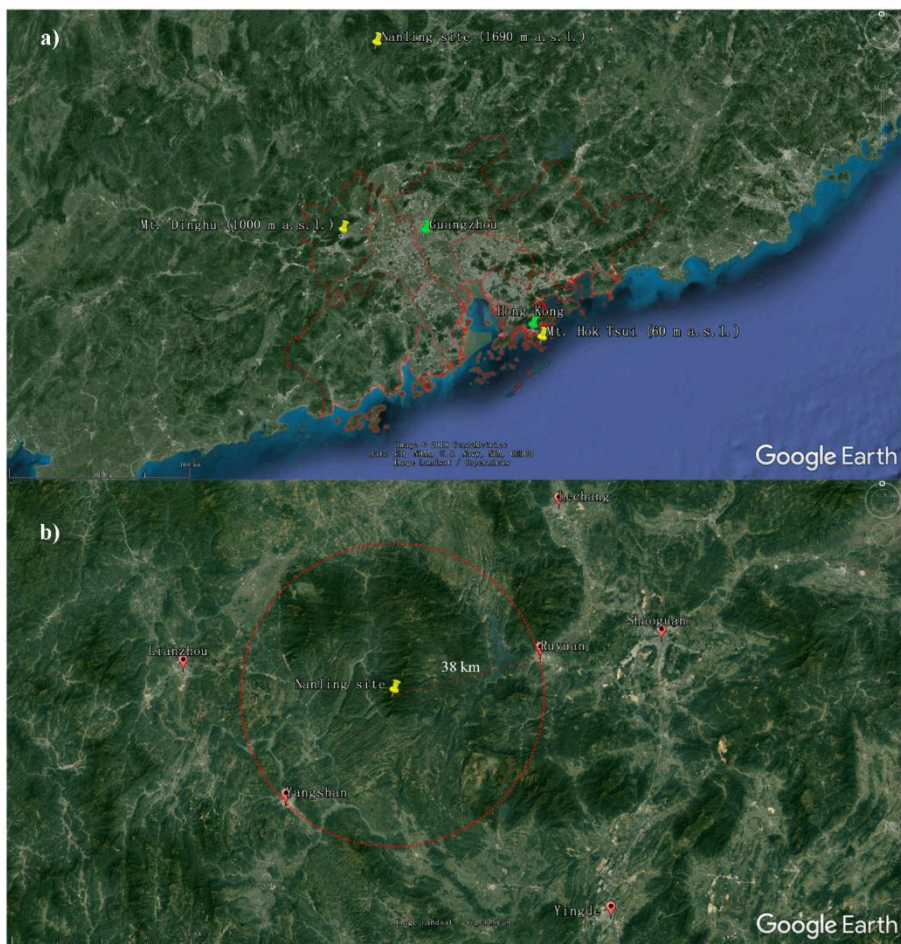


Fig. 6. (a) Location of the Nanling site, Dinghu Mountain site, Hok Tsui site, Guangzhou and Hong Kong. The Nanling site is 174 km northeast to the Dinghu Mountain site. Red outlined domain represent the Pearl River Delta region. (b) Map showing the nearest urban centers (Yangshan County, Ruyuan County, Lechang City, Lianzhou City, Shaoguan City and Yingde City) around the site.

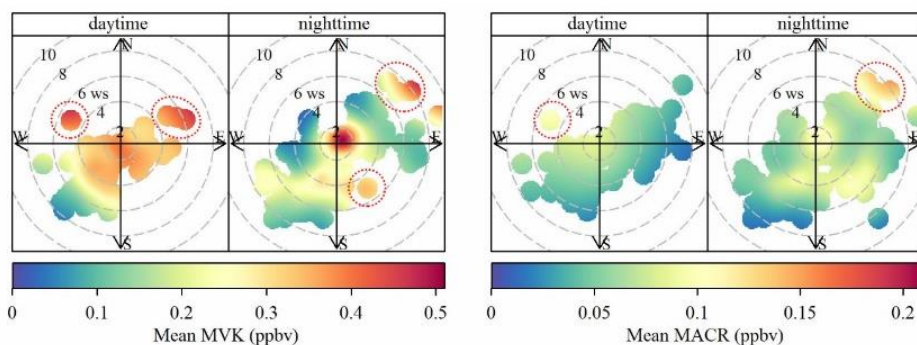


Fig. 7. Daytime and nighttime polarplots of MVK and MACR during the sampling period (July 15–August 17 2016). Concentrations varied by wind speed (ws, unit in m/s) and wind direction. Red dotted sectorial domains represent the interferences of regional transport from nearby urban centers.

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-18. Page 10, Line 17, “the observed relationship of observed MVK/isoprene”: delete one “observed”

Response: Many thanks, correction made.

-19. Table 1: provide the standard deviation of the average concentrations if available.

Response: Many thanks, done.
