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Atmospheric Chemistry and Physics Discussions

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.

Daocheng Gong and Hao Wang et al.

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Dear Referee #3,

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 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**).

Gong et al. presents their results of online observations of isoprene and its first-stage oxidation products MVK and MACR in summer 2016 at a remote, high-altitude mountain forest site to the north of the air-polluted PRD region in southern China. They found that the isoprene level was significantly lower and attributed it to the strong regional atmospheric oxidative capacity. The PBM-MCM model was used to estimate the OH and NO_3 concentrations to support their assumptions. The paper is well written and organized. The reviewer would recommend the manuscript for publication after some specific comments.

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

Specific Comments:

-**1.** O_3, OH_x, PAN, and NO_3 are indicators of atmospheric oxidative capacity. Since OH and NO_3 were not determined in the observation, the observed O_3 concentration is a more powerful tool to express the atmospheric oxidative capacity. The diurnal variations of O_3 peaked at 20:00 is very interesting, because the changing trends of O_3 and sun radiation were not accordant. The temporal variations of O_3 also show different trends during the observation. Could regional transport contribute O_3 to the measurement site? The authors had better add more discussion on the variations of O_3 concentration.

Response: Many thanks for spotting this. We noticed that the high levels of O_3, as well as its distinct diurnal variations, were observed at the site, and we are preparing another paper to discuss these points in details. In this revised manuscript, discussions about the high abundances of O_3 at the site has been added in the Section 3.1. As for the interesting O_3 diurnal variations, a number of studies have observed a similar pattern at mountaintops, that is, high concentrations at night and low concentrations during the daytime (Gallardo et al., 2000;Gao et al., 2017). Some previous studies have concluded that the factors closely related to the distinct O_3 diurnal patterns at mountaintops were the boundary layer diurnal cycles (Gao et al., 2017), the mountain-valley breezes (Zaveri et al., 1995;Yang et al., 2012;Cristofanelli et al., 2013), the regional transport effects (Naja et al., 2003;Li et al., 2008;Zhang et al., 2015;Gao et al., 2017), the location and altitude of a mountain (Chevalier et al., 2007;Monteiro et al., 2012), and ozone vertical distributions (Forrer et al., 2000;Zellweger et al., 2003;Gheusi et al., 2011). Overall, the distinct diurnal variations in O_3 concentrations are the result of a combination of various physical and chemical processes. This point has been added to the Section 3.2.

In the Section 3.1:" High abundances of O_3 at this site likely indicate strong oxidizing power of the present remote atmospheres."

In the Section 3.2:" Some previous studies at mountaintops observed distinct diurnal variations in O_3 concentrations that featured with high levels at night and low levels during the daytime (Zaveri et al.,

1995;Gao et al., 2017), which are the result of a combination of various physical and chemical processes (e.g., boundary layer diurnal cycles, mountain-valley breezes, regional transport, photochemical reactions)."

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-**2.** The modelled OH and NO_3 concentrations were regarded as the most important evidence for the conclusion of this manuscript. However, the PBM-MCM model is not a good tool to estimate OH concentrations at low NO_x concentrations at remote site like this study. The reviewer strongly recommend the authors add some other models to support their conclusions.

Response: Thanks for this comment. We agree with the referee that PBM-MCM indeed needs improvement and further optimization for its application under low-NO_x environments.

Thus on one hand we conducted sensitivity analyses of the PBM-MCM modelled OH concentrations with certain uncertainties. The results showed that the current PBM-MCM may have 19 ± 9% overestimation of the daytime OH mixing ratios at the present study. See also our response to Referee #2, comment #2 and #4 for more detailed discussion on this point.

On the other hand, a widely-used parameterization method with measured aromatic hydrocarbons has been applied to estimate the regional mixing ratios of daytime OH radicals (Shiu et al., 2007). This additional approach can provide 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 revised manuscript and supplement. See also our response to Referee #2, comment #1 for more detailed discussion of this point.

We sincerely appreciate the suggestions made by the Referees, and agree that more observations and modeling studies will be needed to address this question. We will consider the application of other models as a better diagnostic tool in the future, e.g., OBM-AOCP (Observation-Based Model for investigating Atmospheric Oxidative Capacity and Photochemistry) developed by Xue et al. (2016).

References:

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chemistry in the polluted atmosphere of Hong Kong and Pearl River Delta region: analysis of a severe photochemical smog episode, Atmos Chem Phys, 16, 9891-9903, 10.5194/acp-16-9891-2016, 2016.

-**3.** Page 1, Line 22-23, this sentence is incomplete.

Response: Many thanks for spotting this, the correction has 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.".

-**4.** Page 4, Line 32, the specifications of the Teflon filter should be clarified.

Response: Many thanks for spotting this, corrections have been made to read "…a Teflon filter (0.25 μm pore size, 47 mm OD, Millipore, USA) was placed in front of the sample inlet.".

-**5.** Page 5, Line 21-23, it is confused that "daily" and "every two days". Secondly, it seems that SO_2, NO_x, and CO analyzers are usually calibrated with domestic standard gases which are not NIST-traceable. The NIST-traceable standard was only applied to calibrate O_3 analyzer.

Response: Many thanks for spotting this mistake, corrections have been made to read "All instruments were calibrated weekly by using a multi-gas calibrator (Model 146i, Thermo Scientific, Inc.) throughout the study. The NIST-traceable (National Institute of Standards and Technology, USA) standard was applied to calibrate the O_3 analyser. For NO_x, SO_2 and CO, standard gases provided by NRCCRM (National Research Center for Certified Reference Materials, China) was applied. Zero and span checks of all analysers were performed every two days.".
