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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.

Anonymous Referee #2

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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.

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.

-Some previous studies have suggested that the MCM model may not work well for reproducing the HOx concentrations at high-BVOCs and low-NOx conditions, which seems to be the case of 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.

-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.

-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.

-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.

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.

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.

Minor comments:

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

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.

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 NOx 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.

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

Page 4, Line 19: Southeast Asia

Change “atmospheric boundary layer (APL)” to “planetary boundary layer (PBL)” throughout the manuscript.

Page 5, Lines 18-19: it has been confirmed that this commercial NOx 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 NOx 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.

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.

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

Page 8, Lines 13-14: rephrase this sentence “Although . . .”

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?

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

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

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