

Anonymous Referee #3

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This paper presents results from a 0-D box model constrained by observations of radical sources and sinks in order to evaluate the oxidation capacity of several Chinese megacities, including Beijing, Shanghai, Guangzhou, and Chongqing. The models suggest that while there are similarities in the chemistry of each urban area, such as ozone production being VOC-limited in each, there are some distinct differences in predicted radical concentrations, rates of ozone production, and OH reactivity, which may help provide insights into specific control strategies for each area.

While the paper provides some interesting contrasts between the cities, it is unfortunately somewhat difficult to read due to issues related to both the amount of information and how it is presented as well as style and grammar. In particular, section 3.3.2 describing the radical budget analysis reads more like a stream of thought rather than an organized discussion.

Answer:

The manuscript is restructured by moving the VOC description to section 4.1 and moving the OH-HO₂-RO₂ budget analysis (originally section 3.3.2) to section 4.2.

We have edited the manuscript substantially on the style and grammar and please find the modification in the revised manuscript.

A major assumption in the paper is that the model can accurately reproduce concentrations of OH, HO₂, and RO₂ radicals in order to predict the oxidation capacity of each region. Unfortunately, there is no discussion of whether this is a reasonable assumption. As mentioned in the introduction, previous measurements of radical concentrations in urban areas often exhibit significant discrepancies with model predictions, suggesting that chemical models are unable to accurately reproduce the oxidation capacity of these areas (see for example Whalley et al. (2018), Griffith et al. (2016), in addition to references cited in the Introduction). As summarized in the Lu et al. (2018) review cited in the paper, “: : current tropospheric chemical mechanisms cannot explain the OH radical concentrations in China, which strongly underestimated the OH concentrations and the local ozone production for the

low and high NO_x range, respectively.” The authors should expand the discussion of these discrepancies and discuss in much more detail their potential impact on their model predictions and conclusions.

Answer:

As shown in Rohrer, the OH is relative well captured by the model in moderate and high NO_x regime.

As the presented observation were conducted in megacities, which were mainly located in the high NO_x regime. The model should be able to predict the OH concentrations well. The major question is the model underestimation for HO₂ and RO₂ concentrations and thus the local ozone production rate. We added sentences in Line 24 Page 6 “As previous field campaign in China shown that the OH concentrations could be underestimated in the low NO_x conditions (Tan et al., 2018b; Tan et al., 2017; Fuchs et al., 2017; Rohrer et al., 2014; Lu et al., 2013; Lu et al., 2012; Hofzumahaus et al., 2009). In this study, the NO_x concentration are in moderate and high range, where the model is capable to reproduce the OH concentrations relatively good (Rohrer et al., 2014). For the high NO_x regime, the prominent feature is the underestimation of HO₂ and RO₂ concentrations (Tan et al., 2018a; Tan et al., 2017; Tan et al., 2018c). This is also found in other urban site outside China (Griffith et al., 2016; Whalley et al., 2018; Kanaya et al., 2007; Dusanter et al., 2009; Shirley et al., 2006; Brune et al., 2016; Ren et al., 2013), indicating a common defect in current chemical mechanisms. Such model defect will lead to underestimation of local ozone production. The explanation of model underestimation is out of the scope of this study but the possible impact will be discussed in section 4.3.”

We also added the discussion on potential underestimation of P(O₃) in Line 14 Page 9 “As mentioned in section 3.3, the current model could have defects for high NO_x conditions, which underestimated the peroxy radical concentrations and thus local ozone production China (Tan et al., 2017; Griffith et al., 2016; Whalley et al., 2018; Kanaya et al., 2007; Dusanter et al., 2009; Shirley et al., 2006; Brune et al., 2016; Ren et al., 2013). However, the quantitative estimation is not possible due to the absence of in-situ radical measurements. To our knowledge, no field campaigns have been conducted to perform in-situ radical measurements in city center area in China. However, a field campaign in downwind area of Beijing (YUFA) found local ozone production rate was underestimated due to the underestimation of HO₂

concentrations (Lu et al., 2010). Another field campaign in a rural site in NCP also found model underestimation of $P(O_3)$ by 20 ppbv per day compared a daily integrated ozone production of 110 ppbv derived from the measured HO_2 and RO_2 (Tan et al., 2017). Therefore, the ozone production rate presented derived from model calculations in this study should be considered as a lower limit. Nevertheless, the underestimation of peroxy radical concentration will not affect the O_3 - NO_x -VOC sensitivity diagnosis (Tan et al., 2018c).”

Additional comments:

1) The paper would benefit from a more detailed description of what was measured and how they were measured, perhaps with a table in the supplement. In particular, the specific VOCs that were measured should be described in more detail.

Answer:

We added a table to describe the instrumentation in the supplement (Table S1). We also prepared the table in supplement to state what are measured, modelled, and parameterized in this study (Table S2). The measured VOCs and their concentrations are presented in table S3.

2) Instead of just showing the total AHC (or preferably AVOC as indicated elsewhere in the manuscript), it would be more informative to illustrate the diurnal mixing ratios of some important individual VOCs that demonstrate the similarities and differences in the areas as described in the manuscript.

Answer:

We changed all AHC to be AVOC in the revised manuscript.

We added a table about measured VOC in supplement (Table S3) and a table showing top 10 k_{OH} contributing VOCs (Table 2). The mean diurnal profiles of top 10 VOCs are added in supplement (Fig. S6). A detail discussion on the measured VOCs is added. Please find the answers in the response to referee #1 who has the similar comments.

3) In addition, it should be clarified which VOCs and/or OVOCs were measured and which were modeled as part of the radical budget. For example, were HCHO and other carbonyls measured or was their contribution to radical production based on modeled concentrations?

Answer:

The VOC are measured and OVOCs are modelled. Therefore, the alkene ozonolysis is observation constrained. We make this point clear by adding a sentence in the radical budget analysis section “”

We added the discussion of modelled OVOCs results in the end of section 4.1 VOC compositions and ozone production efficiency in the revised manuscript. The modelled OVOCs concentrations are comparable to previous studies for these regions, indicating the model is capable to reproduce the OVOCs formation. The added content is “The OVOCs concentrations are simulated by the box model. The modelled HCHO concentrations were in the range of 3 to 8 ppbv (Fig. S7), which are consistent with the previous studies in these regions (Zhang et al., 2012; Song et al., 2018; Chen et al., 2016; Tang et al., 2009). The modelled acetaldehyde concentrations are in the range of 2 to 3 ppbv in Beijing, Shanghai, and Chongqing but 1 ppbv larger in Guangzhou because the larger contribution of aromatics VOCs which produce acetaldehyde from their OH degradation.”

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