Authors' responses to review comments

Atmospheric Chemistry and Physics (egusphere-2024-2568)

Differences in the key volatile organic compound species between their emitted and ambient concentrations in ozone formation

1. The authors have responded to the comments of the reviewers well. There are a couple of edits necessary prior to publication:

Response: Thank you for reviewing our manuscript.

2. Line 133: change "consumption by both OH and photon" to "losses either by photolysis or photooxidation"

Line 144: should be e-benzene/e-styrene?

Line 209: change "For daytime OH and hv consumption" to "For photolysis and photooxidation loss"

Fig. 2: please move legend out of panel a (make it at top or something that is easier to find) with it having larger font and/or bold. Right now it takes a while to find, which makes interpreting the figure more difficult.

Please ensure references to supplemental figures include an S. Right now, there are references to figures that I assume are in main document (no s) but they don't exist or match text.

Line 351: Change "According to Table 2" to "As shown in Table 2"

Response: Done.

3. Please reflect biogenic, anthropogenic, and OVOCs in figure as there is not a direct connection now between those methods and the figures. The figures with them by class can remain in SI for reference.

Response:

The emitted and ambient concentrations of OVOCs are presented in Figure 2, Tables S1 and S2. Emitted concentrations can be categorized into anthropogenic and biogenic sources. Anthropogenic emissions account for 26%±21% to 62%±12% of the total emitted concentrations, while biogenic sources contribute 38%±12% to 74%±21%. Details will be referenced to Zheng et al., unpublished, Characteristics and sources of volatile organic compounds and their influences on ozone and fine particulate nitrate production sensitivities at five sites in the Chengdu Plain, China.

4. Fig 1 & 3: please consider a different color for either alkenes or alkanes to better differentiate them for color blind people

Response: Done. We also revised the Figures S7, S10, and S11.

5. Please review abstract and conclusion with the guidelines prior to resubmission: https://www.atmospheric-chemistry-and-hysics.net/policies/guidelines_for_authors.html

Response:

We revise the sentences (please check lines 8-21 in Abstract and 371-384 in Conclusion).

'Volatile organic compounds (VOCs) emissions and their secondary transformations play a significant role in ozone (O_3) formation. Previous studies have often relied on ambient VOCs concentrations to identify key VOCs species. However, ambient concentrations represent the residual concentrations after the emitted VOCs have been consumed, which can introduce substantial uncertainties. To address this issue, this study proposes a novel method to identify the key VOCs species in both anthropogenic and biogenic emissions. The emitted VOCs concentrations are calculated during both nighttime and daytime in summer using the nitrate radical, O_3, and hydroxyl radical reaction rates and ambient concentrations of 99 VOCs measured at Deyang, Chengdu, and Meishan, China. The emitted concentrations of alkenes and aromatics are higher than the ambient concentrations. The largest differences between emitted and ambient concentrations are 1.04 ppbv for cis-2-butene at Deyang, 0.81 ppbv for isoprene at Chengdu, and 1.79 ppbv for isoprene at Meishan. In contrast, due to secondary production, the emitted concentrations of oxygenated VOCs are lower than the ambient concentrations. The largest differences are -0.54 ppbv for acetone at Deyang, -0.58 ppbv for acetaldehyde at Chengdu, and -0.5 ppbv for acetone at Meishan. Based on the emitted concentrations, isoprene is one of the top three species contributing to O_3 formation at all three sites, which may be overlooked in observed concentrations. Comprehensive calculation of the emitted VOCs concentrations enables the key VOCs species in O_3 formation to be accurately identified.'

'Using NO_3, O_3, and OH reaction rates along with hourly ambient concentrations of 99 VOCs measured at Deyang, Chengdu, and Meishan in Southwest China, we calculate the emitted VOCs concentrations during both nighttime and daytime in summer. These emitted VOCs concentrations are compared with the ambient concentrations in terms of their OFP. Because the emitted VOCs concentrations are directly linked to MIR values, this novel method substantially enhances the accurate identification of the key VOCs species in O_3 formation. The emitted concentrations of alkenes and aromatics are significantly higher than the ambient concentrations. In contrast, because of the secondary production, the emitted OVOCs concentrations are lower than the ambient ones. Based on the emitted VOCs concentrations, the top three species contributing to OFP are cis-2-

butene, isoprene, and m,p-xylene at Deyang; m,p-xylene, acetaldehyde, and isoprene at Chengdu; and isoprene, ethylene, and acetaldehyde at Meishan. These results emphasize the importance of isoprene in O_3 formation and differ from those based on ambient concentrations. While many current environmental policies focus on reducing emissions of non-isoprene alkenes and aromatics, our study shows that isoprene emissions are also important. Therefore, the control of isoprene emissions should be considered in the mitigation of O_3 pollution. Our study provides new insights into improving the scientific understanding of the VOCs emissions, their secondary transformations, and serves as a reference for managing key VOCs species in future control strategies.'