

1. The authors have not provided the answer to the following initial query in their responses:

From laboratory tests, what is the conversion efficiency of an alkene RO₂ to OH at 5 ppm and 2.5 ppm NO? Furthermore, if the HO₂ signal measured with the high NO injection is 6% higher than the HO₂ signal that is measured with the low NO injection, then I think that this does indicate that there is an RO₂ interference being observed. I suggest the authors attempt to put an upper limit on the RO₂ interference using the methodology described in Whalley et al., (AMT, 2013) (equations 7 and 8).

Answer:

Previous laboratory experiments of another LIF system (FZJ-LIF) with the same cell design and operating parameters to PKU-LIF indicated the conversion efficiency of isoprene derived RO₂ to OH was lower than 0.1 at NO concentration of $4 \times 10^{12} \text{ cm}^{-3}$ (Fuchs et al., 2011) (Figure 5, 0.4 mm nozzle). Therefore, the conversion efficiencies for the NO concentrations of 5 ppm and 2.5 ppm used in this study (i.e. $5 \times 10^{11} \text{ cm}^{-3}$ and $2.5 \times 10^{11} \text{ cm}^{-3}$ at cell pressure of 4 hPa) were expected to be less than 0.1.

According to Equation 7 and 8 in Whalley et al. (2013), the HO₂ interference from RO₂ radical can be calculated by multiplying the complex RO₂ concentrations (RO_{2*i*}) with corresponding conversion efficiency (α). Unfortunately, RO₂ was not measured during this campaign while one would expect a strong correlation between RO₂ (or RO_{2*i*}) and HO₂. Previous summer campaigns in China demonstrated that the RO_{2*i*} to HO₂ ratio varies from 0.6 in a rural site in Wangdu (Tan et al., 2017) to 2 in an urban site in Beijing (Whalley et al., 2021). As the chemical condition encountered in YRD was more similar to that of Wangdu (the Beijing campaign was conducted at an urban site), it was reasonable to assume the RO_{2*i*} to HO₂ ratio in this study was closer to 0.6. By applying the conversion efficiency of 0.1 as an upper limit and assuming RO_{2*i*} to HO₂ ratio to be 0.6, the maximum HO₂ interference from RO₂ radicals should be closer to 6% of the HO₂ measurement in this study. But we acknowledge that the interference would increase, if RO_{2*i*} to HO₂ ratio become larger.

We revised the paragraph as ‘To minimize the potential interference from RO₂, the added NO mixing ratio was switched between 2.5 ppm and 5 ppm every 2 minutes, corresponding to the HO₂ conversion efficiencies of 10% and 20%, respectively. The expected RO₂ conversion efficiency for both modes was below 10% for this experimental setup for isoprene derived RO₂ from laboratory tests (Fuchs et al. 2011). The extent of the RO₂-interference was also proportional to the complex-RO₂-to-HO₂ ratio. Unfortunately, RO₂ was not measured during this campaign but one would expect a strong correlation between RO₂ (or complex-RO₂) and HO₂ (Tan et al., 2017; Whalley et al., 2021). Previous field summer campaigns in China showed that, the ratio of complex-RO₂ to HO₂ varies from 0.6 at a rural site in Wangdu (Tan et al., 2017) to 2 at an urban site in Beijing (Whalley et al., 2021). As

the chemical condition encountered in YRD was more similar to that of Wangdu (the Beijing campaign was conducted at an urban site), it was reasonable to assume the complex-RO₂ to HO₂ ratio in this study was closer to 0.6. Therefore, by applying the RO₂ conversion efficiency of 0.1 as an upper limit, the maximum HO₂ interference from RO₂ radicals should be closer to 6% of the HO₂ measurement in this study assuming complex-RO₂ to HO₂ ratio to be 0.6.’

2. The authors have not responded fully to the following:

How well did the model predict the diurnal variation of PAN/ other model-generated species such as formaldehyde and glyoxal? Could the authors include the modelled and observed formaldehyde and glyoxal profiles in the SI and with modelled and observed PAN?

Answer:

The diurnal variations of modelled and observed PAN, formaldehyde and glyoxal were shown in Fig. S2. As discussed in the last version of revision, the modelled PAN concentration agreed to measurements from late morning to the midnight but slightly lower than measurements in the early morning, and the discrepancy was not caused by the effect of boundary layer height variation. While the model under-predicted the HCHO concentrations and over-predicted the glyoxal concentrations, which might be related to the significant primary emission of HCHO and missing sinks of glyoxal in the current mechanisms. However, the missing sources and sinks of HCHO and glyoxal are not the scope of this study. To avoid interruption from incapability of model performance, both HCHO and glyoxal were constrained to observations in this study.

We added some discussions about the observed and modelled HCHO and glyoxal in the model description section as ‘In addition, sensitivity test without HCHO and glyoxal constrained indicated that model would under-predicted the HCHO and over-predicted the glyoxal concentrations (Fig. S2), which might be related to the significant primary emission of HCHO and missing sinks of glyoxal in the current mechanisms. However, the missing sources and sinks of HCHO and glyoxal are not the scope of this study. To avoid interruption from incapability of model performance, both HCHO and glyoxal were constrained to observations in this study.’

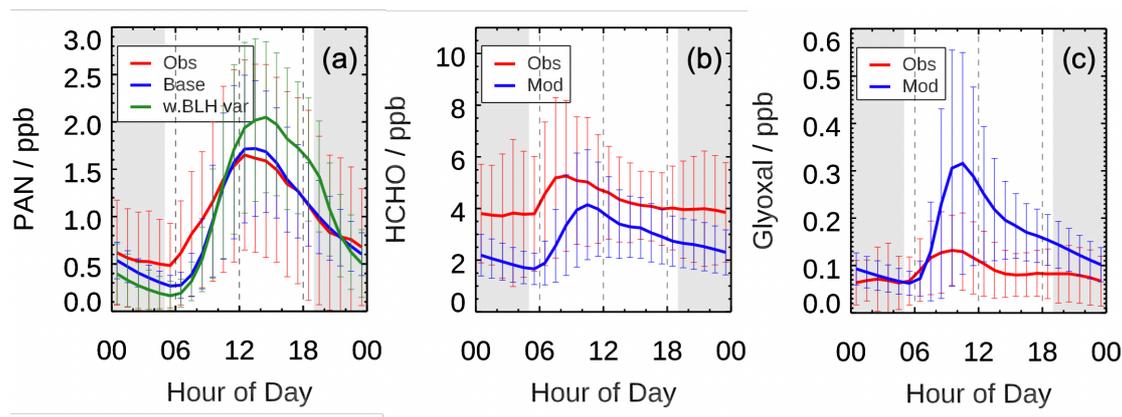


Figure S2. The mean diurnal profiles of measured and modelled PAN (a), HCHO (b), and glyoxal (c) concentrations. (a) The base model run (Base) applied a first-order loss term equivalent to a lifetime of 8 hours to all species. The other model run (w. BLH var) imposed a boundary layer height (BLH, derived from ECMWF) dependent loss rate to all species. (b) and (c) The model run (Mod) free the HCHO and glyoxal compared to the base model run (Base) in (a). The grey areas denote nighttime.

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