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***Interactive comment on* “Observation and modelling of OH and HO<sub>2</sub> concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere” by K. D. Lu et al.**

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In Fig. 3 of our paper, we compare measured and modelled relative detection sensitivities ( $\alpha_{\text{RO}_2}$ ) for specific RO<sub>2</sub> that are detected by our LIF system in the HO<sub>2</sub> cell. As noted in the text (Sect. 2.3), the modelled  $\alpha_{\text{RO}_2}$  values (blue symbols, MCMv3.1) reproduce the pattern of the experimental values relatively well. However, some underprediction is evident for particular peroxy radicals, e.g. of cyclohexane, MACR and MVK. After paper submission, we have recalculated the  $\alpha_{\text{RO}_2}$  values using the newly published Master Chemical Mechanism MCMv3.2 (<http://mcm.leeds.ac.uk/MCM/home.htm>). In-

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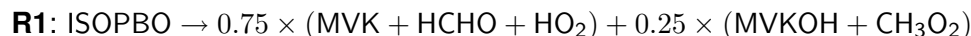
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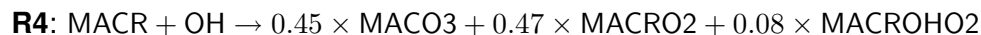
terestingly (and as one would hope), the new MCM version yields generally improved agreement between the simulated and experimental  $\alpha_{\text{RO}_2}$  values (see Fig. 1, below). More specifically, for peroxy radicals from isoprene, MACR and cyclohexane,  $\alpha_{\text{RO}_2}$  is much better described by MCMv3.2 rather than by MCMv3.1. Thus, the measurements by Fuchs et al. (2011) give indirect support to the revisions made for these species in MCMv3.2. It should be noted that the modelled target parameter,  $\alpha_{\text{RO}_2}$ , is related to a short time scale (2.7 ms), high NO mixing ratio (1500 ppm), low pressure (3.5 hPa) and dark conditions, quantifying the  $\text{RO}_2$  to  $\text{HO}_2$  conversion at chemical conditions where peroxy radicals preferentially react with NO.

The improved model results for the peroxy radicals from isoprene, MACR and cyclohexane are caused by enhanced  $\text{HO}_2$  formation.

Isoprene: the  $\text{HO}_2$  yield from the unimolecular decomposition reaction of ISOPBO radicals ( $\beta$ -hydroxyalkoxy radicals from 1,2 OH addition) is enhanced due to replacement of reaction **R1** (MCMv3.1) by reaction **R2** (MCMv3.2).



MACR: the yield of  $\beta$ -hydroxyperoxy radicals (MACRO2, MACROHO2), which undergo fast decomposition to  $\text{HO}_2$ , is enhanced due to replacement of reaction **R3** (MCMv3.1) by reaction **R4** (MCMv3.2). The yield of MACO3, which does not contribute to the interference, is diminished.



Cyclohexane:  $\alpha_{\text{RO}_2}$  is strongly enhanced by the newly included ring-opening reaction pathway for the cyclohexoxy radical in MCMv3.2. In the ring-opening mechanism (missing in MCMv3.1), the major product CO1C6O undergoes 1,5 H-atom shift and isomerization to  $\delta$ -hydroxyalkoxy radicals (CO1H63O). The latter product decomposes to

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HO<sub>2</sub> as fast as  $\beta$ -hydroxylalkoxy radicals.

**Figure 1** Relative detection sensitivities ( $\alpha_{\text{RO}_2}^i$ ) for specific RO<sub>2</sub> compared to HO<sub>2</sub>. The experimental values (red stars) and their 1 $\sigma$  error bars were determined for the instrument configuration applied at PRD for HO<sub>2</sub> detection (Fuchs et al., 2011). Modelled values (blue circles for MCMv3.1 and green crosses for MCMv3.2) are shown for major VOCs which contributed more than 90% to the VOC reactivity in PRD. Original and mechanistic names of the VOCs are shown at the lower and upper x-axis, respectively.

**Reference** Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and Wahner, A.: Detection of HO<sub>2</sub> by laser-induced fluorescence: calibration and interferences from RO<sub>2</sub> radicals, *Atmos. Meas. Tech. Discuss.*, 4, 1255–1302, doi10.5194/amtd-4-1255-2011, 2011.

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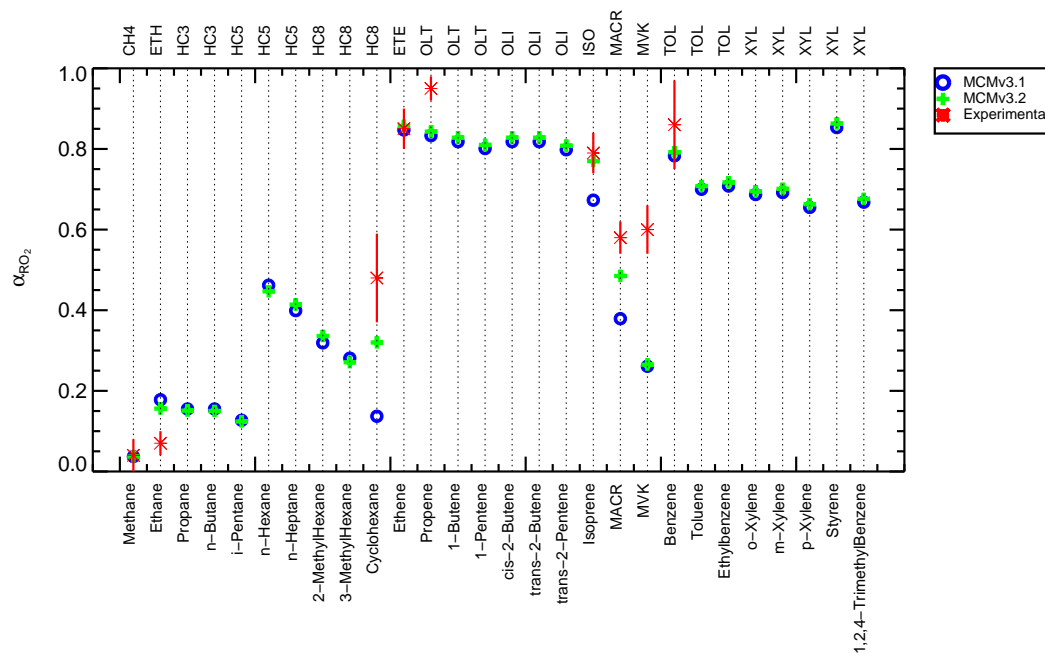
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**Fig. 1.** This updated figure is planned to replace Fig. 3 of the manuscript

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