

## ***Interactive comment on “Oxidation processes in the Eastern Mediterranean atmosphere: Evidence from the Modelling of HO<sub>x</sub> Measurements over Cyprus” by Chinmay Mallik et al.***

### **Anonymous Referee #2**

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This paper presents measurements of OH and HO<sub>2</sub> radical concentrations over Cyprus during the CYprus PHotochemistry EXperiment (CYPHEX) in 2014. Measurements of OH and HO<sub>2</sub> using an LIF-FAGE instrument were compared to the results of a box model constrained by observations of O<sub>3</sub>, CO, NO<sub>x</sub>, hydrocarbons, and others. The model used agrees well with the measured OH to within 10% when constrained to all measured species, including NMHC, but tends to underestimate HO<sub>2</sub> by 17%. Excluding terpenes from the model improves the modeled agreement with the measured HO<sub>2</sub>. Increasing the concentration of terpenes was found to increase the modeled underprediction of the measured HO<sub>2</sub>. The authors suggest that the reason for the discrepancy is an increase in radical-radical termination reactions from terpene-generated

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organic peroxy radicals. Adding a simple autooxidation scheme that decreases the terpene peroxy radical concentration improves the modeled agreement with the measured HO<sub>2</sub>.

The paper presents some interesting results that are appropriate for ACP and will be suitable for publication after the authors have addressed the following questions.

1) The authors state that an OH artifact generated internally on average accounted for approximately 45% of the total signal (page 6). While a detailed analysis of the interference is beyond the scope of the paper, the authors should expand the description of the interference and its variability. Unfortunately, the figure in the supplement does not provide much information on the day-to-day variability of the interference given that the background signal is displayed in arbitrary units. Can the authors display the interference as an equivalent OH concentration together with the total measured signal and the atmospheric OH signal as they have done previously (Novelli et al., 2014a)? Did this interference vary with ozone and biogenic VOC concentrations, as observed previously?

2) To reduce the potential interference in their HO<sub>2</sub> measurements from RO<sub>2</sub> radicals, the authors reduce the conversion efficiency of HO<sub>2</sub> to OH to 30% (page 6). It is not clear whether the authors calibrated the conversion efficiency of RO<sub>2</sub> radicals such as isoprene-based hydroxy peroxy radicals at this HO<sub>2</sub>-to-OH conversion efficiency to insure that potential interferences from RO<sub>2</sub> radicals were indeed minimized. This should be clarified in the revised manuscript.

3) While the paper describes the range of observed concentrations of some of the other chemical parameters, it would be useful to show the time series of the measurements to illustrate their day-to-day variability and allow a comparison with the OH and HO<sub>2</sub> measurements. Given the dependence of the model on the concentration of terpenes, the authors should also show the time series of the ambient isoprene and terpene concentrations to allow a comparison with the OH and HO<sub>2</sub> measurements. A time

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series of the NO<sub>2</sub> mixing ratios would also be useful to allow comparisons with other environments.

4) While the correlation plots provide an overall picture of the agreement of the model with the measurements, they do not provide any information regarding the day-to-day variability of the model-measurement agreement as well as the ability of the model to reproduce the diurnal variations of OH and HO<sub>2</sub>. The authors should illustrate the modeled time series of OH and HO<sub>2</sub>, perhaps illustrating periods of better model agreement when measured terpene concentrations were lower than 80 ppt.

5) The description of the MOM chemical mechanism used by the authors gives a reference of Taraborrelli et al., 2015 (page 7), which is not in the reference list. Have the authors updated the MIM3 mechanism described in Taraborrelli et al. (2012) reflecting the updated LIM1 mechanism (Peeters et al., J. Phys. Chem. A, 118, 8625–8643, 2014) and used in the latest version of the MCM (Jenkin et al., Atmos. Chem. Phys., 15, 11433–11459, 2015)? While recycling of HO<sub>x</sub> radicals by isoprene may not be important in this environment, the isoprene mechanism used in the model should be clarified.

6) While Figure 5 illustrates the improved agreement with measurements when a simplified autooxidation scheme in the terpene oxidation mechanism is added, there is little discussion of the resulting modeled OH concentrations. Does the increase in the modeled HO<sub>2</sub> lead to an increase in the modeled OH? Did the authors make any assumptions regarding the fate of the products of the H-shift reactions (photolysis, etc.)?

7) The radical budget illustrated in Figure 7 are difficult to read, especially the contributions to OH loss. While O<sub>3</sub> and HONO photolysis and recycling by HO<sub>2</sub> + O<sub>3</sub> and NO contribute to approximately 80% of OH production (page 16), what contributes to the remaining 20% (“other” in Figure 7)? Ozonolysis? OH recycling from isoprene? For the loss of HO<sub>2</sub>, the “other” category appears to be a significant contribution on several days - is this category due to RO<sub>2</sub> +HO<sub>2</sub> reactions from terpenes as discussed in sec-

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tion 3.3 and 3.4? Is the agreement with the measured HO<sub>2</sub> better on the days when this “other” loss is small? The paper would benefit from some additional discussion of the radical budget.

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