This paper presents measurements of OH and HO2 radical concentrations over Cyprus during the CYprus PHotochemistry EXperiment (CYPHEX) in 2014. Measurements of OH and HO2 using an LIF-FAGE instrument were compared to the results of a box model constrained by observations of O3, CO, NOx, 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 HO2 by 17%. Excluding terpenes from the model improves the modeled agreement with the measured HO2. Increasing the concentration of terpenes was found to increase the modeled underprediction of the measured HO2. The authors suggest that the reason for the discrepancy is an increase in radical-radical termination reactions from terpene-generated organic peroxy radicals. Adding a simple autooxidation scheme that decreases the terpene peroxy radical concentration improves the modeled agreement with the measured HO2.

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.

>> Thank you very much for your positive comments and encouragement. We have provided a point-to-point reply to your other comments below.

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?

Response:- We have now modified the plot as per comments. We have, however, not shown the total OH signal, as it can be estimated from the sum of background and atmospheric signals, hence redundant. We do not see a clear variation of the background OH with either O_3 or terpenes alone. However, when we plot the background OH with a proxy for Crigee (CI) production rate, there seems to be some relationship at low and moderate CI concentrations, which needs to be studied in detail. This will be attempted in a future work as CI is not within the scope of the present MS as the reviewers themselves point out.
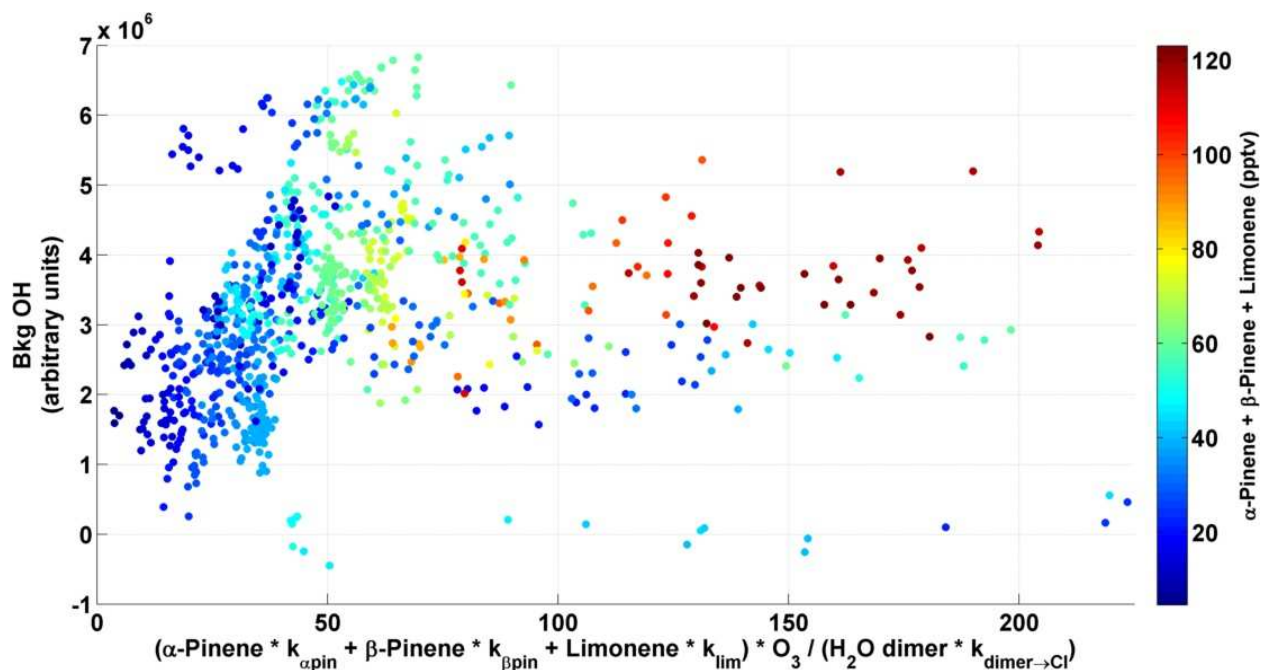
Figure. Background OH plotted against a simplified proxy for crigee (CI) concentrations, assuming that the major production term for CI is the ozonolysis of terpenes and the major loss term is its reaction with water dimer. While the O_3 and terpene concentrations are based on measurements, the concentration of H_2O dimer is based on the Caaba/Mecca output.

Changes in MS:- Supplementary figure 1 modified
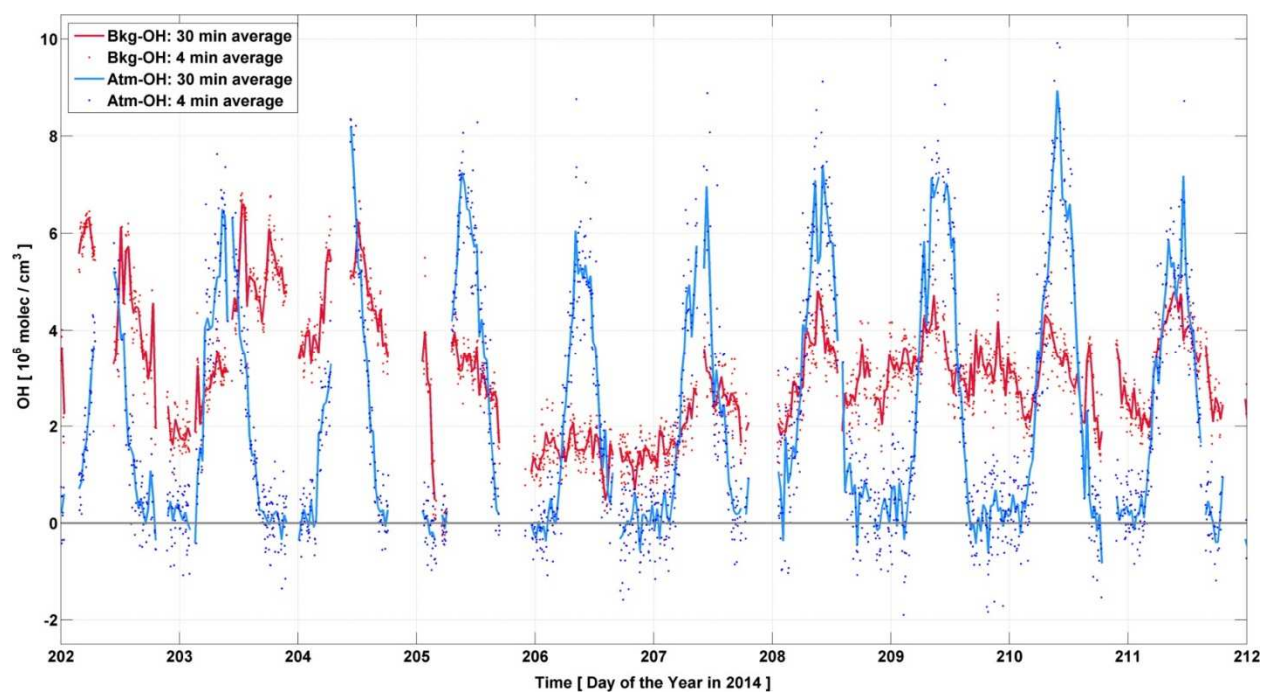
Supplementary Figure 1: *Variation of atmospheric and background OH during CYPHEX.*

Response:- Due to low OH reactivity during Cyphex, we expect the RO_2 production from the oxidation of hydrocarbons to be low. Hence the interference due to potential conversion of atmospheric RO_2s into HO_2 due to NO injected to convert HO_2 into OH in the low pressure detection volume is expected to be low compared to regions with high OH reactivities like the boreal forest in Finland. In order to reduce the conversion of RO_2 to HO_2, we used a reduced NO flow resulting in ~7 x 10^{12} cm^{-3} of NO in the detection cell, thus converting only about 30% of HO_2 to OH while simultaneously reducing the RO_2-HO_2 conversion efficiency. We did not conduct experiments to measure the conversion efficiencies of all possible RO_2s in the atmosphere. To estimate the interference due to RO_2s on our measured signal, we made model calculations using CAABA/MECCA where most of the RO_2s from higher hydrocarbons directly form HO_2 on reacting with NO skipping the reaction step of alkoxy radicals with O_2 which is slower at reduced pressure inside the instrument compared to ambient.

The model is run at ~4 hPa to see how OH and HO_2 evolve with time in the low pressure detection volume at different NO concentrations and is validated for calibration conditions (manuscript under preparation). The RO_2s in the model are initialized with the concentrations generated from the model run for the base case (case III in Figure 3 of the original MS) for our study while OH, HO_2 are initialized with measured concentrations.
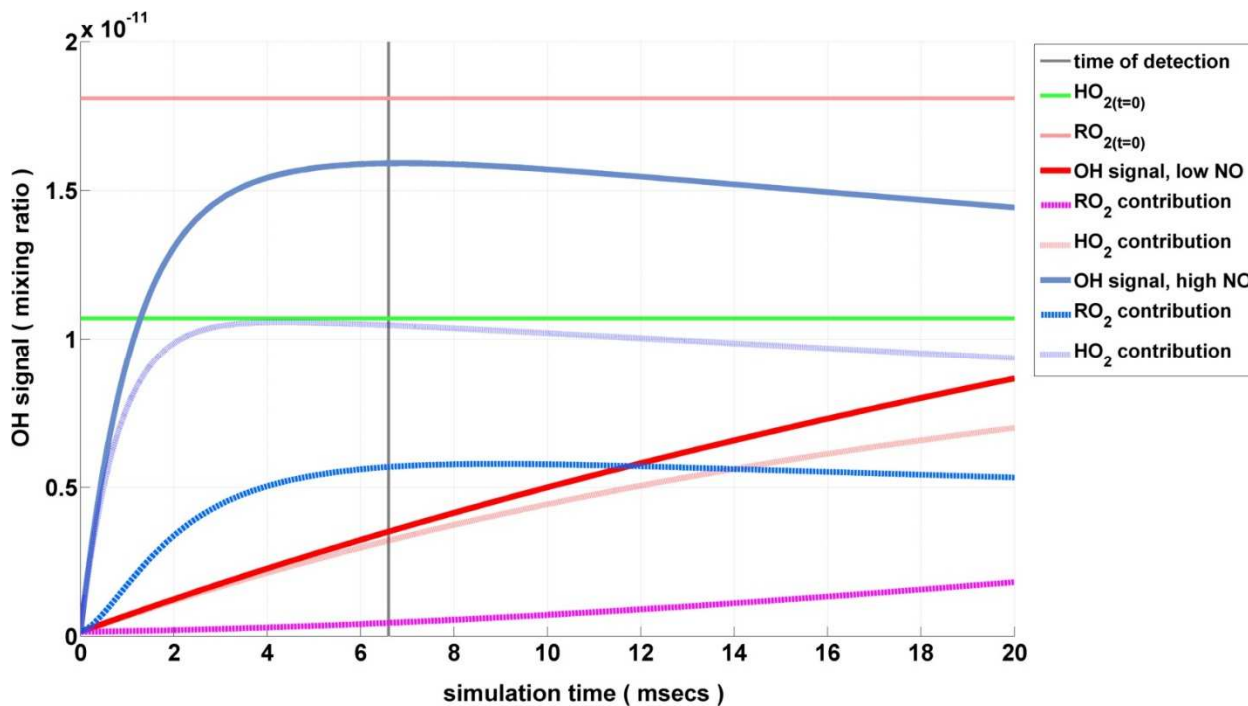
Supplementary Figure 2a: Internal evolution of the OH signal in the low pressure detection cell with increasing residence time at 2 different NO concentrations (high NO: 1.71 x 10^{14} cm^{-3} shown in blue; low NO: 7.1 x 10^{12} cm^{-3} shown in red). The initial HO_2 and RO_2 signals are 10.7 and 18.1 pptv respectively.

In the **Supplementary Figure 2a,** we show the evolution of OH and HO$_2$ inside the detection cell after injection of NO (t=0) for NO concentrations of 7.1×10^{12} and 1.71×10^{14} cm^{-3} respectively. The converted OH signal is detected after 6.6 msecs (time of detection). For the high conversion efficiency case, the contribution of the RO$_2$ to the OH signal at 6.6 ms is about 35% or 31% of the initial RO$_2$ mixing ratio. This value matches with estimates from previous study by Hens et al., 2014. For the low conversion efficiency case that represents the CYPHEX measurement mode, the estimated contribution of RO$_2$ to the measured signal is about 12 % or 2.5% of the initial RO$_2$ mixing ratio.
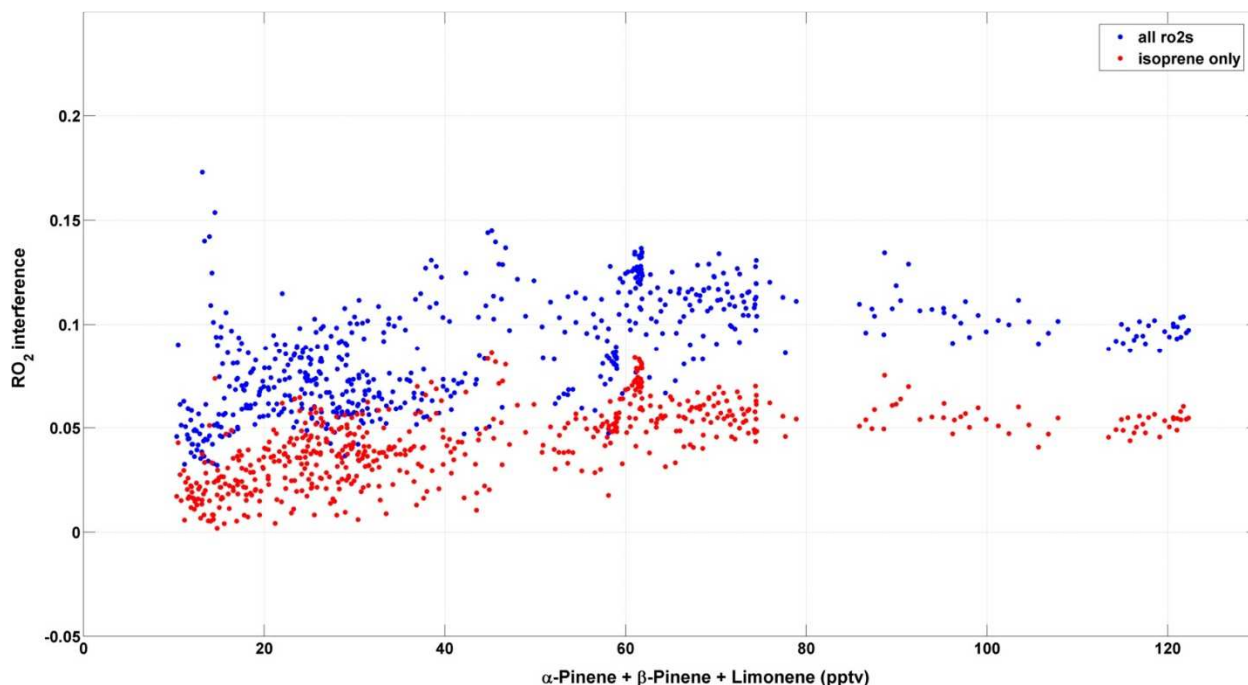
Supplementary Figure 2b: Estimated RO$_2$ interference from all RO$_2$ and only from Isoprene based RO$_2$ during CYPHEX-2014 as function of the terpene concentrations

Further, we estimate that more than 50% of the RO$_2$ interference is due to isoprene oxidation products. This is due to the fast conversion of isoprene-based hydroxy peroxy radicals towards HO$_2$ and OH. These isoprene-based hydroxy peroxy radicals have one of the largest conversion efficiencies of up to 90 % (Fuchs et al., 2011, Lew et al., 2018). Moreover, we see that the RO$_2$ interference does not increase with increasing terpene concentrations and is nearly constant at terpene levels greater than 80 pptv (**Supplementary Figure 2b**), mostly because during the course of the day HO$_2$ concentration increases during this time faster than terpene based RO$_2$ concentration. This indicates that the RO$_2$ interference effects cannot explain the deviation of modelled HO$_2$ w.r.t. measurements at high terpene mixing ratios.

Lew, M. M., Dusanter, S., and Stevens, P. S.: Measurement of interferences associated with the detection of the hydroperoxy radical in the atmosphere using laser-induced fluorescence, *Atmospheric Measurement Techniques*, **11** (1), 95-109, Doi 10.5194/amt-11-95-2018, 2018.

Changes in MS:- Added the above text in Page 8 and the figures as supplementary

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 HO2 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 HO2 measurements. A time series of the NO2 mixing ratios would also be useful to allow comparisons with other environments.

Response:-We have now modified figure 2 as per suggestions.

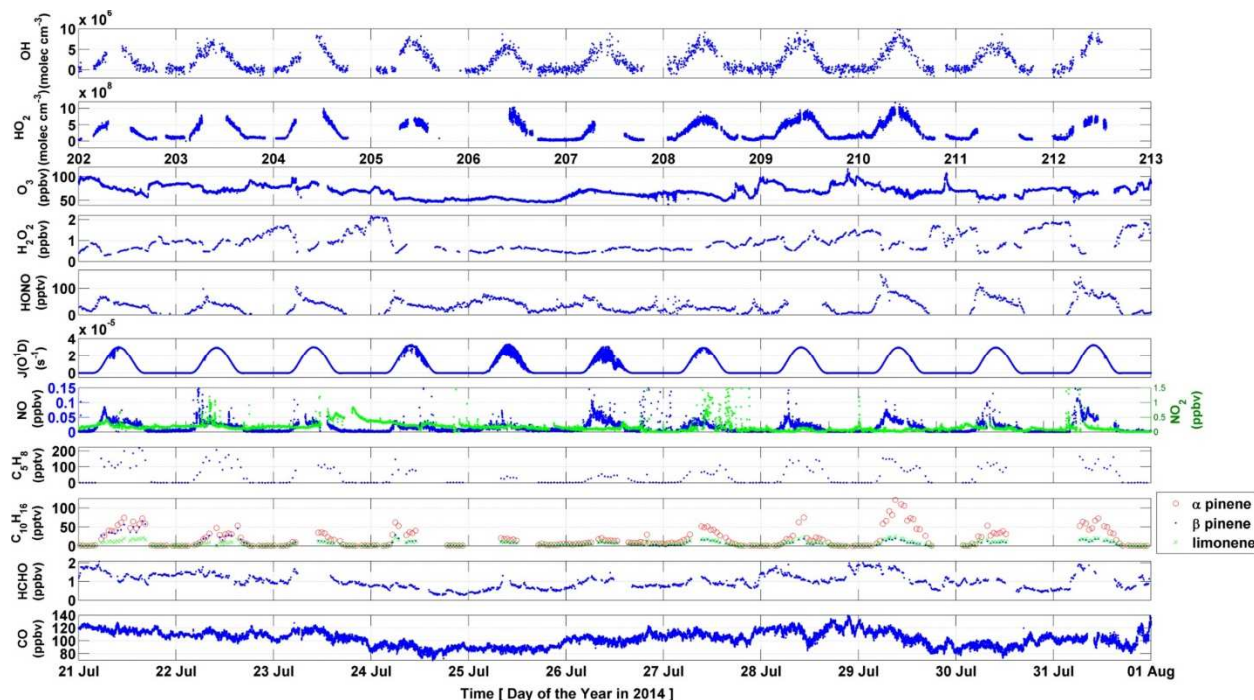Changes in MS:- Modified figure 2 as per suggestion

Figure 2. *Measurements of OH, HO₂ along with selected chemical and radiation parameters relevant to HOₓ chemistry during the CYPHEX campaign. Time is in UTC. Local time in Cyprus during summer is UTC+3.*

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 HO2. The authors should illustrate the modeled time series of OH and HO2, perhaps illustrating periods of better model agreement when measured terpene concentrations were lower than 80 ppt.

Response:-We have added the following figure as suggested.

Changes in MS:- Added text on Page 17 and supplementary figure 5 as per suggestion

The large deviation between observations and modelled HO₂ around middays on 205, 208 and 210 occur during periods with high terpene concentrations. On day 205 and 208, the simulation with the autoxidation scheme shows much better agreement to observations compared to the base case (Case III in figure 3) while on day 210, when terpene concentrations are much higher, even the autoxidation scheme fails to reproduce the HO₂ observations. In this case the simulation where the rate coefficient of

RO₂-R'O₂ reactions was drastically increased shows a much better agreement compared to both the base case and the autoxidation case.
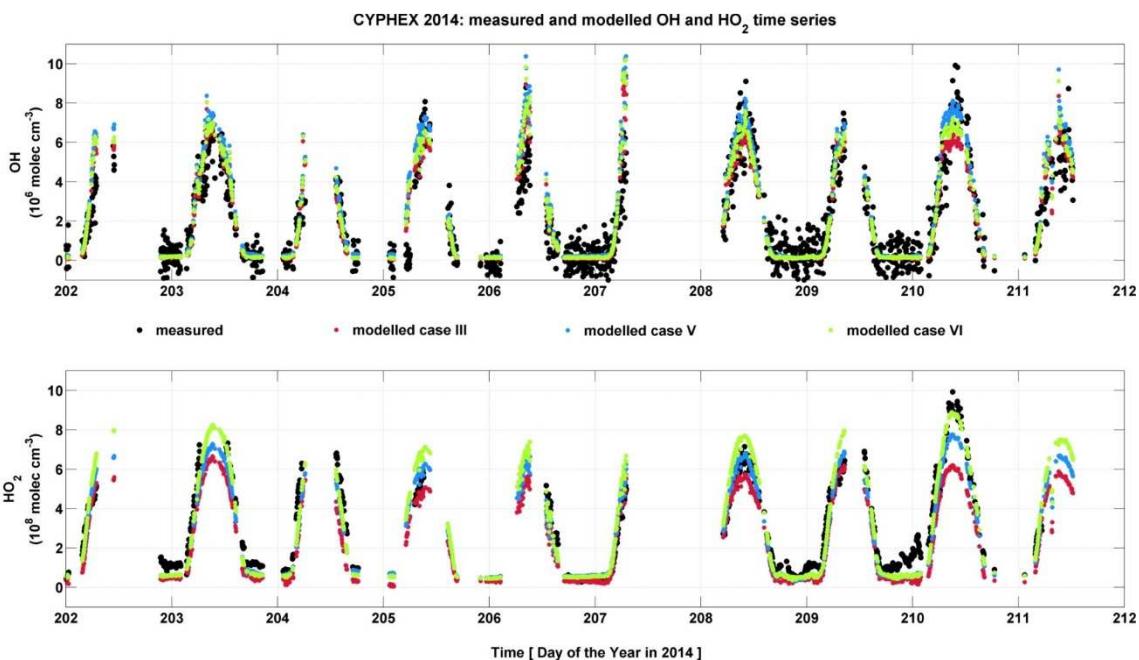
Supplementary Figure 5. *Time series of LIF-FAGE measurements of OH (top panel) and HO₂ (bottom panel) along with various model simulations with CAABA/MECCA; model simulations using base case i.e. initialized with all measured species (case III), simulations emulating the autoxidation scheme (case V), after increasing the rate coefficient of RO2 – R'O2 reactions close to the gas kinetic limit (case VI). Time is in UTC. Local time in Cyprus during summer is UTC+3.*

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 HOx radicals by isoprene may not be important in this environment, the isoprene mechanism used in the model should be clarified.

Response:- The reference to Taraborrelli et al is an EGU conference abstract is towards the end of the reference list (page 25 of original submission). As per comments, we have now expanded the model description as described below.

Changes in MS:-Page 10

MOM has been first presented and used in the study by Lelieveld et al. (2016). It represents the gas-phase oxidation of more than 40 primarily emitted VOCs. The structure and the construction methodology mirrors the one of the MCM. The oxidation mechanism for aromatics has been presented in Cabrera-Perez et al., (2016). The terpene oxidation scheme includes previous developments for modelling HOx field measurements (Taraborrelli et al. 2012; Hens et al. 2014; Nölscher et al. 2014). Most of the known and/or proposed HOx-recycling mechanisms under low-NO conditions are taken into account. Finally, isoprene

chemistry follows to a large extent Peeters et al. (2014) and Jenkin et al. (2015) with modifications by Nölscher et al. (2014). Chemistry of the pinenes (monoterpenes) is a reduction of the MCM with modifications proposed in the past by Vereecken et al., (2007); Nguyen et al., (2009); Vereecken and Peeters, (2012); Capouet et al., (2008).

Cabrera-Perez, D., Taraborrelli, D., Sander, R., and Pozzer, A.: Global atmospheric budget of simple monocyclic aromatic compounds, *Atmos. Chem. Phys*., **16**, 55 6931–6947, https://doi.org/10.5194/acp-16-6931-2016, http://www.atmos-chem-phys.net/16/6931, 2016.

Capouet, M., Müller, J.-F., Ceulemans, K., Compernolle, S., Vereecken, L., and Peeters, J.: Modeling aerosol formation in alpha-pinene photo-oxidation experiments, *J. Geophys. Res*., **113D**, https://doi.org/10.1029/2007JD008995, 2008.

Jenkin, M. E., Young, J. C., and Rickard, A. R.: The MCM v3.3.1 degradation scheme for isoprene, *Atmos. Chem. Phys*., **15**, 11 433–11 459, https://doi.org/10.5194/acp-15-11433-2015, 2015.

Nguyen, T. L., Peeters, J., and Vereecken, L.: Theoretical study of the gas-phase ozonolysis of b-pinene (C10H16), *Phys. Chem. Chem. Phys*., **11**, 5643–5656, https://doi.org/10.1039/b822984h, 2009.

Nölscher, A., Butler, T., Auld, J., Veres, P., Muñoz, A., Taraborrelli, D., Vereecken, L., Lelieveld, J., and Williams, J.: Using total OH reactivity to assess isoprene photooxidation via measurement and model, *Atmos. Environ*., **89**, 453–463, https://doi.org/10.1016/j.atmosenv.2014.02.024, 2014.

Peeters, J., Müller, J.-F., Stavrakou, T., and Nguyen, V. S.: 30 Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: the upgraded LIM1 mechanism, *J. Phys. Chem. A*, **118(38)**, 8625-8643.

Vereecken, L. and Peeters, J.: A theoretical study of the OH-initiated gas-phase oxidation mechanism of b-pinene (C10H16): first generation products, *Phys. Chem. Chem. Phys*., **14**, 3802–25 3815, https://doi.org/10.1039/c2cp23711c, 2012.

Vereecken, L., Müller, J.-F., and Peeters, J.: Low-volatility poly-oxygenates in the OH-initiated atmospheric oxidation of a-pinene: impact of non-traditional peroxyl radical chemistry, *Phys. Chem. Chem. Phys*., **9**, 5241–5248, 30, https://doi.org/10.1039/b708023a, 2007.

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 HO2 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.)?

Response:-The autoxidation scheme used by us is based on Crounse et al (2013). In this scheme (Figure 1 in Crounse et al., 2013), the hydrogen shift reactions lead to generation of a hydroperoxide compound along with an OH. This directly leads to an increase in OH as can be observed from the supplementary figures 4 & 5. Since there is not sufficient information regarding the compounds that would be formed during the autoxidation of peroxy radicals that we considered for this analysis, we have used dummy species for the hydroperoxide products formed. These dummy species will not further participate in the chemical scheme.

Changes in MS:- Supplementary figures 4 & 5 added to show how both modelled OH and HO_2 vary against measurements for the autoxidation scheme w.r.t. the base case.
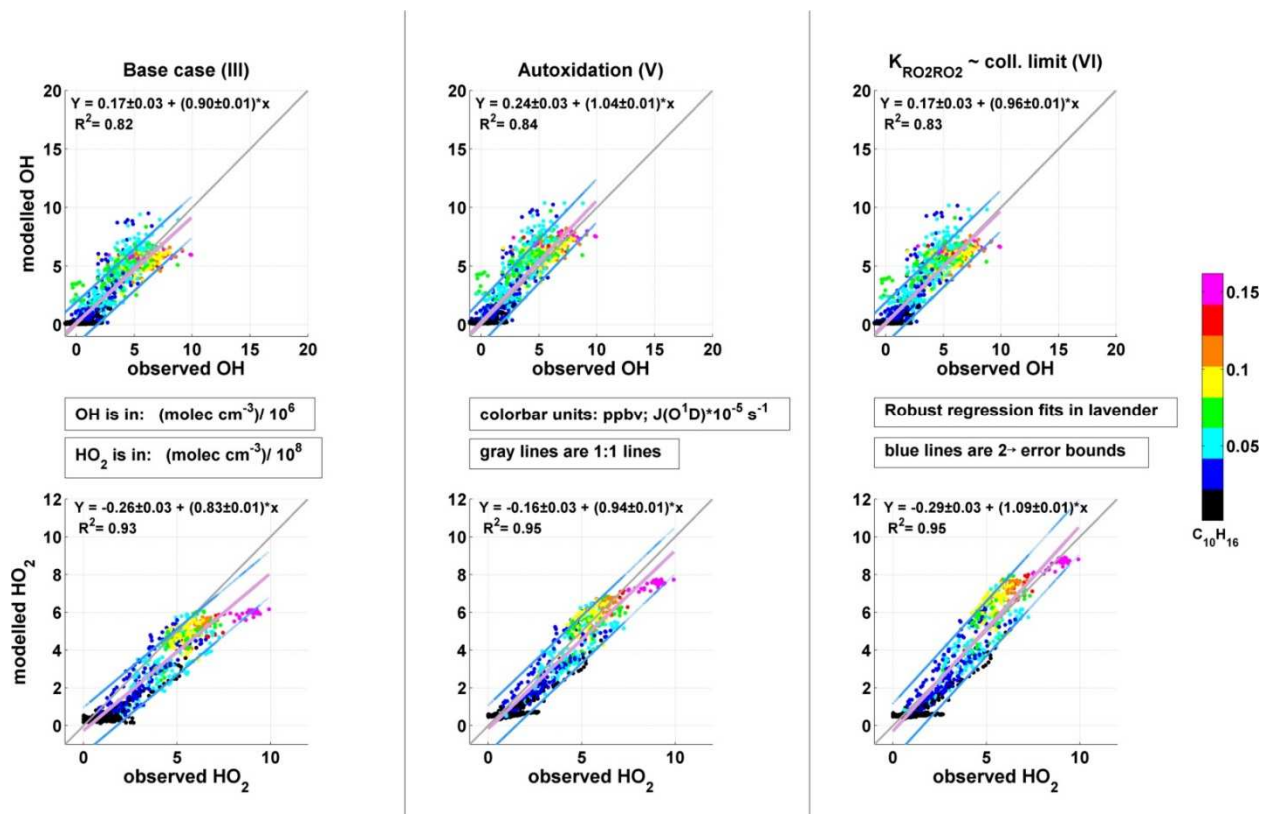

Supplementary Figure 4. *LIF-FAGE measurements of OH (top panel) and HO_2 (bottom panel) vs model simulations with CAABA/MECCA. From left to right: model simulations using base case i.e. initialized with all measured species (case III), simulations emulating the autoxidation scheme (case V), after increasing the rate coefficient of RO2 – R'O2 reactions close to the gas kinetic limit (case VI).*

7) The radical budget illustrated in Figure 7 are difficult to read, especially the contributions to OH loss. While O3 and HONO photolysis and recycling by HO2 + O3 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 HO2, the "other" category appears to be a significant contribution on several days - is this category due to RO2 +HO2 reactions from terpenes as discussed in section 3.3 and 3.4? Is the agreement with the measured HO2 better on the days when this "other" loss is small? The paper would benefit from some additional discussion of the radical budget.

Response:- We have now modified figure 7a so that the panel for the OH sink as well as the text look bigger and clearer. There was a slight mistake in the budget calculation whereby the reactions of the category ROOH + OH = product + OH; e.g. 'C96OOH + OH = NORPINAL + OH'; which are neither a OH source or sink, were not omitted. Now they taken out of the budget and the numbers in the text are revised, although the resulting changes are very minor and always less than 2 %. Further, more reactions are added to the legend in the plot of OH production and loss budget to reduce the 'others' part and these described in the text. The others category is now about only about 7 % compared to nearly 18 % previously. This 7% is made up of numerous reactions which contribute less than 1% individually, so not

worthy of discussion here. Similarly, in the OH loss category we have added a group of reactions of the category ROOH + OH = RO2, e.g. 'C85OOH + OH = C85O2', which makes up about 8.4 %. The associated changes are documented in the text. Further, we have now shown the HO_2 sinks in much more detail by modifying figure 7b. The peroxy radicals together account for nearly 95% of the other term and described in the revised budget plot. You are right that the model increasingly underpredicts the measurements when 'other' loss is large and these occur at higher terpene concentrations (supplementary figure 6).
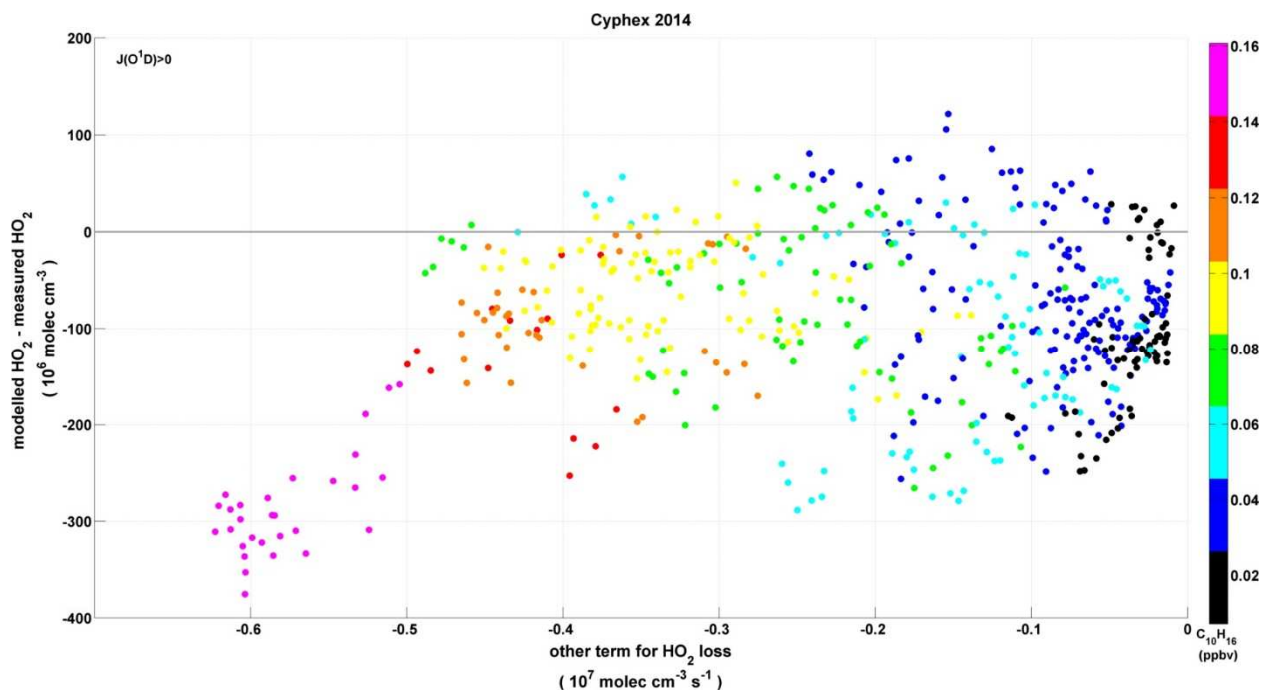
Supplementary Figure 6. *Variation of the difference between modelled and measured HO_2 w.r.t. the 'other term' in the last version of the MS, most of which is constituted by the reactions of peroxy alkyl and acyl radicals with HO_2.*

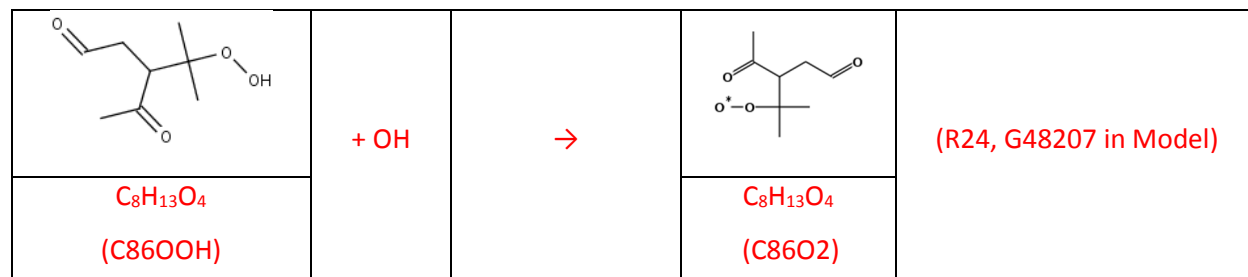Changes in MS:- Text (**only the red portions**) and modified fig 7a

For CYPHEX, the major OH as well as HO_x producing channel is the reaction of atmospheric water vapor with O^1D generated from the photolysis of O_3 (Figure 7). Peak daytime contributions of this channel towards OH production exceeded 45 % for most of the days, and about 60 % on days 205, 208 and 209. The midday values coinciding with peak OH production on day 205 was marked by conspicuous influence of aged air masses originating over south-west Europe and considerably processed over the Mediterranean before reaching the site. The peak HO_2 values on this day were about 11% lower than the average peak HO_2 values during the study period. The peak HO_2 values for $J(O^1D) > 2.5e^{-5}$ s^{-1} was 6.4×10^8 molec/cm^3 for the study period while this value was only 5.7×10^8 molec/cm^3 on day 205. While, on average, the recycled OH via reactions of HO_2 with NO and O_3 (R6-R7) contributed 33.6 % to the total OH production, this value was about 6 % lower for days 205-206. It may also be noted that although O_3 was very low on both days 205 and 206, with predominant influence of aged marine air, the contribution from $O^1D + H_2O$ to the total OH production still exceeded 50 %. Due to lower HONO mixing ratios, the fractional contributions of HONO photolysis towards peak OH production during midday on day 208 was significantly low at about 2.5-3.5 %. On all other days, for which values are available, this channel contributed more than 6 % to peak OH production during noon time. The photolysis of HONO has the largest fractional contribution to the early morning OH production on day 211, reaching above 30 %. Overall during CYPHEX,

the average daytime (JO^{1}D>0) contribution to OH production from O$_3$ photolysis and subsequent reaction of O^{1}D with water vapor was about 39.1 %, the average daytime contribution from HONO photolysis was 12.3 %, while recycled OH from reaction of HO$_2$ with O$_3$ and NO account for 15.2 and 18.4 % of the total OH production, respectively. The four major OH producing channels (Figure 7) contribute up to 95 % of daytime OH production on most occasions, with 85.3 % on average. Further, the reactions of acyl peroxy radicals (RCO$_3$) with HO$_2$ contribute about 3.1 % to the OH production which the photolysis of H$_2$O$_2$ and the ozonolysis of pinene contribute 1.85 % and 2 % respectively.

The single major sink of OH during CYPHEX was CO, followed by CH$_4$, HCHO, C$_5$H$_8$, CH$_3$CHO and O$_3$, on average accounting 20.9, 10.0, 7.8, 5.1, 4.9 and 4.1 % of OH losses respectively. The reactions of various peroxides with OH to form peroxy radicals e.g.R24 contribute 8.4 % to the OH loss. Further, oxidation of CH$_3$OH, pinal, C2-C4 alkenes, α-pinene, HO$_2$, NO$_2$, CH$_3$O$_2$ by OH contributed 2.7, 2.4, 2.4, 2.2, 1.6, 1.4, 1.4 % respectively. During these days (205-206), the modelled OH loss (Figure 7) as well as the calculated OH reactivity (Figure 4) were lowest of the study period. It is likely that the air masses arriving to the site were already much processed, spending considerable time over the Atlantic and Mediterranean, leading to depleted OH reactivity. During this period of marine influence, the contribution of long-lived gases to the daytime OH loss increased by about 15 % while the contribution of shorter lived gases like HCHO and CH$_3$CHO decreased by 34 % and 39 % respectively.

Added text in page 19

The reactions of peroxy radicals (RO$_2$ and RCO$_3$) with HO$_2$ contribute 24.6% to the HO$_2$ loss, resulting in increased underprediction of HO$_2$ by the model with increasing terpene concentrations (Supplementary Figure 6).
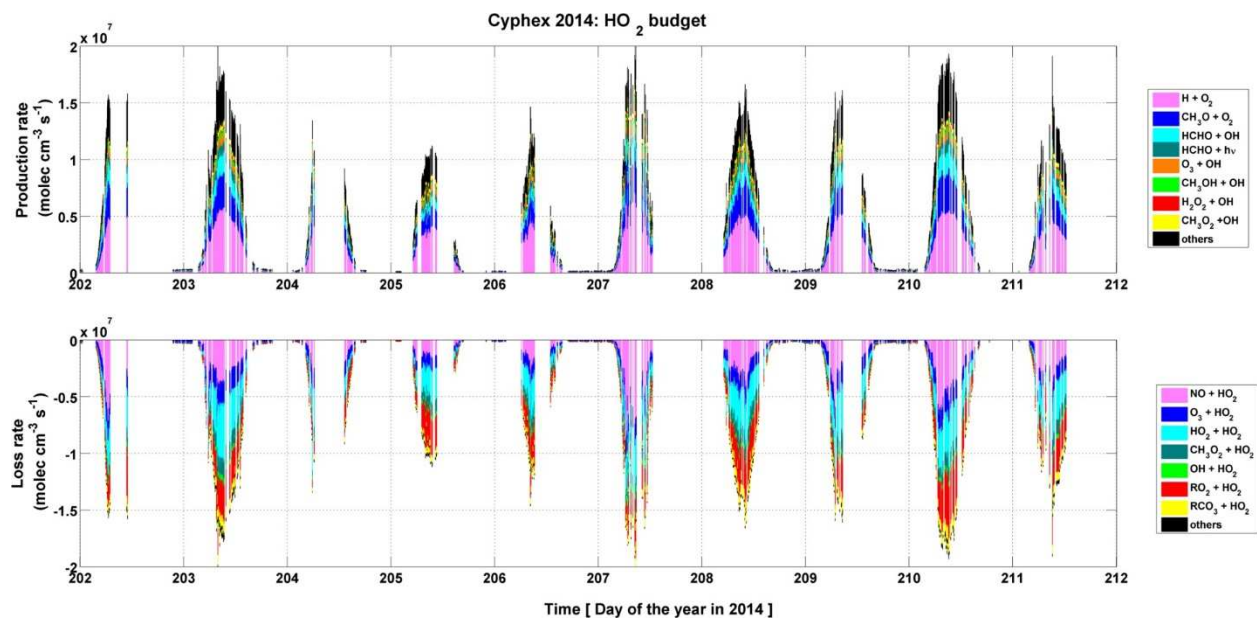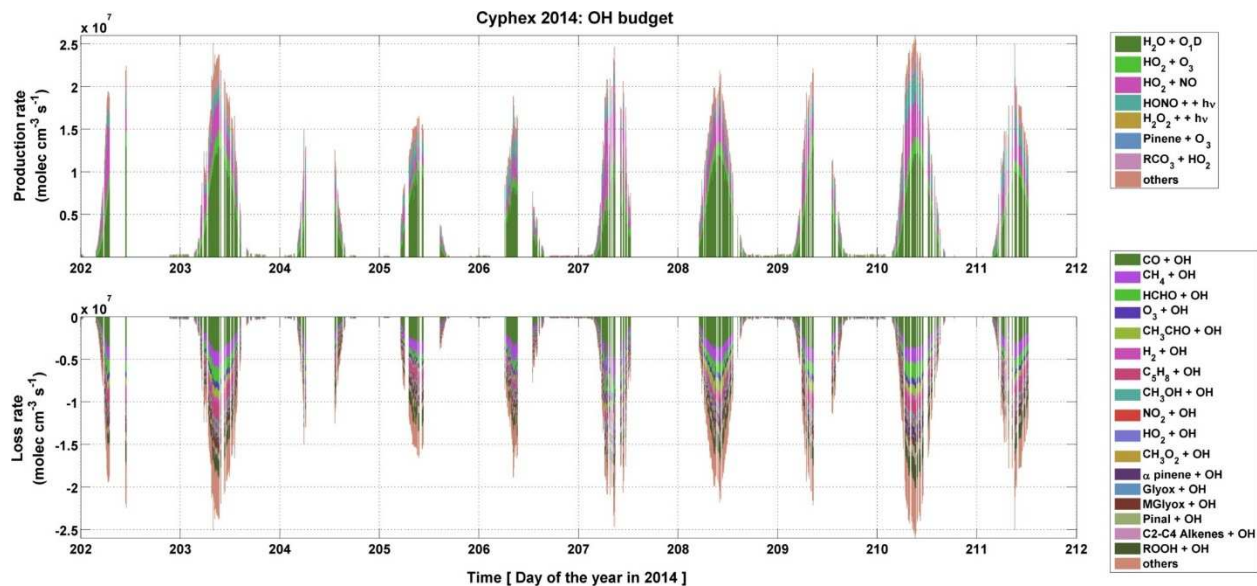
C$_8$H$_{13}$O$_4$ (C86OOH)	+ OH	→	C$_8$H$_{13}$O$_4$ (C86O2)	(R24, G48207 in Model)

Figure 7 a & c.