We would like to thank the reviewers for their helpful and positive comments which have improved the paper. The specific comments of the reviewers are in bold below together with our responses.

### Referee #1

Although the analysis the authors make is very detailed and makes use of the appropriate tools, the level of detail in the implementation of the Peeters mechanism is not very high and with some inaccuracies. For example, there is no separation between E and Z isomers of ISOPAO<sub>2</sub> and ISOPCO<sub>2</sub> (Paulot et al., ACP (2009) proposed 15:85 initial production ratio).

We apologise if we did not make this clear. The isoprene peroxy radicals (ISOPO<sub>2</sub>) included in the representation of the Peeters mechanism are as described by Peeters et al. (2009) and Peeters and Muller (2010), which does include *E* and *Z* isomers for the 1,4-peroxy radicals. These were included in the model as ISOPAO<sub>2</sub> (Z-1-OH-4-OO-isoprene), ISOPCO<sub>2</sub> (*E*-4-OH-1-OO-isoprene), ISOPEO<sub>2</sub> (*E*-1-OH-4-OO-isoprene) and ISOPGO<sub>2</sub> (*Z*-4-OH-1-OO-isoprene). The chemistry of these radicals is referred to on page 10370 (line 25) and described in Table 7, and uses MCM chemistry for ISOPAO2 as an analogue for reactions of ISOPEO<sub>2</sub> and ISOPGO<sub>2</sub> with HO<sub>2</sub>, RO<sub>2</sub> and NO.

### The photolysis products of PACALD proposed by Peeters and Müller (2010) are OH and ketenes. However, ketenes are not included in the model and the photolysis of PACALD2 is set to give $CH_3COCH_2OH + CO + OH + HO_2$ (Table 7).

As discussed on page 10371 (lines 12-15), we treat the products of PACALD photolysis in analogy with their nearest MCM structural analogues in our base simulation for the Peeters mechanism. While we aim to represent the Peeters mechanism as comprehensively as possible, the mechanism unfortunately does not describe full degradation schemes for ketenes expected to be produced on photolysis of the PACALD species. In order to fully simulate the degradation of the organic fragments of the PACALD photolysis it was necessary to use the MCM structural analogues at this point in the scheme. Given the uncertainty in the chemistry up to this point, devising a full ketene oxidation scheme seemed excessive. We have attempted to investigate the sensitivity of the model output to the use of the MCM analogues at this point, with results shown in Table 8 and discussed below.

We will include the following on page 10371 (line15) to describe this in more detail:

'Although the Peeters mechanism expects production of ketenes on photolysis of the PACALDs, further oxidation chemistry for such ketene species is, at the present, unavailable. Thus we use the photolysis products of the PACALD MCM analogues  $HC4ACO_3H$  and  $HC4CCO_3H$  at this point in the scheme in an attempt to provide a full isoprene degradation scheme. Sensitivity of the Peeters mechanism to the PACALD photolysis products is shown in Table 8.'

This makes a significant but unfaithful HO<sub>2</sub> production of about  $10^7$  cm<sup>3</sup> s<sup>-1</sup> (Figure 7h) in the Peeters mechanism. Furthermore, Peeters and Müller (2010) proposed a production of 2 OH radicals after PACALD photolysis and not 1 OH as in this case. Therefore, simulations for the Peeters mechanism should be repeated after at least having eliminated the above mentioned HO<sub>2</sub> production and introducing a production of 2 OH radicals. Although, the authors seems to have done sensitivity simulations with PACALD2 photolysis not resulting in HO<sub>2</sub>, the description provided in Table 8 is not clear and probably is a result of a typo.

We apologise for the typographical error in Table 8. This has now been corrected, and describes the results of sensitivity studies in which  $HO_2$  production from photolysis of PACALD2 was switched off. We also now include the results of simulations in which the only difference made to the base Peeters simulation is the removal of  $HO_2$  production from PACALD2 photolysis, and in which 2 OH radicals are produced in the PACALD photolysis.

# Since the requested changes will likely improve both OH and HO<sub>2</sub> results with the Peeters mechanism, satisfactory results may be achieved for both OH and HO<sub>2</sub>. Therefore, this may weaken (or even reverse) the major conclusions of the manuscript.

Table 8 has been updated to amend the typographical error and to include the simulations described above (base case simulation with no HO<sub>2</sub> produced from PACALD photolysis, and base case simulation with production

of 2 OH from PACALD photolysis). As the results show, there is still no single simulation which is able to simultaneously reproduce the measurements of both OH and  $HO_2$ . The general conclusions of the manuscript are thus unaltered.

I agree with the comment of D. Kubistin concerning the modelling studies of Lelieveld et al., (2008) and Kubistin et al., (2010) in which the OH-recycling mechanisms  $C_5H_8 + OH \rightarrow ISOPO_2 + nOH ISOPO_2 + HO_2 \rightarrow ISOPOOH + mOH$  were used only as proxies and in both articles it was explicitly stated. Therefore, all the paragraphs (p10346 114, p10362 113, p10362 126, p10372 125) in which these articles are mentioned and commented should be reformulated accordingly.

We have reformulated the appropriate paragraphs as requested. Please see response to D. Kubistin below.

## p10346 I18 : Lelieveld et al. (2008) did not present box model results. Instead, global simulations as in Butler et al. (2008) were shown. Therefore, the citation should be put next to Butler et al. (2008).

We have included the additional reference next to Butler et al. (2008), although it should be noted that Lelieveld et al. (2008) did also show the results of box model simulations described in more detail by Kubistin et al. (2010).

#### Referee #2

1) As discussed by the authors, Fuchs et al. (2011) have reported a potential interference in FAGE HO<sub>2</sub> measurements from alkene-based peroxy radicals, including isoprene-based peroxy radicals. As pointed out in the paper, this interference will depend on the instrument configuration, including the concentration of added NO and the reaction time before OH detection. The authors claim that because the observed to modeled ratio for HO<sub>2</sub> is independent of the concentration of isoprene (as shown in Figure 6b) it is possible that their instrument is insensitive to isoprene peroxy radicals. However, if the measured HO<sub>2</sub> does include an interference from peroxy radicals, then this could have a more significant impact on the model/measurement agreement for HO<sub>2</sub> and the ability of the proposed recycling mechanisms to reproduce both OH and HO<sub>2</sub>. Although this may not change the overall conclusions of the paper, the authors should include a brief discussion of the potential impact of an interference on their conclusions.

The potential for HO<sub>2</sub> interferences in FAGE measurements is discussed on page 10361. Since the submission of this manuscript, the ground-based FAGE instrument has been tested for HO<sub>2</sub> interferences resulting from alkene-based peroxy radicals, and was found to be relatively insensitive to RO<sub>2</sub> species. The results of this work are described in the author comments to Whalley et al. (ACPD, 2011, 11, 5785-5809 <u>http://www.atmos-chem-phys-discuss.net/11/5785/2011/acpd-11-5785-2011.html</u>). While investigation of the Leeds AirFAGE instrument has yet to be completed, the results described by Whalley et al. (2011) further emphasise the strong dependence of any potential interference on the instrument configuration.

We have amended our conclusions section (page 10374) as follows:

'Further laboratory experiments are required to elucidate the mechanisms involved in the oxidation of isoprene. Such studies may provide a solution which enables reproduction of observations of both OH and HO<sub>2</sub> by the model. However, until this has been achieved, our results indicate that in order to obtain model to observation agreement for OH we require additional loss processes for HO<sub>2</sub>. Any potential interference in the HO<sub>2</sub> measurements derived from alkene-based peroxy radicals, as discussed by Fuchs et al. (2011), will lead to a greater model discrepancy for HO<sub>2</sub> when agreement is achieved for OH, and the need for much greater additional loss processes for HO<sub>2</sub>.

2) I am confused with the author's treatment of the photolysis of the PACALDs produced from HPALD photolysis in Table 7, which has been updated in Peeters and Muller, 2010 (not Muller and Peeters as indicated in the Table). The updated reaction PACALD photolysis mechanism in Peeters and Muller leads to the formation of 2 OH radicals rather than 1 OH and 1 HO<sub>2</sub> radical as listed in Table 7. It is not clear how this change would affect their model results, but it could bring the modeled HO<sub>2</sub> into better agreement with the observations. It appears that the sensitivity study described in Table 8 removed HO<sub>2</sub> as a product of PACALD2 photolysis (indicated by the "i.e. no HO<sub>2</sub>" statement), however this is not clear as the reaction shown in Column 1 for PACALD2 photolysis is the same as the base mechanism in Table 7.

Please see above comments for referee #1. We apologise for any confusion arising as a result of the errors in Table 8. We have amended the caption for Table 7 to reference Peeters and Muller, and not Muller and Peeters.

3) The radical budget in Figure 7 suggests that NO is a major propagator of HO<sub>x</sub> radicals, although it is not clear what NO mixing ratio was used for this particular calculation. It is also unclear why the radical budget is not balanced (the production of OH from the HO<sub>2</sub> + NO reaction in Figure 7a is much less than the loss of HO<sub>2</sub> due to HO<sub>2</sub> + NO in Fig. 7b). Unfortunately the model/measurement comparisons are not binned according to different NO concentrations as they are for isoprene, as it appears that there was some variability in NO concentrations during the campaign (52.6 ± 109.0 ppt, range of 0.02 to 1240 pptv from Table 2). Was the model/measurement agreement better at higher NO concentrations than lower NO concentrations?

We apologise for the confusion here. The radical budgets shown in Figure 7 were for separate data points for OH and  $HO_2$ , and have now been updated to show the same data point throughout. The NO concentration (42 ppt) has been included in the caption to the figure.

### Comment by D. Kubistin

Kubistin et al., 2010, is cited to have introduced the reaction  $C_5H_8 + OH \rightarrow ISOPO_2 + OH$  for the GABRIEL campaign as an explanation for a direct additional OH recycling. This is misleading as this reaction was chosen only to investigate a possible OH recycling inside the whole isoprene oxidation scheme. This sole reaction should only be understood as a proxy for additional recycling within the subsequent oxidation scheme. The factor n = 1.3 shows that at some point or points within the oxidation process a total of 1.3 OH have to be produced for each OH destroyed in the initial step.

The factor n in the reaction  $C_5H_8 + OH \rightarrow ISOPO_2 + nOH$  was determined by Kubistin et al. for the GABRIEL campaign by modifying the reaction  $C_5H_8 + OH \rightarrow ISOPO_2$  to  $C_5H_8 + OH \rightarrow ISOPO_2 + nOH$  inside the chemical reaction scheme. The reaction constant used was  $k = 2.54 \times 10^{11} \exp(410/T)$ . By varying the factor n in the range of 1.0 to 1.5 (0.1 steps), best agreement between observed and modelled OH concentrations during GABRIEL was obtained with the factor n = 1.3 (OH<sub>obs</sub> / OH<sub>mod</sub> = 1.4 ± 0.5).

We apologise if the text appeared to represent the work of Kubistin et al. (2010) in a misleading manner. We have amended the text on page 10362 (lines 13-17) as follows:

'A simple, but chemically unlikely, recycling scheme in which OH is produced directly by isoprene+OH ( $C_5H_8$  +OH  $\rightarrow$  ISOPO<sub>2</sub> +*n* OH) was investigated to determine the extent of OH recycling required for the GABRIEL campaign (Kubistin et al., 2010). The best fit between the observation and the model required *n*=1.3 (Kubistin et al., 2010).'

We have removed the statements 'However, the mechanism for recycling was not specified' on page 10362 (line 17) and 'However, details of how this value was derived by Kubistin et al. are not provided' on page 10363 (line 2).