

Response to referees

We would like to thank the referees for taking the time to read this paper and for providing useful comments and suggestions. We will respond to the individual points below.

Response to Referee #1:

>>(1.1) The main aims of this paper, however, are unclear. If the purpose of the paper is to provide an >>appreciation of the processes controlling atmospheric reactivity throughout the canopy, this has not >>been achieved in the manuscript at present. The bulk of the text is devoted to validating different >>aspects of the model and so perhaps this manuscript should be viewed as a more technical paper? As >>such, this work may be more suited for publication in ACP's sister paper, AMT.

We feel that the detailed comparison of measured and modelled reactivity has provided sufficient insight into oxidative processes in the boreal forest to warrant publication in ACP rather than its more technical counterpart (AMT). Model validations (by comparison to measurements) are included in order to investigate the accuracy of our model results.

>>(1.2) The paper introduces the concept of 'relative oxidative strength' and suggests when >>considering the importance and strength of an oxidant, both the reactivity and concentration of the >>oxidant need to be considered. Utilising this concept, the authors find that O₃ is the oxidant able to >>remove compounds fastest from the atmosphere. The authors state that O₃ almost exclusively (91%) >>reacts with NO, however. The reaction of O₃ with NO may be classified as a null cycle as the NO₂ >>formed readily photolyses during the day to reform O₃ and NO. Taking this into consideration, 91% >>of O₃ reactivity should be considered null and, therefore, the ability of O₃ to remove/process >>compounds in the atmosphere is, in reality, considerably lower than presented in the paper. As the >>reactions each oxidant undergoes must also be considered, the term 'relative oxidative strength', as >>presented in the manuscript currently, actually provides very little useful information. The authors >>themselves briefly comment that 'oxidative strength is not equal to oxidative importance', but only >>after a lengthy introduction and discussion of this fundamentally flawed concept. The manuscript, as >>is, provides a skewed view on the chemistry responsible for the processing of compounds in the >>atmosphere with statements in both the abstract and conclusions that O₃ is the oxidant capable of >>removing pollutants fastest. This is not the case. Discussions in section 7.4.5 and reaction R13 could >>be adapted to reflect the reactivity (and, hence, relative oxidative strength) of a particular oxidant >>towards organic compounds only. It may be informative to integrate oxidative strength over the >>whole day (24 hrs) for comparison. A sizable chunk of the paper is given over to this concept, >>however, and the authors should seriously consider how much credence they want to give to this.

We thank the referee for these very good suggestions. We will change Fig. 11 to only cover the oxidation strength when organic compounds have been taken into consideration. We will re-write and shorten Sec. 7.4.5 (and equation R13), the abstract and conclusion accordingly and provide the 24 hrs integrated oxidative strength.

>>(1.3) The modelled and measured OH reactivity diurnal profiles do not agree well. The differences >>in the diurnal trends displayed by the model and measurements should be discussed more critically. >>Although previous model measurement comparisons of OH reactivity at forested sites tend to show >>an under-prediction, the diurnal trends are often similar for both; see for example Edwards et al., >>ACP, 13, 9497-9514, 2013. This is not the case here and so the validity of the emission scheme used >>needs to be discussed. The authors state on page 30975, line 5 'the modelled forest is too >>homogeneous to capture the variability in the measured OH-reactivity' which raises the question: Is >>a model, constrained to modelled emissions that are too homogeneous, appropriate to compare to in- >>situ observations? The authors need to provide evidence that this application of the 1D model is

>>robust and that this approach is providing something in addition to that presented in Nölscher et al, >>ACP, 12, 8257 – 8270, 2012.

The environment studied in Edwards et al. (2013) is very different from the one studied in this manuscript, thus we cannot expect the model results to differ from the measurements in a similar way. The observed differences in the diurnal trend between the modelled/calculated and measured OH reactivity was discussed for the same campaign in Nölscher et al. (2012) and for the same site, also during a different campaign in Mogensen et al. (2011), and thus it was not treated in detail in this paper.

While Table 2 in our manuscript provides the statistics on how well the same data set of measured and modelled OH reactivity compares, Figure 7 seeks to show the general pattern throughout the campaign period using all available data. As also stated in the Sec. 7.4.2., the modelled data used for Figure 7 includes all data during non-pollution periods, while the measurement data only includes the available measurements during non-pollution periods. The emission scheme utilised in this manuscript is widely used and accepted by the community, while the emission factors are from measurements from the particular site (in case of the monoterpenes, the emission factor is measured continuously). Further, a combination of the different schemes for meteorology, emission and chemistry was validated in Mogensen et al. (2011). That paper provided comparisons of the measured and modelled monoterpene concentration for several heights and showed that the concentration agreement is good. Monoterpenes were chosen for this comparison, since they are the group of organic compounds that contribute to the largest fraction of the OH reactivity at the site. In Sec. 7.4.2 on P30973 after L10, we will mention the validation study by Mogensen et al. (2011). Since the SMEAR II site is well studied with respect to tree emissions (e.g. Hakola et al., 2003, Hakola et al., 2006, Tarvainen et al., 2005, Bäck et al., 2012, Aalto et al., 2014), we are quite confident which specific VOCs are emitted, and it seems unlikely that the missing OH reactivity is due to emitted VOCs (that are measurable with GC-MS and PTR-MS). The missing reactivity is more likely due to either emitted VOCs that are not detectable by GC-MS and PTR-MS and/or unknown oxidation products of the known emitted compounds. We will add this statement to the manuscript. Lastly, we would like to mention to the referee that we are currently working on implementing a BVOC emission scheme into a LES (Large Eddy Simulation) model, whereby we can test if our 1D model simulations are sufficient.

>>(1.4) Title: Does not mention OH reactivity at all currently. A more encompassing title should be >>chosen

We will change it to “Simulations of atmospheric OH, O₃ and NO₃ reactivities within and above the boreal forest”

>>(1.5) Pg 30948, line 17: ‘conditions of the campaign’ mention temperature specifically here. OK.

>>(1.6) Pg 30949, line 17: There are earlier field measurements of OH than 1987. The Beck et al paper >>referenced actually discusses measurements made in 1984, although these have been discredited. >>More appropriate references should be chosen.

OK. We will refer to Wang and Davis (1974) instead.

>>(1.7) Pg 30949, line 22: ‘common to all investigations..is the large missing fraction of the OH- >>reactivity’ - this is not the case, for example, in the Lou et al study referenced, good agreement >>between modelled and measured OH reactivity was found.

OK. We will reword this to “common to most investigations..is the large missing fraction of the OH- reactivity”

>>(1.8) Section 3: The details provided for the different instruments is not consistent, sometimes limits of detection are given, sometimes not (CO measurement). Descriptions should be standardised. We will provide the recording interval, detection limit and total accuracy for all instruments mentioned in this section. For the SMEAR II measurements we will also keep the sampling interval, since the trace gas concentrations are measured at several heights.

>>(1.9) Pg 30952, line 21: Just because there was only one instrument measuring SO₂, this shouldn't exclude a description or reference. Please provide some details. The original idea was not to include info on the SO₂ measurement, since the data were not intercompared in the paper. However, we will provide the required measurement information and add a reference to Rosman et al. (2001).

>>(1.10) Pg 30953, line 3: 'campaign' is spelt incorrectly
OK, this will be corrected.

>>(1.11) Section 3.2: were either O₃ instruments calibrated against an ozone standard?
The SMEAR II O₃ instrument was calibrated directly after the campaign with our (the Physics Department at the University of Helsinki) laboratory's O₃ transfer standard photometer which is in turn regularly (once a year) calibrated at the Finnish Meteorological Institute against ozone standards (photometers) traceable to the Finnish national O₃ standard photometer (SRP-37). The instrument set-up and handling of the MPI O₃ instrument is similar to the set-up described in Hosaynali Beygi et al. (2011). This instrument was calibrated using a commercial O₃ calibrator, (model TE49C, Thermo instruments GmbH, Germany) several times during the campaign. We will mention that both instruments were calibrated against ozone standards.

>>(1.12) Page 30954: lines 2 – 4 are not necessary.
OK, we will erase them.

>>(1.13) Pg 30954, line 21: 'poorer' – please state by how much?
No particular value was provided in Bohn et al. (2008). After personal communication with Birger Bohn, we were made aware that the accuracy of our rates were better, since the filter radiometers were compared with a reference spectroradiometer instrument at FZJ before and after the campaign. Moreover, the J(1OD) measure has been technically improved since the 2008 paper, however, there exist no paper on this. We will include a note on that in the manuscript.

>>(1.14) Pg 30958, line 8: It is not clear what is meant by 'other monoterpenes than those mentioned here'? Are other monoterpenes included? Is there a lumped monoterpene emission in addition to those explicitly considered? Please clarify.
Yes, we included a lumped monoterpene emission in addition to those explicitly mentioned. This was done, since Bäck et al. (2012) detected small emissions of other monoterpenes (camphene, terpinolene and p-cymene) than α -pinene, β -pinene, limonene and 3-carene, however, the gas phase chemistry of those other monoterpenes is unknown. We will clarify this in the text.

>>(1.15) Section 5.3.1 – unclear what exactly has been done here and why analysis of this type was needed?
In this section we suggested how to convert our measured spectral irradiance into actinic flux. This was necessary, since we needed more photolysis rates than what were measured. Further, we needed the photolysis rates throughout the canopy and not just at two vertical points (which were the available measurements). In the very beginning of this section, we will write what measurement data we had

available and why we needed to include this conversion.

>>(1.16) Section 5.3.2 – What is the impact of adding these additional photolysis reactions?
The impact is small (and at times neglectable), but those are the suggestions from Atkinson et al. (2004).

>>(1.17) Pg 30960, line 18: ‘This includes information..’ It is not clear what is being referred to here?
>>The reference?

When re-reading this sentence, we agree with the reviewer that the sentence is not clear. The reason for adding something like this was to emphasize that the calculation of the photolysis rates are done using wavelength and temperature dependent cross sections and quantum yields and not just some function as was done in MCM version 3.1. Since the sentence is not strictly necessary, we will erase it.

>>(1.18) Pg 30962, line 21 onwards: What is the impact of the different rate coefficients for the
>>reaction of N₂O₅ with H₂O(v)? Does the reaction with H₂O represent a significant N₂O₅ sink?
>>Incidentally, I couldn’t find this reaction on the MCM website when I browsed.

We forgot to add, that a few inorganic gas phase reactions listed in Atkinson et al. (2004), that are not included in the MCM subset, were also included in the chemistry. This also covers the N₂O₅ water channel, and this rate is therefore not from the MCM. We apologise for the mistake. During our study there is no impact due to the different rate coefficients since the temperatures were high and the loss of N₂O₅ is strongly dominated by thermal dissociation. The reaction with H₂O does therefore not represent any accountable sink of N₂O₅ and in order not to confuse the reader, we will leave out this whole discussion.

>>(1.19) Pg 30963, lines 3 – 8: I presume the authors are referring to rate of production/destruction
>>analysis. This whole paragraph is confusing, however.

In this paragraph we describe how the reactivity calculation was computationally handled. We will remove this paragraph from Sec. 5.5 and make it a separate subsection (Sec. 5.5.1). We will also rewrite the section.

>>(1.20) Pg 30965, line 6: should surface deposition be considered here as well as the aerosol surface
>>area as it was included in R7 loss processes on the previous page?

We agree and will include this in the calculation.

>>(1.21) Pg 30966, lines 16-18: The specific pollution event times are not necessary.
OK, this will be left out.

>>(1.22) Pg 30968, line 9: add ‘with’ after ‘coincides’
OK, this will be added.

>>(1.23) Pg 30968, line 19: replace ‘with’ with ‘by’
OK, this will be changed.

>>(1.24) Section 7.1.1: A brief discussion on the impact of underestimating the [H₂O] should be
>>provided
OK

>>(1.25) Pg 30970, line 13: This is not an appropriate title for this section which simply compares the
>>concentration of the measured gases using different instruments – there is no ‘model validation’

OK, we will change the title to “Comparison of trace gas measurements”.

>>(1.26) Pg 30971, line 4: please state the albedo used in the TUV calculations

OK, we will add “The surface reflectivity was assumed to be independent of wavelength and was fixed to 0.1.”.

>>(1.27) Pg 30971, line 7: remove ‘as required’

OK

>>(1.28) Pg 30971, line 15: it is not difficult compare. The comparison is necessary to assess how good >>the canopy penetration factor is.

We do not agree. Since the ground measurements were done in a clearing, they do not represent the photolysis rates at ground level inside the canopy.

>>(1.29) Pg 30972, line 26: ‘modelled OH-reactivity shows little variability..’ Due the very different y >>axis ranges displayed in Fig. 7, it looks like the modelled OH reactivity has a more pronounced >>diurnal structure than the measurements.

The calculated ratio (minimum reactivity / maximum reactivity) is 0.17 for the measurements (both heights) and 0.84-0.85 for the model results (the ratio is 0.85 for 18 m and 0.84 for 24 m). We will add this information to the section.

>>(1.30) Pg 30973, line 27: ‘the largest fraction’ please give this fraction.

We will add the specific fraction to the sentence.

>>(1.31) Pg 30974, line 6: ‘with a bit more than 2/5..’ this sentence needs improving.

OK, we will reformulate.

>>(1.32) Pg 30974, line 12: ‘partly due to..’ what else is contributing to the differences?

Both the emission and the chemistry scheme have been updated since the Mogensen et al. (2011) paper and this also contributes to the difference. We will add this information into the manuscript.

>>(1.33) Pg 30977, line 1: ‘..suggesting that we would not expect a similarly large missing NO₃- >>reactivity as the missing OH-reactivity’ This is an interesting point, suggesting it may be possible to >>combine two oxidant reactivity measurements to aid identity of the missing reactivity fraction.

This sentence might be a bit too crude extrapolation. In reality, the contribution of oxidised BVOCs to the NO₃ reactivity might be much larger, but currently the NO₃ chemistry has not been explored enough. We will remove the sentence and we will elaborate on the unexplored NO₃ chemistry.

>>(1.34) Pg 30978, line 5 – 7: This argument cannot explain the consistent bias.

The text deals with averaged values but we see from Figure 10 that the bias is not consistent. As the text from lines 7 -21 indicates, there are other sources of bias (including overestimation of terpene emissions in the model and NO₃-recycling from organic nitrates) and, in the end, we leave this issue open by identifying which measurements would be necessary to resolve the issue. We shall amend the text to indicate that in general the model over-predicted the measured (and corrected) NO₃ reactivity but that on some occasions reasonable agreement was obtained (e.g. on day 08/03).

>>(1.35) Pg 30979, line 15: ‘resisting’ to ‘remaining’

OK

>>(1.36) Pg 30981, line 7: 'least' to 'lowest'
OK

>>(1.37) Pg 30983, line 15: It is unclear why a conversion of spectral irradiance to actinic flux from
>>measurements of $j(\text{NO}_2)$ and $j(\text{O}_1\text{D})$ is useful? If measurements of $j(\text{O}_1\text{D})$ and $j(\text{NO}_2)$ are available,
>>it would be straightforward to estimate other photolysis rates directly from these.

Please see the response to your comment on Section 5.3.1. Further, continuous measurements of $j(\text{O}_1\text{D})$ and $j(\text{NO}_2)$ are not conducted at the SMEAR II stations. However, for other projects, we also want to simulate periods when these measurements were not conducted, thus we need some way to convert the measured irradiance, thus we took the opportunity in this paper, since the measurements were available.

>>(1.38) Pg 30984, line 14: 'resisting' to 'remaining'
OK

>>(1.39) Tables 2: A correlation plot of OH reactivity modelled vs measurements would be more
>>informative than the information provide in Table 2 alone.
We can add such a plot in addition to Table 2.

>>(1.40) Table 3: I suggest replacing this table with either pie-charts or a figure equivalent to figure 8.
In principle this is a good idea, however, some of the groups contribute with such a small fraction, that it is difficult/impossible to see their contribution on a pie-charts or a figure equivalent to figure 8.

>>(1.41) Figure 1: isn't necessary

We agree with the referee that this figure is not crucial for our manuscript. However, we find that it gives a good overview of the model structure (which is important). We expect that the reader finds it easier to understand how the model works with this figure included, which is the reason why we prefer to keep it.

>>(1.42) Figure 8: I suggest plotting absolute contribution (s^{-1}) rather than fractional contribution so
>>the inorganic reactivity of these different oxidants can be compared and contrasted.

If we would do as the reviewer suggests, then we would loose the time dependent importance of the individual inorganic compounds, since the oxidant reactivities are not constant as a function of time. We would therefore prefer to keep the figure as it is, but we will add another figure including the absolute contributions as the reviewer suggests.

>>(1.43) Figure 11: should be updated to reflect oxidative strength relating to the removal of organic
>>compounds only.
Yes we agree and this will be done.

Response to Referee #2:

>>(2.1) Overall, I truly appreciate that the authors' effort to study unexplored area and draw the
>>attention about importance of NO_3 and O_3 reactivities in the forest environment to the atmospheric
>>chemistry community. However, this manuscript is still poorly written and needs to be improved in
>>many parts of the sections, particularly in the discussion of the reactivities of oxidants by organics.
We are very happy that the referee acknowledges that we made first attempts to investigate an unexplored scientific area. We are confident that the changes suggested by both referees will strongly improve the manuscript. In particular, we will rewrite the section on the relative oxidation strength to only cover reactions with organic compounds. Please also read the response to comment 2.17.

>>(2.2) The title seems that this MS intended to focus on O₃ and NO₃ reactivities. Throughout the MS, >>however, description and discussion of OH and NO₃ reactivities are much more allocated than O₃ >>reactivity.

Please read the response to the comment 1.4.

>>(2.3) In addition, reactivities of each oxidant by reacting with organics are poorly explained despite >>of their importance in the forest area.

We will change Sec. 7.4.5 to only cover organic compounds and in this section we will also emphasize the fact that the organic O₃ and NO₃ chemistry is not well explored.

>>(2.4) One big concern is that the authors did not use BVOC measurement data or did not justify >>BVOC input data when comparing the modeled value by MEGAN to any other available data at the >>site or to the similar vegetation types. This may cause substantial error in reactivity calculation. Since many of the organic compounds that are relevant for our study have a short lifetime, they will also have a distinct vertical profile. Therefore, it is not possible to constrain our 1D model by BVOC measurements. About validation of the emission scheme, please read the response to the comment 1.3.

>>(2.5) As the referee #1 pointed out, I agree that discrepancy of modeled vs observed OH reactivity >>needs to be thoroughly discussed.

Please read the response to the comment 1.3.

>>(2.6) As well as, during daytime NO+O₃ → NO₂ +O₂ reaction is null cycle since O₃ returns back >>by NO₂ photolysis, so it is hard to say that O₃ is reacted with NO. To improve this, I suggest >>focusing more on organic compounds than inorganic compounds.

Please read the response to the comment 1.2.

>>(2.7) Moreover, the lifetime of oxidant is equivalent to the inverse of reactivity, thus lifetime of O₃ >>is estimated ~13 hours based on the result in the abstract. This is considerably slow and not >>plausible in the forest environment if trees emit BVOCs. Further, when considering NO+O₃ reaction >>as null cycle, the O₃ lifetime is going to be even much slower. This is also required to discuss in the >>MS.

The calculation is based on known and published (MCM) chemistry and validated emission input (e.g. Mogensen et al. (2011)). Also, the lifetime is within the range of what Peräkylä et al. (2014) report.

>>(2.8) Abstract: Overall, this part should be rewritten after revision of the MS.

We will revise the abstract to reflect the general manuscript in its state after revision.

>>(2.9) P.30948, L23: ‘removing pollutants fastest’, this sounds like inappropriate since O₃ also reacts >>with BVOC as mentioned previously in the MS, as well as O₃ by itself is generally not the fastest >>oxidant to remove either organic or inorganic compounds.

Since we will change Section 7.4.5 to cover mostly/exclusively organic compounds, we will delete L23. Also see the response to comment 1.2.

>>(2.10) P.30949 L18-19: What do you mean by ‘the measurement is tricky’? Be specific here and >>need good references.

We mean that it is difficult to detect such low concentrations of such a reactive compound. We will reformulate the sentence and add references.

>>(2.11) P.30950 L12-14: How did you come with '5% of the global emission of BVOCs'? Did you >>only account for the boreal forests or together with the temperate forests? Clarify this since you >>mentioned both in the previous sentence.

This 5% is from Figure 2b in Guenther, 2013 and the reference is provided in the sentence. The value is only for the boreal forest and we will reformulate the sentence so there is no misunderstanding.

>>(2.12) P.30951 Section 2: Briefly describe the general information for each site such as vegetation >>type, climate, wind pattern, anthropogenic influences, and etc. . .

Such a description will be added to Sec. 2.

>>(2.13) Section 3.1-3.3: Even though table 1 shows some information for measured gases, it does not give any information for diurnal profile. So, I suggest describing general diurnal patterns for each gas at the site or generating some figures similar as figure 7 for measured gases.

OK, we will add a figure with the daily averaged profiles.

>>(2.14) P.30955 L6-8: Explain what method you used to calculate uncertainty or add a reference. We used propagation of uncertainty and will add this information to the manuscript.

>>(2.15) Section 4.4: What was the measurement uncertainties for NO₃ and N₂O₅?

Total uncertainty is reported as 15 % (at least 2 pptv) and 15 % (at least 3 pptv) for NO₃ and N₂O₅ respectively (Crowley et al., 2010). We will add this to the manuscript.

>>(2.16) Section 5: How was treated the deposition in the model (e.g. surface removal and stomatal >>uptake) In addition, how does the SOSAA deal with partitioning between gas and particle?

During the last months we have included and tested the multiple-layer deposition module from Prof. Laurens Ganzeveld in SOSAA. However, using a constant sticking probability for all gases resulted in an overestimation in the deposition from the volatile compounds. Currently, we are working on a molecule-specific sticking coefficient based on the functional groups of the individual molecules, but this input was and will not be available for the model simulations we provided for this manuscript.

Concerning the partitioning between gas and particle phase, the simulations presented in this manuscript were done without our aerosol dynamic module (as also mentioned in Sec. 5). Instead we calculated the sink term for certain gases like sulfuric acid or nitric acid using the calculated condensational sink values from the measured aerosol size distributions.

>>(2.17) Section 5.2: This section is poorly written and need to be more specific because BVOCs are >>presumably very important source in reactivity calculation in the forest environment. So, please >>describe a little more in detail how you estimated LAI or add a reference, and explain a bit more >>about vegetation composition such as dominant tree species and understory plants. In order to >>calculate reactivities of oxidants by reacting with BVOCs, mixing ratios of each BVOC at different >>heights are necessary, so describe how the BVOC mixing ratios were considered in detail rather than >>just stating use of MEGAN. Also, it needs to be discussed whether or not the BVOC input data used >>in the model were reliable when comparing them to the measurement data from the same site (or >>other similar sites, if not applicable).

We would like to emphasize that this paragraph does only serve as an overview, since the emission module has been repeatedly described in previous papers. We will add that references to the used LAI and write that the dominant tree species is Scots pine. The above-ground understory vegetation consists of ~60% vascular plants (mostly shrubs) and ~40% mosses (Ilvesniemi et al., 2009). We will also add that the leaf area density distribution is based on observations at the site. Further, we will write that the BVOC mixing ratio at each level in the model depends on the predicted BVOC emission in that level,

the concentration of reactants in that level, and the transport to/from that level. About validation of the MEGAN output, please read the response to the comment 1.3.

>>(2.18) P.30960 L13: 'MCM v3.2' is mentioned first here, so give the full name here than in the >>section 5.4.

OK

>>(2.19) P.30960 L22-23: Justify or add a reference why you used a constant mixing ratio of H₂ and >>CH₄.

The concentration of H₂ was to our knowledge never measured at the site. The value used, is in line with what has been measured by CDIAC at other stations. After personal communication with Prof. Vesala's group it was decided that it was a good assumption to use a constant mixing ratio of CH₄ during the campaign period.

>>(2.20) P.30969 L25-26: Discuss the reason why the time window of 7 pm-8pm was chosen to >>validate the turbulence. Also discuss what result was come out if you do this for daytime or at >>nighttime. Because 7pm should be nearly neutral condition of the air and it apparently cannot be >>representative for turbulence scheme.

The choice for the time window was not considered thoroughly enough, and we will change the figure to show the average profiles for 1-2 am and pm, to better represent turbulent midday conditions and the difference to stable or neutral night time.

>>(2.21) P.30972 L24-26: This sentence is not true, particularly for daytime measurement which >>apparently shows higher at ROH in-canopy than above-canopy in figure 7.(b). Moreover, modeled >>ROH result shows consistent lower value at above-canopy in figure 7.(c). Improve this >>appropriately.

We will remove the sentence and instead write that during noon-early afternoon, the difference in measured above and in-canopy reactivity increases and the in-canopy reactivity is almost twice that of the above-canopy reactivity. Also we will add that the modelled in-canopy reactivity is consistently higher than the above-canopy reactivity.

>>(2.22) P.30973 L3-10: It is not clear whether or not the same size of data set was used to compare >>'Measured' vs 'Modelled'. In figure 7. (a), it indicates maximum 10-12 days of measurement data >>were used for one month campaign period. Is it the same for the model? Please clarify this. In case >>they used different set, justify how those can be compared each other.

As also stated in the text, the dataset is different, since the modelled reactivity covers the entire study period, while the measured reactivity covers the available measurements. Since we have filtered out periods influenced by pollution, we are only considering 'natural' conditions. We included this plot in order to get a picture of how the modelled and measured summer time OH reactivity generally behaves. For statistical purposes, we have considered only the periods with available measurements in Table 2, thus this table compares the same dataset of measured and modelled reactivity.

>>(2.23) P.30973 L22-23: Give specific number of isoprene concentration range rather than stating just >>'very low'.

OK, we will add this.

>>(2.24) P.30979 L6-8: As explained in general comment, with given number of O₃ reactivity, the >>lifetime of O₃ can be calculated by inverse number of reactivity, thus O₃ lifetime is estimated by >>~11 hours during daytime and ~5.8 days at night. This is pretty slow, particularly at night. Was

>>there decreasing trend in nighttime ozone concentration? If so, discuss what major processes of
>>ozone removal take place at the site. Also, provide diurnal trend of O₃ and NO during the campaign.
>>I think the model only accounts for very limited number of chemical reactions with O₃, so I believe
>>there should be missing parts of O₃ reactivity for unknown/unaccounted compounds and reactions.
>>At the end of this section, even though possibility of underestimation is mentioned, authors
>>should thoroughly discuss about how much of reactivities they expect to underestimate. Otherwise,
>>this whole manuscript will be less meaningful in terms of O₃ reactivities.

About the lifetime of O₃, please see the response to comment 2.7. The concentration of O₃ was less during night time than during day time, which is observed in both the SMEAR II mast measurements and the MPI measurements. We expect that the major night time removal process of ozone is by deposition (Rannik et al., 2012), and we can add this reference in the manuscript. For daily trends of O₃ and NO (and other measured trace gases), please see the response to comment 2.13. As stated in P.30972 L13, according to the known (MCM) chemistry that is relevant for our simulation, O₃ only reacts with 28 oxidised BVOC species, so indeed the model only accounts for a very limited number of chemical reactions between O₃ and organic compounds. We are also of the belief that O₃ must be reacting with much more organic compounds in the atmosphere, but that the chemistry of O₃ has just not received as much attention as e.g. OH. We will clearly state this in the Sec. 7.4.5, however, we currently have no way to say (or even guess) how large the missing O₃ reactivity is.

>>(2.25) P.30981 L1: As mentioned above, O₃ molecule by itself is not the fastest oxidant, but O₃
>>removes reactants much more than other oxidants do because it is the most abundant oxidant at the
>>site. State this very clearly.

We will write the following sentence or similar "O₃ is by itself not the fastest oxidant at any time, however, at times, O₃ removes reactants more than other oxidants, since it is much more abundant in concentration at the site."

>>(2.26) P.30982 L4-5: Explain in detail how OH and NO₃ are reformed and why not for O₃?
We will remove this sentence.

>>(2.27) P.30982 L5-8: Again, rephrase 'how fast can the oxidant remove pollutants from the
>>atmosphere,'. 'pollutants' is not appropriate here since BVOCs are not the pollutants.
OK.

>>(2.28) P.30982 L11-13: With this sentence, it seems authors think opposite way to the rate of
>>reaction between OH and O₃. The statement 'though it is only capable of doing it at a slow rate.' is
>>generally wrong except for a few very reactive compounds with O₃ (e.g. beta-caryophyllene). For
>>example, when comparing reaction rate for isoprene and most monoterpenes, the reaction with OH
>>is much faster than O₃.

We agree that this sentence is not very good. We are referring to the oxidative strength and not rate of reaction. We will reformulate the sentence.

>>(2.29) P.30982 L16-19: I do not agree with this statement, because O₃ can react with the second or
>>even higher generation products from primary reactants. Methacrolein and methyl-vinyl-ketone are
>>good example since those are the second products from isoprene oxidation and those can react with
>>O₃, though the reaction rates are relatively much slow with either isoprene or MVK&MACR
>>compared to reaction with OH. The reason why O₃ has much less number of reactions than OH does
>>is due to the reaction mechanism by O₃ for a variety of compounds has not broadly studied yet,
>>particularly for high order generation products from organic compounds.

We will emphasis that this statements is made for known O₃ chemistry. We will add that O₃, however,

also reacts with some higher generation products (e.g. those 28 that we have included from the MCM). We will also add that O₃ chemistry is not well explored and e.g. make a reference to Ehn et al. (2014) that found O₃ generated ELVOC.

>>(2.30) P.30983 L26: Again, the word 'fast' is improper. Please consider it to replace with a relevant word or rephrase it.

OK. We will replace "how fast" with "the rate at which".

>>(2.31) Section 8: This part needs to be rewritten after revision.

We will change the text connected to the conclusions reached about the oxidative strength.

>>(2.32) Table 1: I suggest replacing this table to diurnal profile plots for each compound.

We will keep the table, but add the figure as explained earlier in the response to comment 2.13.

>>(2.33) Table 3: List more specified compounds for monoterpenes and sesquiterpenes used to the model and show each reactivity rather than using total MTs and SQTs.

We will keep MTs and SQTs totals, but add the contribution from the individual terpenes also.

>>(2.34) Figure 6: It is not easy to compare. I suggest making this figure to 1:1 scatter plots, with regression curves. (e.g. in a figure, Meas vs TUV with black dots and Meas vs 2015 MODEL with red triangles.)

OK, we will also add scatter plots as suggested.

>>(2.35) Figure 8: I suggest generating similar area plots that show contribution of each organic compound used in the model in addition to this plot. With this figure alone, it seems inorganic compounds are more important in the reactivities of oxidants.

We include more than a 1000 organic compounds in the model, thus such figure would not be meaningful.

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