#### 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 it's 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 is 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 faction 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, O<sub>3</sub> and NO<sub>3</sub> 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 <u>most</u> 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 SO<sub>2</sub> 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 Meterological Institute against ozone standards (photometers) traceable to the Finnish national O3 standard photometer (SRP-37). The instrument setup 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(10D) 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 a-pinene, b-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 where 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 emphasis 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 NO<sub>3</sub>-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) NO<sub>3</sub> 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(NO2) and j(O1D) is useful? If measurements of j(O1D) and j(NO2) 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(O1D) and j(NO2) 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 NO3 and O3 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 emphasis 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  $\sim$ 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 NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> 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 emphasis 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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List of changes

\*) We added an additional affiliation for S. Smolander "\* now at NOAA/Geophysical Fluid Dynamics Laboratory - Princeton University, Cooperative Institute for Climate Science, Princeton, NJ, USA."

\*) We added the sentence "The turbulence closure scheme is known to perform best under near-neutral stratification. However, the overestimation of friction velocity was found persisting for all stability conditions." to the end of chapter 7.1.3.

List of changes required by the referees

1.1) Nothing specific was currently done.

1.2) We added a new version of Figure 11 that only takes the organic (and not the total) reactivity into account. We further changed the abstract and conclusion so that they now include the information when only organic compounds are considered for the oxidation strength. We changed equation R13, added the 24 hour integrated oxidant strength and changed the text in Sec. 7.4.5.

1.3) We mentioned the Mogensen et al. (2011) study in Sec. 7.4.2 and we elaborated on the missing OH reactivity.

1.4) We changed the title to "Simulations of atmospheric OH, O<sub>3</sub> and NO<sub>3</sub> reactivities within and above the boreal forest".

1.5) We added "(with typical temperatures of 20–25 C)" to the sentence.

1.6) We changed the reference.

1.7) We changed the wording to "Common to most investigations..is the large missing fraction of the OH-reactivity".

1.8) We included the recording interval, detection limit and total accuracy for all instruments mentioned in this section. Also we corrected two typos in Table 1.

1.9) In the section "Measured gases used as input to the model" we added a subsection on the SO<sub>2</sub> measurements.

1.10) The typo was corrected.

1.11) We mentioned that both instruments were calibrated against ozone standards.

1.12) We erased the lines.

1.13) We mentioned that the uncertainty on the photolysis rates are less than reported by Bohn et al., 2008.

1.14) The sentence was reworded to "The monoterpenes included are  $\alpha$ -pinene,  $\Delta$ 3-carene,  $\beta$ -pinene, limonene, cineol and a lumped group of minor monoterpenes and their emission distribution is based on the average chemotype presented in Bäck et al. (2012).".

1.15) In the beginning of Sec. 5.3.1, we justified the conversion.

1.16) Currently nothing was done.

1.17) The sentence "This includes the information on wavelength and temperature dependent cross sections and quantum yields." was erased.

1.18) We erased the discussion about the reaction rate.

1.19) We removed the paragraph into a sub-paragraph (Sec. 5.5.1) and rewrote the section.

1.20) We included loss due to dry deposition of N2O5 into our calculation.

1.21) The text was erased.

1.22) 'with' was added to the sentence.

1.23) 'with' was replaced with 'by'.

1.24) We make a sensitivity test to check how the underestimation affects the reactivities and added a short description of the results in the end of this section.

1.25) The title of the subsection was changed to "Comparison of trace gas measurements".

1.26) We added the sentence "The surface reflectivity was assumed to be independent of wavelength

and was fixed to 0.1.".

1.27) We deleted 'as required' from the sentence.

1.28) Currently nothing was done.

1.29) The ratios were added to Sec. 7.4.2.

1.30) We added the fraction to the sentence and also, we changed the word 'compounds' (in the sentence "Since SMEAR II is a monoterpene dominated environment, the reactivity of OH due to reactions with these terpenes is significant and they make up the largest fraction of the OH-reactivity due to primary emitted compounds) to 'terpenoids'.

1.31) The sentence was reformulated.

1.32) We mentioned that the difference also arises due to updates in the emission and chemistry schemes.

1.33) We removed the sentence and added discussion in Sec. 7.4.3.

1.34) We specified that in general the model over-predicted the measured (and corrected) NO<sub>3</sub> reactivity, but that on some occasions reasonable agreement was obtained (e.g. on day 08/03).

1.35) 'resisting' was changed to 'remaining'.

1.36) 'least' was changed to 'lowest'.

1.37) Currently nothing was done.

1.38) 'resisting' was changed to 'remaining'.

1.39) We added scatter plots for the OH reactivity at both heights. Currently this figure is called "Figure 12".

1.40) Currently nothing was done.

1.41) Currently nothing was done.

1.42) We added a figure with the absolute reactivities due to reactions with inorganic compounds. Currently this figure is called "Figure 13".

1.43) We added a new version of Figure 11 that only takes the organic (and not the total) reactivity into account.

2.1) The manuscript underwent significant changes. For specifics, we refer to the remaining points on this list.

2.2) see 1.4.

2.3) see 1.2.

2.4) see 1.3.

2.5) see 1.3.

2.6) see 1.2.

2.7) Currently nothing was done.

2.8) The abstract was rewritten.

2.9) The sentence was deleted.

2.10) The sentence was reformulated and we added three references.

2.11) The sentence was reformulated.

2.12) We added a brief description to Sec. 2, where we provided general information on the vegetation, meteorological conditions and anthropogenic influences during the campaign.

2.13) We added a figure with the daily averaged profiles of the NO, NO2, O3, CO and SO2. Currently this figure is called "Figure 15".

2.14) We added that we used propagation of uncertainty in order to calculate the measurement uncertainty.

2.15) The uncertainty and a reference were added.

2.16) Currently nothing was done.

2.17) We added references to the used LAI, wrote that Scots pine is the dominant species at the site, and also informed about the above-ground understory vegetation and the used LAD distribution. Lastly,

we specified how the concentration of each BVOC at each level depends on the emission, reactant concentration level and meteorology. About validation of the MEGAN output, please see 1.3.

2.18) We introduced the MCM abbreviation in Sec. 5.3.2. instead of in Sec. 5.4.

2.19) Currently nothing was done.

2.20) We changed the figure to show the average profiles for 1-2 am and pm.

2.21) The sentence was changed.

2.22) Currently nothing was done.

2.23) We added the average isoprene concentration during the campaign.

2.24) A reference to the night time sink of ozone was added in Sec. 7.4.5 as we also discussed the unexplored ozone chemistry in the same section.

2.25) This was changed as Sec. 7.4.5 was changed.

2.26) The sentence was deleted.

2.27) This was erased.

2.28) This was changed as Sec. 7.4.5 was changed.

2.29) Sec. 7.4.5 was changed and we emphasised the unexplored ozone chemistry.

2.30) We changed the wording.

2.31) We changed the text connected to the conclusions reached about the oxidative strength.

2.32) See 2.13.

2.33) We add the reactivity due to individual terpenes in Table 3.

2.34) We improved Fig. 6 and added scatter plots comparing the measured photolysis rates with the modelled and the TUV predicted rates. Currently this figure is called "Figure 14".

2.35) Currently nothing was done.

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### The oxidation capacity of the boreal forest: first simulated reactivities Simulations of atmospheric OH, O<sub>3</sub> and NO<sub>3</sub> reactivities within and above the boreal forest

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## Discussion Paper

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#### Abstract

Using the 1D atmospheric chemistry-transport model SOSAA, we have investigated the atmospheric reactivity of a boreal forest ecosystem during the HUMPPA-COPEC-10 campaign (summer 2010, at SMEAR II in Southern Finland). For the very first time, we present vertically resolved model simulations of the NO<sub>3</sub>- and O<sub>3</sub>-reactivity (R) together with the 5 modelled and measured reactivity of OH. We find that OH is the most reactive oxidant  $(R \sim 3s^{-1})$  followed by NO<sub>3</sub>  $(R \sim 0.07s^{-1})$  and O<sub>3</sub>  $(R \sim 2 \times 10^{-5}s^{-1})$ . The missing OHreactivity was found to be large in accordance with measurements ( $\sim 65\%$ ) as would be expected from the chemical subset described in the model. The accounted OH radical sinks were inorganic compounds ( $\sim$  41%, mainly due to reaction with CO), emitted monoter-10 penes ( $\sim 14\%$ ) and oxidised biogenic volatile organic compounds ( $\sim 44\%$ ). The missing reactivity is expected to be due to unknown biogenic volatile organic compounds and their photoproducts, indicating that the true main sink of OH is not expected to be inorganic compounds. The NO<sub>3</sub> radical was found to react mainly with primary emitted monoterpenes ( $\sim 60\%$ ) and inorganic compounds ( $\sim 37\%$ , including NO<sub>2</sub>). NO<sub>2</sub> is, however, only 15 a temporary sink of NO<sub>3</sub> under the conditions of the campaign (with typical temperatures of 20-25 °C) and does not affect the NO<sub>3</sub> concentration. We discuss the difference between instantaneous and steady state reactivity and present the first boreal forest steady state lifetime of NO<sub>3</sub> (113s). O<sub>3</sub> almost exclusively reacts with inorganic compounds ( $\sim 91$  %, mainly NO, but also NO<sub>2</sub> during night) and less with primary emitted sesquiterpenes ( $\sim 6\%$ ) 20 and monoterpenes ( $\sim 3\%$ ). When considering the concentration of the oxidants investigated, we find that OH is the oxidant that is capable of removing pollutants fastestorganic compounds at a faster rate during daytime, whereas NO<sub>3</sub> can remove organic molecules at a faster rate during night time. O<sub>3</sub> competes with OH and NO<sub>3</sub> during a short period of time in the early morning (around 5 am) and in the evening (around 7-8 pm). As part of this 25 study, we developed a simple empirical parameterisation for conversion of measured spectral irradiance into actinic flux. Further, the meteorological conditions were evaluated using radiosonde observations and ground based measurements. The overall vertical structure of the boundary layer is discussed, together with validation of the surface energy balance and turbulent fluxes. The sensible heat and momentum fluxes above the canopy were on average overestimated, while the latent heat flux was underestimated.

#### 1 Introduction

As most biogenically and anthropogenically emitted trace gases are oxidised within the Earth's boundary layer, the oxidising capacity of this layer may be considered to be approximately that of the atmosphere. The concentrations of oxidants and their reactivity towards a vast amount of compounds and pollutants, together with the concentration of these pollutants, impact on the local air quality. Anthropogenic activity, resulting in increased sources
 of air pollution and more intense forest management (e.g. deforestation), results in changes in the composition of the atmosphere and potentially in its oxidation capacity.

The OH radical is considered the main atmospheric cleaning agent and consequently, it has received a lot of attention (e.g., Levy, 1971; Mount and Eisele, 1992; Lelieveld et al., 2008; Mogensen et al., 2011, and references therein). Being highly reactive, OH has a short lifetime (depending on the conditions, but usually much less than one sec-15 ond Jacob, 1999), and is capable of reacting with most functional groups. The concentration of OH was first measured in 1987 (??) the 1970's (Wang and Davis, 1974), but even with great advances in instruments the measurement is still tricky and instrument development, it is still difficult to detect such low concentrations of such a reactive compound (Mao et al., 2012; Novelli et al., 2014a, b) . The measurement is therefore still 20 associated with large uncertainties. The reactivity of OH, its summed first-order loss rate constant from the atmosphere, has been measured in both urban (e.g., Ren et al., 2003; Lou et al., 2010) and remote and forested environments (e.g., Kovacs et al., 2003; Nölscher et al., 2012a; Sinha et al., 2010). Common to all-most investigations, especially those in forested areas, is the large missing fraction of the OH-reactivity. This means that OH is lost

due to unaccounted processes that is most often attributed to unmeasured and unidentified

compounds either originating from direct emission or formed via oxidation processes (e.g., Mount and Eisele, 1992; Di Carlo et al., 2004; Sinha et al., 2010).

While the OH concentration has a clear daily profile with a daytime peak due to its large photolytic source, it is absent or present at much lower concentrations during the night when
other oxidants such as the NO<sub>3</sub> radical or O<sub>3</sub> play an increasingly significant role. Typical O<sub>3</sub> mixing ratios are in the range of tens of ppb, whereas NO<sub>3</sub> is rarely present at mixing ratios more than a few hundred ppt and typically less than 100 ppt. While the reactivity of NO<sub>3</sub> has never been directly measured (e.g. Brown et al., 2011, and references therein), some recent studies have addressed O<sub>3</sub>-reactivity (Park et al., 2013; Matsumoto, 2014). So
far no one has modelled the reactivity of either O<sub>3</sub> nor NO<sub>3</sub>.

After the tropical forest, the boreal forest zone together with the temperate forests represent the largest forested area worldwide (Guenther, 2013) and it produces a large amount of different volatile organic compounds (VOCs). It is estimated that this the boreal forest zone accounts for about 5% of the global emission of biogenic VOCs (BVOCs) (Guenther, 2013). These VOCs can react with the abovementioned oxidants and thereby alter the atmospheric oxidation budget and produce new products with different chemical and physical properties. These compounds often have lower vapour pressures than their parent molecule and have the potential to participate in aerosol formation and growth, and in production of cloud condensation nuclei (CCN) and thereby affect the climate (e.g., Makkonen et al., 2012; Ehn et al., 2014).

An accurate description of vertical fluxes, and therefore validation of the overall meteorological situation, is essential to reach our main goals, which are the following:

25

- to evaluate model uncertainties due to the use of measured input gas concentrations.

- to create a simple empirical parameterisation for conversion of measured spectral irradiance into actinic flux in order to calculate photodissociation rates.
- to model the reactivity of OH and, for the first time that of O<sub>3</sub> and NO<sub>3</sub>, and to investigate their reactivity towards specific groups of compounds, thereby mapping the diel bahaviour of their relative importance.

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Our method in order to achieve these goals is a 1D chemical-transport model, so that we are also able to investigate the vertical importance of the compounds of interest. Our location of choice is the SMEAR II station, which is very well characterised and also located in the boreal forest zone.

#### 5 2 The site

All compounds presented here were measured during the HUMPPA-COPEC-10 campaign (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry 2010). This extensive campaign was carried out at the SMEAR II station (Station for Measuring Ecosystem–Atmosphere Relations), Hyytiälä,

- Southern Finland (e.g., Hari and Kulmala, 2005; Vesala et al., 1998; Kulmala et al., 2001a). The campaign took place between 12 July–12 August 2010, and the aim of the campaign, including instrumental set-up, is provided by Williams et al. (2011). Continuous measurements (with less instrumentation than during the campaign) are carried out at the SMEAR II site.
- <sup>15</sup> The SMEAR II station is located in the southern boreal forest zone. The vegetation mostly consists of conifer trees, in particular Scots pine (Haapanala et al., 2007). Williams et al. (2011) describe the meteorological situation, including anthropogenic influences, during the campaign in details, thus we only provide a short summary here: The campaign took place during an anomalously warm summer, with an average temperature
- <sup>20</sup> of 20 °C. During the campaign, air advected to the site mostly from the SW (53.7%), but also from the SE (20.7%) and from the NW (10.3%). The site was impacted by periods of advected biomass burning emissions, emissions from urban centers in the SW and occasionally by a nearby sawmill. The periods with anthropogenic influences were not considered in this study.

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#### 3 Measured gases used as input to the model

The ambient concentrations of NO, NO<sub>2</sub> (=  $[NO_X] - [NO]$ ), SO<sub>2</sub>, O<sub>3</sub> and CO are continuously measured at the SMEAR II station and their averaged daily profiles are illustrated in Fig. 15. Since their sources are mostly of anthropogenic origin, we use the concentration of these compounds as input to our model. Some model uncertainty stems from the 5 uncertainty in the concentration of these input gases. For this reason, in Sect. 7.2, we intercompare critical trace gases from the SMEAR II site with additional campaign measurements. Since the concentration of SO<sub>2</sub> was only measured by one instrument, we will obviously exclude this data from the intercomparison, which is why we also do not give a description of the instrumentation here. Below we go through the measurement details of 10 , and the mentioned trace gases. All of the belowmentioned campaign based input gases were measured by researchers from the Max Planck Institute (MPI) at 24 m, while the with an original recording interval of 1 s. The SMEAR II gases are continuously measured at several heights; 67.2, 50.4, 33.6, 16.8, 8.4, and 4.2 m above the SMEAR II mast base. The original time resolution recording interval was 1 min at 6 min time interval for each measure-15 ment height. For the later intercomparison, we chose to only focus on the averaged data from 33.6 and 16.8 m. In case of CO the measurements were performed only at 16.8 m. The campaign based measurements were carried out on a tower approximately 30 m from the SMEAR II mast. For details on the non-SMEAR II trace gas measurements, we refer to

<sup>20</sup> Williams et al. (2011).

#### 3.1 NO and NO<sub>X</sub> measurements

The continuous SMEAR II NO and NO<sub>X</sub> concentrations were measured with one chemiluminescence analyser (TEI 42C TL, Thermo Fisher Scientific, Waltham, MA, USA). NO<sub>2</sub> was measured indirectly by using a NO<sub>2</sub> specific photolytic converter (Blue Light Converter,

<sup>25</sup> Droplet Measurement Technologies, Boulder, CO, USA). The NO<sub>2</sub> concentration was calculated as the difference between the measured NO<sub>X</sub> and NO concentrations. The detection limit was 0.1 ppb for NO and 0.15 ppb for NO<sub>2</sub>. The precision (signal noise) was total accuracy for NO was  $\pm$  0.05 ppb for and 0.08 and  $\pm$  0.09 ppb for NO<sub>2</sub>. Lastly, the relative accuracy was  $\pm 10$ . The effect of oxidation of NO to NO<sub>2</sub> by the reaction between NO and O<sub>3</sub> inside the sample lines was estimated to be smaller than the measurement accuracy. The concentrations of both NO and NO<sub>2</sub> were additionally measured specifically for this campaign by MPI using a modified commercial Chemiluminescence Detector (CLD 790 SR)

- <sup>5</sup> paign by MPI using a modified commercial Chemiluminescence Detector (CLD 790 SR) originally manufactured by ECO Physics (Duernten, Switzerland) (Hosaynali Beygi et al., 2011). NO<sub>2</sub> was measured indirectly by conversion to NO using a blue light converter. The detection limits for the NO and NO<sub>2</sub> measurements were 10 and 80 ppt, respectively for an integration period of 2 s. The original time resolution of the sampled data is 1, and the total
- <sup>10</sup> uncertainty of that total accuracy of the original NO data is (at 2 sigma) 10.3 ppt + 5of the readingwas  $\pm$  0.01 ppb, while the total uncertainty accuracy of that NO<sub>2</sub> data is (at 2 sigma) 14.2 ppt + 6of the readingwas  $\pm$  0.03 ppb.

The high detection limit of the SMEAR II chemiluminescence analyser is a problem, since the concentrations of NO and NO<sub>2</sub> are generally low at our site (~ 0.02 and ~ 0.3 ppb, respectively for this camapigncampaign). For previous studies (e.g., Mogensen et al., 2011), we have defined the concentration of both NO and NO<sub>2</sub> to be 5 ppt when the measured concentrations were below the detection limit. Since one of the main aims of this paper is to investigate the reactivity of NO<sub>3</sub>, and since the concentrations of NO and NO<sub>2</sub> are crucial in order to obtain this, we chose to use the MPI measured NO<sub>X</sub> concentrations for our simulations due to the high sensitivity of the MPI instrument, unless otherwise specified. For SO<sub>2</sub>, O<sub>3</sub> and CO we used the SMEAR II data.

3.2 O<sub>3</sub> measurements

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The  $O_3$  concentration is continuously measured at SMEAR II using one ultraviolet light absorption analyser (TEI 49C, Thermo Fisher Scientific, Waltham, MA, USA). The detection limit is 1 ppb, while the relative accuracy is  $\pm 3$ total accuracy is  $\pm 1$  ppb. The  $O_3$  concentration was further measured for this campaign by MPI using a UV instrument, sharing the inlet line with the MPI chemiluminescence detection system (CLD) for measuring NO and NO<sub>2</sub>. The uncertainty on this measurement is detection limit was  $\sim 1$  ppb, while the total accuracy was  $\pm$  4 ppbor 1depending on which is greater. Both instruments were calibrated against ozone standards during (MPI instrument) or after (SMEAR II instrument) the campaign.

#### 3.3 CO measurements

The CO concentration was measured on the SMEAR II mast with one infrared light absorption analyser (API 300EU, Teledyne Monitor Labs, Englewood, CO, USA). The detection limit was 50 ppb, while the relative accuracy was ±3total accuracy was ±25 ppb. Additionally, the CO concentration was also measured during the campaign by MPI using a commercial vacuum UV resonance fluorescence CO instrument (AeroLaser GmbH, Garmisch-Partenkirchen, Germany). The accuracy is reported to be detection limit was ~ 1 ppb, while
 the total accuracy was ± 10 ppb.

#### 4 Measurements during the HUMPPA-COPEC-10 campaign

#### 3.1 SO<sub>2</sub> measurements

Here we are briefly going through the measurements that we have made use of in our study. For details, we refer to already published articles. For all measurements we use 30The SO<sub>2</sub> concentration was measured on the SMEAR II mast with one fluorescence analyser (TEI 43 CTL, Thermo Fisher Scientific, Waltham, MA, USA). The detection limit was 0.1 ppb and the total accuracy was  $\pm$  0.05 averaged datappb. The measurement principle is described in Rosman et al. (2001) though the same analyser is no longer in use at the site.

#### 4 Measurements during the HUMPPA-COPEC-10 campaign

#### 20 4.1 Meteorological sondes

Ouwersloot et al. (2012) studied the convective boundary layer during the HUMPPA-COPEC-10 campaign and describe in detail the radiosondes measurements. In short: dur-

ing the entire campaign, 175 GRAW DFM-06 radiosondes were launched at a distance of  $\sim$  300 m from the SMEAR II station. Five radiosondes were launched every day except for four days when the measurements were made every second hour. The radiosondes operated on-line and contained temperature and humidity sensors together with a GPS. The GPS was accurate within 10 m, the temperature sensor within 0.2 °C, while the humidity sensor measured with an accuracy of 2%.

#### 4.2 Photolysis rates

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Filter radiometers (from Forschungszentrum Jülich and the Max Planck Institute for Chemistry) were used to measure the atmospheric photolysis frequencies  $J(NO_2)$  (NO<sub>2</sub>+ $h\nu(\lambda \leq$ 420 nm)  $\rightarrow$  O(<sup>3</sup>P) + NO) and  $J(O^1D)(O_3 + h\nu(\lambda \leq 340 \text{ nm}) \rightarrow O(^1D) + O_2)$  (Bohn et al., 10 2008). It is very difficult to estimate the measurement uncertainty on photolysis rates measured by filter radiometers, however, Bohn et al. (2008) report that when intercomparing  $J(NO_2)$ , the results differ by 5–8% and the instrument correlation for  $J(O^1D)$  is poorer with larger scatter at large solar zenith angles. Since the filter radiometers were compared with a reference spectroradiometer instrument before and after the campaign, and since 15 recent technical developments have improved the measurement of  $J(O^{1}D)$ , we expect that the uncertainty on our measured photolysis rates are less than what is reported by Bohn et al. (2008) (after personal communication with Birger Bohn). Both rates were measured at ground level in a clearing partly blocked by trees, and above the canopy at 24 m, with a full view of the upper hemisphere. 20

#### 4.3 Measurements of OH-reactivity

The total OH-reactivity was measured using the Comparative Reactivity Method (CRM, from the Max Planck Institute for Chemistry) (Sinha et al., 2008) at 18 and 24 m. We refer to Nölscher et al. (2012a) and Nölscher et al. (2012b) for details on the setup. The instrument operated with a detection limit of  $3-4 \, \text{s}^{-1}$  with respect to the baseline noise (2 sigma). The overall measurement uncertainty is estimated to be 16 % based on errors in the detection.

tor (5%), rate coefficient (14%), gas standard (5%) and dilution (2%). The uncertainty is calculated based on propagation of uncertainty.

#### 4.4 Measurement of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>

NO<sub>3</sub> (and N<sub>2</sub>O<sub>5</sub>) mixing ratios were measured using a two-channel, cavity-ring-down system, which has recently been described in detail (Crowley et al., 2010b; Schuster et al., 2009). The reported random noise limited detection limits for NO<sub>3</sub> is 1–2 ppt in 3 s integration. By averaging data over several minutes, this is reduced significantly (to < 1 ppt) at which point fluctuations in the zero measurement (obtained by adding NO) prevent further reduction of the detection limit. The total uncertainty is reported as 15% (at least 2 ppt) and 15% (at least 3 ppt) for NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> respectively (Crowley et al., 2010b). The instrument for measuring NO<sub>3</sub> was located on the top of the 24 m tower, approximately 1 m from (and at the same height as) the inlets of the MPI-CLD instrument measuring NO and NO<sub>2</sub>.

#### 5 The SOSAA model

- We used the 1D chemistry-transport model SOSAA (model to Simulate Organic vapours,
  Sulphuric Acid and Aerosols) for model simulations. The structure and content of SOSAA have been described in detail in several other papers (e.g. Boy et al., 2011; Mogensen et al., 2011; Boy et al., 2013; Smolander et al., 2014; Zhou et al., 2014; Mogensen et al., 2015). We provide a re-cap here together with included updates.
- SOSAA is programmed in Fortran 90 and consists of modules for (1) planetary boundary
   layer meteorology and turbulent mixing, (2) biogenic tree and soil emission of volatile organic compounds, (3) radiative transfer and gas phase chemical reactions, and (4) aerosol dynamics. The aerosol module is an extension to the original model SOSA (model to Simulate Organic vapours and Sulphuric Acid) and it is described in the paper by Zhou et al. (2014). Since we are not simulating the aerosol phase in this paper, we will not go through
- this particular part of SOSAA. The structure of SOSAA is illustrated in Fig. 1. The inter-

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nal time step for the meteorological module is 10 s, while the time step for the additional modules is 60 s. The chemistry and aerosol modules utilizes parallel computing.

#### 5.1 Meteorology and vertical mixing

The meteorological module in SOSAA is based on the 1D version of SCADIS (Scalar Distribution) (Boy et al., 2011, and references therein). It consists of prognostic equations for 5 temperature, horizontal wind speed, humidity, turbulent kinetic energy (TKE) and the specific dissipation rate of TKE ( $\omega$ ). Since the representation of a three dimensional flow in a one dimensional model is limited, nudging (Anthes, 1974) of temperature, horizontal wind speed and humidity was done in order to represent effects from local to synoptic scale flow patterns. Measurement data from the SMEAR II station and a nudging factor of 0.01 were 10 used. In order to solve turbulent fluxes, a TKE- $\omega$  type closure scheme, also called twoequation closure, was applied (Sogachev, 2009). In this study we used a domain reaching from the surface to 3000 m, with 51 logarithmically distributed vertical layers. The grid density was highest close to the surface and sparser higher up with 19 of the layers being inside

the canopy in the lowest 18 m. 15

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Interactions between the atmosphere and vegetative canopy are described in detail; including plant drag, exchange of heat and moisture, and radiative processes (reflection, penetration, absorption and emission for three wavelength bands) at each modelled canopy layer. For calculating sensible and latent heat fluxes and for solving the energy balance closure, prognostic equations for soil moisture and temperature are included in the model.

Several updates were made in order to improve the model performance. The changes made in the turbulent closure scheme and parameterisations for latent and sensible heat fluxes are described by Sogachev et al. (2012). According to Boy et al. (2011), simulation of thermal radiation from the atmosphere was not succesful due to missing cloud cover records. To overcome this issue, radiation data from ERA-Interim reanalysis (Dee et al., 25 2011) provided by the European Centre for Medium-Range Weather Forecasts (ECMWF) were used as model input. To further improve the accuracy of the surface energy balance, the heat flux and storage into the soil was taken from observations made at SMEAR II,

when available. In case of measurement gaps longer than 4 h, the original parameterisation (Sogachev et al., 2002) was used to estimate the flux, with the addition of using measured soil temperature as input for the deepest soil level (40 cm below the surface). Furthermore, measured soil water content in the humus layer was used as the water content of soil layer 1 (Sogachev et al., 2002) and hence the original prognostic equations for soil moisture were

1 (Sogachev et al., 2002) and hence the original prognostic equations for soil moisture were neglected.

Upper border boundary condition values for wind speed, temperature and its gradient, and humidity are from Era-Interim reanalysis by ECMWF. These data were used instead of the soundings for two reasons. Firstly, the data is available at any location and at a fixed resolution for any day of the year. Secondly, soundings are by nature snapshots of the vertical column, while the Era-Interim data aims to provide an average value of the grid cell presented. The Era-Interim reanalysis data is available with 6 and 3 h (temperature, humidity, horizontal wind speed, and thermal radiation, respectively) temporal resolution. Direct and diffuse global radiation measured at SMEAR II were used as input for the meteorological scheme to improve the accuracy of the energy balance closure. All input data used in the model are linearly interpolated between data points to every model time step.

#### 5.2 VOC emission from trees

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SOSAA includes several modules for calculation of the tree emission of VOCs. For the simulations presented in this paper, we have used a modification of MEGAN (Model of Emissions of Gases and Aerosols from Nature) version 2.04 (Guenther et al., 2006). The tree emissions of VOCs are calculated using the canopy structure, VOC specific standard emission potentials (SEP) and the emission activity of the trees. The dominant tree species is Scots pine, the canopy height is ~ 18.5 m, while the canopy depth is ~ 9 m with a total leaf area index (LAI) of 5.8 (Ilvesniemi et al., 2009; Palmroth and Hari, 2001) and a biomass of 0.0538 g cm<sup>-2</sup>. We included measured The leaf area density distribution is based on observations at the site. The above-ground understory vegetation consists of ~ 60% vascular plants (mostly shrubs) and ~ 40% mosses (Ilvesniemi et al., 2009), but we only considered BVOC emission from the Scots pine. We included SEPs of isoprene,

2-methyl-3-buten-2-ol, monoterpenes and sesquiterpenes measured at the site (Mogensen et al., 2015; Bäck et al., 2012; Hakola et al., 2006; Simpson et al., 1999). The monoterpenes included are  $\alpha$ -pinene,  $\Delta^3$ -carene,  $\beta$ -pinene, limonene, other monoterpenes than those mentioned here, and cineol and cineol and a lumped group of minor monoterpenes and their emission distribution is based on the average chemotype presented in Bäck et al. (2012). Lastly, the emission activity depends on the LAI, and is furthermore controlled by meteorological factors (radiation and temperature). For explicit and recent updates in our

- version of MEGAN, we refer to Mogensen et al. (2015). The calculated concentration of a specific BVOC at each model level depends on the predicted emission of that compound in that specific level, the concentration of reactants in the same level, and the transport to/from
- the level.

#### 5.3 Radiative transfer

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#### 5.3.1 Irradiance and actinic flux

As mentioned in Sec. 4.2, the photolysis rates *J*(NO<sub>2</sub>) and *J*(O<sup>1</sup>D) were measured during this campaign above the canopy and at ground level in a clearing. Further, the spectral irradiance was also measured. In order to calculate all relevant photolysis rates (listed in Sec. 5.3.2) at all simulated levels inside the canopy, we needed to convert the spectral irradiance into actinic flux.

In order to calculate photodissociation of any compound, the following information is crucial: (1) the compound specific wavelength and temperature dependent absorption cross section and quantum yield, and (2) the wavelength and altitude dependent solar actinic flux. Absorption cross sections and quantum yields are measurable laboratory quantities. Measurements of solar actinic fluxes are rare and difficult, instead the spectral irradiance is more commonly obtained, which is also the situation at the SMEAR II station. Here the irradiance is measured by a Bentham DM150 double monochromator (Boy and Kulmala, 2002). The difference in irradiance and actinic flux arises because the irradiance describes the flow of radiant energy through the atmosphere, while the actinic flux concerns probability

of an encounter between a photon and a molecule (Madronich, 1987). Many attempts have been made to develop parameterisations to convert measured irradiance into actinic flux (e.g., Kazadzis et al., 2000; Webb et al., 2002; Kylling et al., 2003; Kazadzis et al., 2004), however, most often the ratio between diffuse and total downwelling irradiance or the ratio of direct to global irradiance is needed. Those ratios are often not measured and it can be 5 difficult to estimate, since it depends on the aerosol load, potential clouds, surface albedo, solar zenith angle and wavelength, which are not all available. We used the radiative transfer tool "uvspec" version 1.7 from the libRadtran package (http://www.libradtran.org/doku.php) to calculate the ratio between diffuse and total downwelling irradiance  $(E_0/E)$  and Eq. (7) in Kylling et al. (2003) in order to convert our measured irradiance into actinic flux. uvspec 10 provides many options to specify the atmosphere, however, we are lacking most of this information, thus we had to estimate the different parameters. Unfortunately this parameterisation (due to lack of input) was not capable of reproducing the measured photolysis rates. Instead a simpler empirical approach was taken. Firstly we modelled the two photolysis rates  $J(NO_2)$  and  $J(O^1D)$  assuming that the measured irradiance equaled the actinic 15 flux. Then the two ratios between the measured and modelled photolysis rates were calculated as a function of solar zenith angle for the entire campaign period and the median was taken for every integer of the solar zenith angle. If the solar zenith angle is zero, then our ratio was also defined as zero. Based on the quantum yield, cross section and irradiance, we estimated that the peak of photolysis of NO<sub>2</sub> was found at 390 nm and at 305 nm in the 20 case of photolysis of O<sub>3</sub> to form O<sup>1</sup>D. Therefore the two calculated ratios were allocated to the wavelengths of 305 and 390 nm. We then linearly interpolated the ratios between 305 and 390 for every solar zenith angle. In the interval 280-305 nm we assume a similar ratio as for 305 nm, and in the interval 390-700 nm we assumed the same ratio as for 390 nm. In the SOSAA model, we then multiplied this wavelength and solar zenith angle dependent 25 ratio with the wavelength and solar zenith angle dependent measured spectral irradiance and obtained new photolysis rates. Though the ratio in theory is expected to be greater than unity (since irradiance refers to radiation weighted with the cosine of the incidence angle, and actinic flux is equally weighted from every direction), we observe that the ratio is only larger than unity at 390 nm, but not at 305 nm. In order to match the measured photolysis rates of NO<sub>2</sub>, we need to multiply the measured spectral irradiance with a value of  $\sim$  1.7–2.8, but in case of obtaining reasonable photolysis rates of O<sup>1</sup>D, we need to multiply the irradiance with a factor of  $\sim$  0.5–0.7 (this shows a strong decrease with increasing solar zenith angle).

For comparison, we also calculated photolysis rates using the Tropospheric Ultraviolet and Visible (TUV) Radiation Model v5.0 (http://cprm.acd.ucar.edu/Models/TUV/). This model calculates the altitude dependent clear sky (there is also an option to add clouds) actinic flux for any given latitude, longitude and time. If the clear sky TUV is used, this would result in maximum photolysis rates. We calculated the radiation with a 4-stream discrete and used the defin2 model input with SMEAR II location, but otherwise only default values were used.

#### 5.3.2 Photolysis reactions

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We have included all available photolysis reactions from MCM (Master Chemical Mechanism) v3.2 (which are originally mostly from Atkinson et al., 2004). More information on MCM is found in Sect. 5.4. Additionally we added the photodissociation of HO<sub>2</sub>NO<sub>2</sub> (via one channel to form HO<sub>2</sub> and NO<sub>2</sub> and via the other channel to form OH and NO<sub>3</sub>) and of N<sub>2</sub>O<sub>5</sub> (via one channel to form NO<sub>2</sub> and NO<sub>3</sub> and via the other channel to form NO<sub>3</sub>, NO and O) (Atkinson et al., 2004). This includes the information on wavelength and temperature dependent cross sections and quantum yields.

#### 5.4 Gas phase chemical reactions

The measured trace gas mixing ratios which were used to constrain the model are described in Sect. 3. Further, we use a constant mixing ratio of  $H_2$  (0.5 ppm) and  $CH_4$  (1.8 ppm). The concentration of all other compounds are calculated based on their emission and their chemical production and/or degradation according to the chemical mechanistic information from the Master Chemical Mechanism, MCM v3.2 (Jenkin et al., 1997; Saunders

et al., 2003; Jenkin et al., 2012) via website: http://mcm.leeds.ac.uk/MCM. The chemical mechanisms from MCM are processed using KPP - Kinetic PreProcessor (Damian et al., 2002) to produce Fortran90 files containing the concentration time derivative functions and their Jacobian for all included compounds, together with the chemical solver LSODE (Radhakrishnan and Hindmarsh, 1993). We have included the necessary inorganic MCM re-5 actions together with the full MCM chemical degradation paths for methane, isoprene, 2methyl-3-buten-2-ol,  $\alpha$ -pinene,  $\beta$ -pinene, limonene and  $\beta$ -caryophyllene. For other emitted organic compounds where no MCM chemistry path is available, we have included their first order oxidation reactions with OH, O<sub>3</sub> and NO<sub>3</sub>. Those compounds include: cineole,  $\Delta^3$ carene, camphene, and "other monoterpenes" than those mentioned here, farnesene, and 10 "other sesquiterpenes" than those mentioned here (Atkinson, 1994). For the reactions of the stabilised Criegee Intermediates (sCI), we diverted from the MCM and instead used newer obtained reaction rates. For the sCI from  $\alpha$ -,  $\beta$ -pinene and limonene, we have used the rates from Mauldin III et al. (2012) similarly to "Scenario C" in Boy et al. (2013). For the sCI from isoprene, we used the rates from Welz et al. (2012) as done in "Scenario D" in 15 Boy et al. (2013). Only biogenic VOC emissions are estimated, thus we do not include the chemistry mechanisms for anthropogenic VOCs. The abundance of anthropogenic VOCs in SMEAR II is generally low and we do currently not have a way to predict their concentration. Sulfuric acid and nitric acid are removed from the gas phase depending on the condensation sink. The condensation sink is based on measurements and calculated according to 20 Kulmala et al. (2001b).

#### 5.5 Instantaneous and steady state oxidant reactivity

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When considering or calculating the reactivity, loss rate, of e.g. OH or NO<sub>3</sub>, we need to differentiate between *instantaneous reactivity* ( $R_{inst}$ ) and the reactivity that defines the *turnover-lifetime* of the radical out of steady-state ( $R_{ss}$ ). The instantaneous OH-reactivity has previously been modelled using SOSAA and we refer to Mogensen et al. (2011) for how this was explicitly done. Since OH is not the only important atmospheric oxidant, we extended our calculations to also cover the reactivities of O<sub>3</sub> and NO<sub>3</sub> (we will denote them

 $O_3$ -reactivity and  $NO_3$ -reactivity, respectively). The reactivity related to a single reaction is calculated by multiplying the reaction rate coefficient (between either of the oxidants and the reactant) by the concentration of the reactant. The total instantaneous reactivity is then the sum of all these terms, which means all sink reactions have been taken into account regardless whether these reactions lead to reformation of the radical or not:

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$$R_{\text{OX,inst}} = \sum_{\text{Reactions}} k_{\text{OX+Y}} \times [Y]$$
(R1)

 $R_{OX inst}$  is the total instantaneous reactivity of the oxidant (where OX is either OH, O<sub>3</sub> or NO<sub>3</sub>), and  $k_{OX+Y}$  is the bimolecular reaction rate coefficient for the chemical reaction between the oxidant and the chemical species Y, where the concentration of Y is given by [Y]. Instead of only considering the total instantaneous reactivities, we also investigated 10 the reactivities with respect to certain groups of compounds (e.g. inorganic compounds, isoprene, monoterpenes and the sesquiterpenes). In our definition of these reactivities, also the reactivities due to reactions between the oxidants and secondary or higher order reaction products arising from a primary reaction, are included. The OH recycling mechanisms available in MCM version 3.2 are taken into account. For NO<sub>3</sub> we also report the 15 instantaneous reactivity, which is why its reaction with NO<sub>2</sub> (forming  $N_2O_5$ ) is included as a loss term even though NO<sub>3</sub> is reformed from thermal decomposition of  $N_2O_5$  (see below). This is then entirely analogous analogous to measured and reported instantaneeous reactivities for . Included in the MCM chemistry is also the homogeneous reaction of with water vapour. We have also considered this reaction, however, it should be mentioned that 20 there exists significant uncertainty regarding its rate constant. Recent measurements of and (Brown et al., 2006; Crowley et al., 2010b) turnover lifetimes in the ambient atmosphere suggest that this reaction is much slower than presented in current literate (e.g. in MCM). The current rate coefficient used in MCM v3.2, and therefore also in our model simulations, is  $2.5 \times 10^{-22}$  (Atkinson et al., 2004), however, the International Union of Pure and Applied 25 Chemistry (IUPAC) suggests to set an upper limit of  $1 \times 10^{-22}$  (see IUPAC Task Group on

In practice we wrote a script in the Python programming language (using the pattern matching operations in the regular expressions module) to find the bimolecular reactions involving instantaneous reactivity of OH, and , and to postprocess them into additional "bookkeeping reactions", to calculate the time evolution of the instantaneous reactivities along with the time evolution of the real chemicals. These reaction were then added to the MCM KPP-format files.

The inverse of the instantaneous reactivity is the instantaneous lifetime ( $\tau_{inst}$ ):

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$$R_{\rm OX,inst} = \frac{1}{\tau_{\rm inst}} \tag{R2}$$

This instantaneous lifetime is distinct from turnover lifetimes ( $\tau_{ss}$ ) derived from steady-state analysis of eg. measured radical concentrations ([radical]) and known production ( $P_{net}$ ) terms:

$$R_{\rm ss} = \frac{P_{\rm net}}{[\rm radical]} = \frac{1}{\tau_{\rm ss}} \tag{R3}$$

As the steady-state lifetime deals with net production and loss terms, it takes into account the reformation of e.g. OH or NO<sub>3</sub> other than in the primary production term(s). We illustrate this below for NO<sub>3</sub>. The formation and loss of NO<sub>3</sub> in the atmosphere can be described by the following set of Reactions (R4)–(R8) with rate coefficients  $k_4$  to  $k_8$ .

$NO_2 + O_3 \rightarrow NO_3 + O_2, k_4$	(R4)
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M, k_5$	(R5)
$N_2O_5 + M \rightarrow NO_2 + NO_3 + M, k_6$	(R6)
$N_2O_5 \rightarrow \text{products}, k_7$	(R7)
$NO_3 \rightarrow products, k_8$	(R8)

Reaction (R7) represents loss of  $N_2O_5$  to aerosol and surfaces and Reaction (R8) represents all gas-phase reactions of  $NO_3$  (mainly with NO and hydrocarbons). We assume that

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ing Reactions (R4) to (R8), the concentration of N<sub>2</sub>O<sub>5</sub> in steady state ([N<sub>2</sub>O<sub>5</sub>]<sub>ss</sub>) is given by: (R9)

Whilst that of NO<sub>3</sub>, ([NO<sub>3</sub>]<sub>ss</sub>) is given by:

 $[N_2O_5]_{ss} = \frac{k_5[NO_2][NO_3]}{k_6 + k_7}$ 

$$[NO_3]_{ss} = \frac{k_4 [NO_2][O_3]}{k_5 [NO_2] - \frac{k_5 k_6 [NO_2]}{k_7 + k_6} + k_8}$$
(R10)

the gas-phase loss of  $N_2O_5$  via reaction with water vapour is not significant as explained

above (IUPAC, 2014) (IUPAC, 2014; Brown et al., 2006; Crowley et al., 2010b) . Consider-

To simplify, we consider two extreme cases. Case 1: the fate of  $N_2O_5$  is dominated by thermal dissociation to NO<sub>2</sub> and NO<sub>3</sub> ( $k_6 \gg k_7$ ). Case 2: the fate of N<sub>2</sub>O<sub>5</sub> dominated by heterogeneous loss to particles/surfaces ( $k_7 \gg k_6$ ). In case 1, the reaction of NO<sub>2</sub> with  $NO_3$  does not represent a sink of  $NO_3$  as the  $N_2O_5$  product regenerates  $NO_3$ . The steady state concentration of NO<sub>3</sub> is then:

$$[NO_3]_{ss} = \frac{k_4 [NO_2][O_3]}{k_8}$$
(R11)

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As discussed above, the numerator is the NO<sub>3</sub> production term so that the steady state reactivity (denominator) is given simply as  $k_8$ . In case 2 the reaction of NO<sub>3</sub> with NO<sub>2</sub> is a sink of NO<sub>3</sub> as the reformation of NO<sub>3</sub> via the thermal dissociation of N<sub>2</sub>O<sub>5</sub> is insignificant. Here, the steady state concentration of NO<sub>3</sub> is given by:

$$[NO_3]_{ss} = \frac{k_4 [NO_2][O_3]}{k_5 [NO_2] + k_8}$$
(R12)

so that the steady state reactivity is given by  $k_5[NO_2] + k_8$  which is the same as the instantaneous reactivity. We can now evaluate which of these two scenarios more closely 20

represents the situation during the HUMPPA-COPEC-10 campaign. We note that the  $N_2O_5$  thermal dissociation rate constant ( $k_6$ ) is highly temperature dependent and for typical HUMPPA conditions (20–25 °C) it is  $\sim 4 \times 10^{-2} \, \text{s}^{-1}$ . In contrast,  $k_7$  is defined by a combination of available aerosol surface area and reactivity and dry deposition and is given by:  $k_7 \sim 0.25 \gamma \tilde{c} A k_7 \sim 0.25 \gamma \tilde{c} A + k_{dd}$ , where A is the aerosol surface area, 5  $\gamma$  the uptake coefficient and  $\tilde{c}$  the mean molecular velocity (Crowley et al., 2010a), while  $k_{dd}$  is the loss frequency of N<sub>2</sub>O<sub>5</sub> due to dry deposition. Combining a typical value of  $A = 1 \times 10^{-7}$  cm<sup>2</sup> cm<sup>-3</sup> at SMEAR II with  $\gamma = 0.03$ –0.001 (Bertram et al., 2009; Chang et al., 2011) with  $\tilde{c} = 24000 \text{ cm s}^{-1}$ , we derive  $k_5 \sim 7 \times 10^{-5}$  and an upper limit of  $3 \times 10^{-5} s^{-1}$  for the loss frequency of N<sub>2</sub>O<sub>5</sub> due to dry deposition in a neutrally stratified 10 nocturnal boundary layer of 100 m height (Geyer et al., 2001) we derive  $k_7 \sim 1 \times 10^{-4}$ - $2 \times 10^{-5} \text{s}^{-1} 5 \times 10^{-5} \text{s}^{-1}$ . This implies that for the warm temperatures encountered during HUMPPA, case 1 is dominant, and the instantaneous reactivity, which includes a contribution from reaction with NO<sub>2</sub> will be larger than the steady state reactivity. Similar arguments apply when considering the reactivity of OH. In this case, due to the many reactions of 15 OH which lead to its reformation on relatively short timescales time scales, the difference between instantaneous and steady state lifetimes will be greater. Examples are the reaction of OH with CO and hydrocarbons in the presence of NO which reform OH (via HO<sub>2</sub>) on timescales time scales of a few minutes. In the rest of the paper, we will refer to the instantaneous reactivity as just "reactivity" but specify when using steady state reactivity. 20

#### 5.5.1 Computing oxidant reactivity

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In order to model the reactivity of the three oxidants, we wrote a script in the Python programming language (using the pattern matching operations in the regular expressions module) in order to find the bimolecular reactions involving OH, NO<sub>3</sub> and O<sub>3</sub> from the MCM files. The reactions were postprocess into additional "bookkeeping reactions", whereby we could calculate the time evolution of the instantaneous reactivities along with the time evolution of the real chemical concentrations.
# 6 Model validation

For the traces gases used to constrain the model, the photolysis rates and the OH-reactivity, the following uncertainty and error analysis is provided: SDs, the Pearson's productmoment correlation coefficient which describes colinearity between the measured and modelled parameters and the coefficient of determination which describes the proportion of the 5 total variance explained by the model. We also provide the slope and the intercept of the linear least-square regression, where the slope will be one and the intercept zero, if the model predicts the measured results perfectly. Also the mean square error (MSE) together with the total root mean square error (RMSE) that shows the actual error, since it has the same unit as parameter investigated, and the systematic (linear error) component, which 10 is the square of the sum of the additive and proportional components of the mean square error together with their interdependence. The unsystematic (= nonlinear error) RMSE is also given. For comparison, Bias, which gives the difference between the mean of the measured and the mean of the modelled variable, is also included. Lastly we also included the "index of agreement" (d) which reflects the degree to which the measured parameter 15 is accurately modelled and is error free. If d is one, the model and measured values are identical, however, if d is zero, the model cannot represent the measured value at all. For

### 7 Results and discussion

In order to provide results for the unperturbed boreal forest, we filtered out the measurement periods during which pollution occurred. The pollution originated from either biomass burning, anthropogenic influence or from the local sawmill. Those periods include (times given in UTC+3): 13 July 18:00–15 July 00:00, 18 July 01:00–06:45, 26 July 00:00–28 July 00:00, 28 July 12:00–30 July 15:00, 3 August 20:10+23:25, 4 August 09:45, 6 August 01:40–04:00, and 7 August 12:00–10 August 00:00. We refer to Williams et al. (2011) for

detailed description on the included validation methods, we refer to Willmott (1981).

the specific times and details on classification of the pollution events.

# 7.1 The meteorological situation

The validation of the meteorological scheme is done firstly for the full vertical domain using data obtained by the radiosonde measurements, and secondly in the surface layer using the continuous measurements conducted at the SMEAR II station. The polluted periods are also included in this analysis, since it will not affect the meteorology.

# 7.1.1 Vertical profiles

5

Examples of vertical profiles of wind speed, potential temperature and absolute humidity on two occasions, 12 p.m. on 12 July and 3 a.m. on the 11 July, are shown in Fig. 2. The model values shown are 30 min averages during which the radiosondes were started. Data
from the SMEAR II tower are included in order to supplement the radiosonde data in the lowest 100 m. This data is also averaged for 30 min, and one should keep in mind that it was obtained with different instruments than those used on the sondes. The upper panel is from 12 p.m.; the mixed layer has been developing throughout the morning and has reached 1100–1300 m which is observed both in the model and by the radiosonde. The model underestimates the depth of the mixed layer, determined here as the depth where the gradient of potential temperature is approximately zero or negative. In the model the height of the atmospheric boundary layer (ABL) is defined as the lowest model level where the Richardson number (Ri) exceeds the limit of 0.25. The figure suggests that this parameterisation is able to set the top of the boundary layer close to the height assessed by the potential tempera-

- ture and wind speed profiles. The underestimation of the height of the mixed layer could be caused by too strong temperature gradients above the boundary layer (clearly visible in the example chosen), that would limit the growth of the mixed layer. However, since the focus in this study is on chemistry close to the surface, we found the agreement between the simulations and observations satisfactory, and the possibilities for improving the accuracy
- <sup>25</sup> of the model close to the top of the boundary layer out of the scope of this work. A single radiosonde flight provides a snapshot from a given moment, whilst the model aims to represent average conditions of 30 min for a horizontally homogeneous area. As a consequence

the simulated horizontal wind speed profile (Fig. 2a) differs significantly from the observed one. In the model the wind speed increases first rapidly in the surface layer and then slower in the boundary layer, having the maximum at the top of the boundary layer, above which it reaches the geostrophic wind speed and stays constant in the free troposphere. The difference in observed and modelled wind speed in the free-troposphere seen in the figure is caused by the difference between the ECMWF reanalysis and the observations and the fact that in the model the wind speed is kept constant above the boundary layer. For accuracy of the reanalysis see Dee et al. (2011).

5

The lower part of Fig. 2 shows a typical nocturnal stable boundary layer at 3 a.m., which is characterised by a stable layer with strong gradients and a residual layer of the previous 10 day's mixed layer where quantities are almost constant with altitude. In these type of cases the top of the boundary layer is ambiguous (Zilitinkevich and Mironov, 1996). The model parameterisation sets the ABL depth at a height that coincides with approximately the layer in the observations which is most stable. Above the stable layer an almost neutrally stratified residual layers is clearly visible in the observations. The residual layers shown in the figure 15 are defined as the layer where water vapour concentration is roughly constant with altitude. The model understimates underestimates the residual layer height, which is a consequence of the tendency to underestimate the height of the mixed layer. The different nature of the radiosonde and ground based observations is evident in the stable layer, and the aim of our model is not to reproduce the profile of the soundings exactly. However, it is obvious that 20 the model understimates underestimates the concentration of water vapour in the air. For the campaign period, the model underestimated the water vapor concentration with vapour concentration by 23.7% on average at 23 m. This underestimation only has a minor effect on the modelled reactivities. A sensitivity test shows that when the water vapour concentration is constrained by the measurements, the reactivity of OH and NO<sub>3</sub> is always smaller than 25

when the modelled water concentration is used. The reactivity of  $O_3$  is also mostly lower, but not always. The maximum changes in the reactivities are 1.4% for OH, 5% (but usually 1-2%) for NO<sub>3</sub>, and 0.4% for O<sub>3</sub>.

# 7.1.2 Surface energy balance

The diurnal averages of the components of the surface energy balance: net radiation, heat flux and storage into the soil, and turbulent fluxes of sensible and latent heat are presented in Fig. 3. The positive values suggest that the atmosphere is gaining heat from the surface

- and vice versa for negative values. The net radiation from the model was calculated as the sum of all radiation components (the direct and diffuse global radiation, atmospheric thermal radiation, PAR and NIR reflected and emitted by the vegetative canopy, and the thermal radiation by the soil surface), and is compared to the net radiation measured for 300–40 000 nm. Using the reanalysis values as input for atmospheric thermal radiation (Sect. 5.1) instead
- <sup>10</sup> of the parameterisation (Sogachev et al., 2002) improved the model performance considerably: RMSE for net radiation improved from 82 to  $69 \,\mathrm{W}\,\mathrm{m}^{-2}$  (for the period studied here). The soil heat flux and storage term in the model would follow exactly what was measured since the values used in the model are based on the observations, hence only observed values are shown.
- <sup>15</sup> The observed turbulent fluxes shown in Fig. 3 are obtained with an eddy-covariance system described by Markkanen et al. (2001). Both the average latent and sensible heat flux differ from the observed most of the day, which is mainly due to the limitations of the utilised turbulence closure scheme that performs best under near-neutral stratification. The underestimation of the latent heat flux in the model can also partly be caused by underestimation of water available to evaporate, which further could lead to increased surface temperature and to overestimated sensible heat flux. The low latent heat flux can also play a role in the underestimation of absolute humidity (Fig. 2). In general, the accuracy of the eddy-covariance method varies between 5–20% and 10–30% for sensible and latent heat flux, respectively (Foken, 2008). Furthermore, the measurements are made in the roughness sublayer, which tends to decrease the observed scalar fluxes (Simpson et al., 1998).
- Hence, the difference between the model and measured values, especially for the sensible heat flux, is too large to be fully explained by inaccuracy of the eddy-covariance method.

Discussion Paper

# 7.1.3 Turbulent mixing

To validate the turbulence scheme, the observed and simulated friction velocity  $(u^*)$  were compared. Friction velocity is defined as the square root of the ratio of momentum flux and air density, and thus describes the amount of turbulent mixing (Stull, 1988, p. 67).

- The diurnal mean  $u^*$  at each model level for the lowest 40 m, together with an aver-5 age horizontal wind profile at 71-2 a.m. and p.m. are shown in Fig. 4. The midday profile represents clearly the turbulent conditions, while in the night time stratification is typically stable or near neutral (Fig., 4b,c). Inside the canopy the horizontal wind speed and friction velocity decrease rapidly. Above the canopy the wind speed continues to increase until
- the top of the mixed layer (Fig. 2), whilst friction velocity has its maximum right above the 10 canopy and slowly decreases towards the top of the boundary layer. The observed values of  $u^*$  (Fig. 4c and d) are obtained from eddy-covariance systems at 3.5 and 23.3 m and calculated from the measured covariances of horizontal and vertical wind fluctuations (u'w'and  $\overline{v'w'}$ ). At both comparison heights the model reproduces the diurnal behaviour, but the
- magnitude is overestimated above the canopy, especially at night time. This is partly due 15 to the strong gradient at the region of the canopy top in the simulations, which causes the comparison to be very sensitive to altitude. Furthermore, the top of the canopy might cause differences just above the canopy (Fig. 4c), since all dynamics caused by scattered tree tops are not necessarily accounted for in a one dimensional model. Horizontal wind speed increases more rapidly with altitude in the model, which could partly also explain the overes-20
- timation of friction velocity by the overestimated wind shear. The turbulence closure scheme is known to perform best under near-neutral stratification. However, the overestimation of friction velocity was found persisting for all stability conditions.

### 7.2 Model validation Comparison of measured input gasestrace gas measurements

In this section we intercompare the measured concentrations of NO, NO<sub>2</sub>,  $O_3$  and CO. 25 For the comparison we have also excluded the pollution periods, since the concentration of these gases are often larger during the pollution events, whereby the uncertainty on the measurements are expected to decrease. For statistical purpose it is therefore better to only consider the same period as our model results.

In general there was satisfactory agreement between the different instruments. The differences between the results (time series in Fig. 5, mean values in Table 1) were within the uncertainty limits in case of the NO and NO. data. In case of the O. concentration results

- <sup>5</sup> uncertainty limits in case of the NO and NO<sub>2</sub> data. In case of the O<sub>3</sub> concentration results there was a systematic difference of 4 ppb. Also the variability in the averaged concentrations were in the same magnitude (Fig 15). In the CO concentration data there was a distinct variability between the SMEAR II and campaign results. The observed difference (22 ppb) was within the uncertainty limits. There were periodical malfunctions of the SMEAR II in <sup>10</sup> strument causing false readings. During post-processing the SMEAR II data was filtered,
- but obviously some inconsistency remained in the data.

#### 7.3 Photolysis

We present the measured *J*(NO<sub>2</sub>) and *J*(O<sup>1</sup>D) in Fig. 6 (time series) and in Fig. 14 (scatter plot) together with the predicted SOSAA values where we used the parameterisation suggested in Sect. 5.3. For comparison, also the TUV predicted rates, which provides the fastest possible photolysis (since clear sky was assumed) are included. The surface reflectivity was assumed to be independent of wavelength and was fixed to 0.1. The performance of our simple parameterisation is good, even though the conversion factor used, is calculated as the median over the entire measurement period. As required, the The modelled rates are always found below the TUV clear sky predicted rates. Different checks for quality of fit are presented in Table 2. Though the index of agreement is 0.98 in case of the modelled *J*(), we observe a clear lag behind the measured rate in both the TUV predicted

and our simulated J(). On average, the modelled noon photolysis peak of NO<sub>2</sub> is slightly underestimated (~ 16%), though when considering the entire day, the difference is larger. Photolysis rates were also obtained near ground, however, not inside the canopy, but instead in a clearing only partly covered by overhanging branches. It is therefore difficult to compare those rates with our predicted below-canopy rates, where we use a canopy penetration factor, that decreases the incoming irradiance when going down through the canopy. At ground the photolysis rates are decreased by  $\sim$  40–80 %. The reduction is by  $\sim$  30–50 % in the measurements.

### 7.4 Oxidant reactivity

The total reactivities of the three most important atmospheric oxidants (OH, O<sub>3</sub> and NO<sub>3</sub>)
have been modelled and will be presented here together with the measured OH-reactivity. No measurements of O<sub>3</sub>- and NO<sub>3</sub>-reactivity were conducted during this campaign. Instead we have measurements of the concentrations and production rate of NO<sub>3</sub> which enable a steady-state turnover lifetime to be calculated and compared to the model result. The daily and seasonal oxidation capacity with respect to monoterpenes at SMEAR II has previously
been estimated based on measurements and is presented in Peräkylä et al. (2014). The HO<sub>X</sub> budget during this campaign has been discussed in detail by Hens et al. (2014). Below we will discuss the daily pattern of the investigated reactivities, together with their vertical profile. In case of the reactivity of OH, we will also discuss the missing OH-reactivity and in case of the NO<sub>3</sub>-reactivity we will present both the modelled instantaneous reactivity and the calculated steady state reactivity.

# 7.4.1 Contribution to the reactivities

We have investigated the compound specific chemical contributions to the three different oxidant reactivities. The contributions at noon and during night (at 18 m) together with the total reactivities are presented in Table 3. The reactivities toward methane, isoprene and all individual monoterpenes and sesquiterpenes are included separately. Furthermore, according to the MCM chemistry, OH is reacting with 1071 other organic species, while an additional BVOC sink consisting of 437 organic species is included for NO<sub>3</sub>, but only 28 other BVOC species react with O<sub>3</sub>. The normalised contribution of the individual inorganic compounds to the total inorganic reactivity of the three oxidants that we consider is presented in Fig. 8 as a daily average for the campaign period (at 18 m), while the absolute contributions are visualised in Fig. 13. The inorganic sink of OH is due to reactions with H<sub>2</sub>,

 $H_2O_2$ ,  $O_3$ , NO, NO<sub>2</sub>, SO<sub>2</sub>, and CO, while the inorganic sink of  $O_3$  includes 3 species; OH, NO, and NO<sub>2</sub>, and lastly the inorganic sink of NO<sub>3</sub> includes NO and NO<sub>2</sub>.

### 7.4.2 OH-reactivity

The daily averaged profiles of the modelled and measured OH-reactivity at 18 and 24 m are presented in Fig. 7b and c. The modelled reactivities includes all values modelled when the pollution periods have been filtered out, while the measured reactivities contains less data due to instrumental disruption. It is clear that the modelled reactivity is much lower than the measured (see also below). The difference between in-canopy During noon-early afternoon, the difference in measured above- and in-canopy reactivity increases and the in-canopy reactivity is found to be almost twice that of the above-canopy OH-reactivity is small both in the measurements and in the simulation results reactivity. The medalled

is small both in the measurements and in the simulation results reactivity. The modelled in-canopy reactivity is consistently higher than the above-canopy reactivity. While the modelled OH-reactivity shows little variability throughout the day (minimum / maximum reactivity = 0.85), excluding a small late afternoon dip due to lower ambient monoterpene concentra-

- tions (Mogensen et al., 2011), the measured reactivity shows a slightly stronger daily trend (minimum / maximum reactivity = 0.17) with a noon-early afternoon maximum. However, as indicated in Fig. 7a, very few measured data points were used for the averaging of the reactivity in the time slot where the peak is observed. The OH-reactivity has previously been both measured and modelled at SMEAR II, and also then a small early afternoon maximum
- <sup>20</sup> was seen from the observations, while the modelled reactivity was found to be more or less constant (Mogensen et al., 2011; Sinha et al., 2010). These new simulations, however, show larger daily variability than in the study by Mogensen et al. (2011) which is mostly due to improvements in the meteorological scheme. A combination of the different schemes for meteorology, emission and chemistry was validated by Mogensen et al. (2011). This study
- <sup>25</sup> showed good agreement between measured and modelled monoterpene concentrations for several heights.

The apportioned and total instantaneous reactivity of OH are reported in Table 3. For the list of specific inorganic compounds, and total amount of compounds that OH reacts

with, we refer to Sect. 7.4.1. The contribution from inorganic compounds and methane is more or less constant at both shown times and together they make up about half of the total OH-reactivity. The contribution from the individual inorganic compounds to the total inorganic reactivity is shown in Fig. 8a, while their absolute reactivities are presented in Fig. 13a. We observe that the contributions from the specified inorganic compounds do not 5 vary significantly throughout the day. One exception is the contribution from the reaction with NO<sub>2</sub>, which is greatest during night time. By far the largest contribution is made up by the reaction with CO ( $\sim$  80 %). The contributions from H<sub>2</sub>, O<sub>3</sub> and NO<sub>2</sub> are similar ( $\sim$  5 %). The contribution from isoprene is 5 times larger during day than night, since the emission of isoprene is controlled by light. However, the reactivity towards isoprene is at all times 10 insignificant due to the very low ambient concentration at the SMEAR II station (campaign average was  $1.8 \times 10^8$  molecules cm<sup>-3</sup>). The reactivity attributable to sesquiterpenes is even lower which is also due to low emissions, but also due to competing reactivity towards other compounds (e.g. O<sub>3</sub>). Since SMEAR II is a monoterpene dominated environment. the reactivity of OH due to reactions with these terpenes is significant and they make up 15 the largest fraction of the OH-reactivity due to primary emitted compounds terpenoids (on average 89% at 18 m). Since monoterpene emissions are driven by temperature and the night time temperature were high during the campaign, while the turbulent mixing was slow, the OH-reactivity due to monoterpenes is clearly largest during night time. Rinne et al. (2012) studied the effect of oxidation chemistry on above-canopy biogenic fluxes during 20 the HUMPPA campaign and found that the chemical degradation had a major effect on the fluxes of sesquiterpenes, while the monoterpene fluxes were only affected during night time. We found that the largest contribution was due to oxidation products (called "other VOCs" in Table 3) with a bit, which were responsible for slightly more than 2/5 of the total reactivity. By far most of these compounds are not usually measured and they are generally 25 not included in the calculated OH-reactivity (e.g., Nölscher et al., 2012a).

The vertical profile of the OH-reactivity covering from the ground to approximately 10 m above the canopy is presented in Fig. 9a as a daily average for the campaign period. The vertical profile of the OH-reactivity is somewhat different than the findings for summer

2008 (Mogensen et al., 2011), which is partly due to an improvement of the meteorological scheme with more vertical mixing, but also due to updates in the emission and chemistry schemes. As in Mogensen et al. (2011) we find that the highest OH-reactivity is during night, which is due to the shallow boundary layer. When the sun rises, the residual layer breaks up and the OH reactive compounds are diluted in a larger volume. Also, a continuously

- <sup>5</sup> up, and the OH reactive compounds are diluted in a larger volume. Also, a continuously high reactivity is found in the entire canopy. After the break-up of the ABL, the OH-reactivity is still high(er) in the crown of the canopy, near the emitting source. The difference between night time and daytime OH-reactivity is approximately  $0.5 \, \text{s}^{-1}$  which is 15% of the night time OH-reactivity.
- A detailed analysis of the measured, calculated (by using measured gas concentrations 10 of OH reactive compounds) together with the missing (the difference between measured and calculated or modelled OH-reactivity) OH-reactivity for the HUMPPA-COPEC-10 campaign is provided by Nölscher et al. (2012a). These researchers divide the measured period into "stressed", "transported pollution" and "normal boreal conditions" (which is not the same as our period, but instead covers 30 July-10 August) and report a missing 15 OH-reactivity of 58% for the last mentioned category, whereas for "stressed" boreal conditions a missing OH-reactivity of 89% was determined. Nölscher et al. (2012a) also aive suggestions for potential missing sources. We calculate the missing OH-reactivity at 18 m as  $10.0 \,\mathrm{s}^{-1} = 64.7 \,\%$  (mean) and  $4.7 \,\mathrm{s}^{-1} = 70.0 \,\%$  (median), and at 24 m as  $8.0 \,\mathrm{s}^{-1} = 68.7 \,\%$  (mean) and  $4.4 \,\mathrm{s}^{-1} = 67.7 \,\%$  (median). As the simulated OH-reactivity 20 shows less variance throughout the day, the variability in the missing OH-reactivity with time (not shown) is mostly due to the measured OH-reactivity. As already pointed out by Mogensen et al. (2011), even though the meteorological description is satisfactory, the modelled forest is too homogeneous to capture the variability in the measured OHreactivity. While the modelled OH-reactivity is only slightly higher than the predicted for 25 the BFORM campaign (Mogensen et al., 2011), the missing OH-reactivity is found to be larger during the HUMPPA-COPEC-10 campaign, which is most probably due to higher temperatures and therefore a higher concentration of unknown BVOCs. Nölscher et al. (2012a) also calculated the OH-reactivity due to some measured anthropogenic gases

(xylene, ethylbenzene, acetonitrile, toluene, butane, pentane, PAA and PAN) that are Discussion Paper not included in our model simulations, due to lack of emission estimates. The missing reactivity of 4.7 s<sup>-1</sup> (median missing fraction for 18 m) corresponds to a concentration in the order of approximately  $9 \times 10^{10}$  molecules cm<sup>-3</sup> for a missing compound that has a similar reaction rate with OH as  $\alpha$ -pinene. Nölscher et al. (2012a) found that these anthropogenic 5 compounds are not significant contributors to the OH-reactivity during non-polluted times as we have considered here. The exclusion of these anthropogenic gases can therefore not explain our missing OH-reactivity. Further uncertainty estimations are provided in Discussion Paper Table 2 and correlation plots are shown for both heights in Fig. 12. All parameter values in the table are calculated based on only those time periods where measurement data 10 was available (after excluding the pollution periods). We observe that the bias is largest at 18 m, inside the canopy, and therefore closer to the emission source. Furthermore, almost the entire RMSE is unsystematic, indicating that it is not a single parameter that drives the missing sink term. One should be aware that evaluating modelled OH-reactivity with observed is not a good measure for quantifying the quality of a model, since it 15 is well known that the missing OH-reactivity is large, and often larger than the known Discussion Paper fraction, especially in forested areas (e.g. Stone et al., 2012, and references therein). Many investigators have speculated on the origin of the missing reactivity and it is mostly thought that the difference between measured and modelled or calculated OH-reactivity is due to unknown organic compounds (e.g. Sinha et al., 2010; Nölscher et al., 2012a; 20 Stone et al., 2012). 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 we are quite confident which specific VOCs are emitted, and it seems unlikely that our missing OH-reactivity is due to emitted VOCs (that are measurable with Gas Discussion Paper Chromatograph – Mass Spectrometer (GC-MS) and Proton Transfer Reaction – Mass 25 Spectrometer (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.

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#### 7.4.3 NO<sub>3</sub>-reactivity

The daily averaged profile of the reactivity of NO<sub>3</sub> at 18 m is presented in Fig. 7d (left y axis). The NO<sub>3</sub>-reactivity is approximately one order of magnitude less than the modelled OH-reactivity. The NO<sub>3</sub>-reactivity steadily increases from around 7 p.m. (reactivity of  $\sim 0.05 \, \text{s}^{-1}$ ) until midnight where it stays approximately constant ( $\sim 0.07 \, \text{s}^{-1}$ ) until 5 a.m. where it increases again and peaks around 7 a.m. ( $\sim 0.1 \, \text{s}^{-1}$ ). Within the following two hours the NO<sub>3</sub>-reactivity decreases rapidly (with  $\sim 0.03 \, \text{s}^{-1}$ ) followed by a more steady decrease until 7 p.m. The averaged maximum variation throughout the day in the NO<sub>3</sub>-reactivity is approximately 50 %, with higher reactivities during night (see below when the contribution to the individual reactivities is discussed).

The contributions to the reactivity together with the total reactivity of NO<sub>3</sub> are presented in Table 3. For the list of specific inorganic compounds, and total amount of compounds that NO<sub>3</sub> reacts with, we refer to Sect. 7.4.1. The inorganic contribution to the NO<sub>3</sub>-reactivity is largest during day time (44 % vs. 20 % during night time). The contribution from the individual inorganic compounds to the total inorganic NO<sub>3</sub>-reactivity is shown in Fig. 8c, while

- vidual inorganic compounds to the total inorganic NO<sub>3</sub>-reactivity is shown in Fig. 8c, while their absolute reactivities are shown in Fig. 13c. During night time the inorganic instantaneous reactivity is due to reaction with NO<sub>2</sub>, while the daytime inorganic reactivity is due to reactions with NO. The other main contributors to the total NO<sub>3</sub>-reactivity are the emitted monoterpenes. During daytime, their contribution is about 50%, though during night
- <sup>20</sup> the contribution from the monoterpenes is 77%. The difference in day time vs. night time monoterpene concentration is partly due to difference in emission (due to difference in temperature and exposed light) and partly due to turbulent mixing. The dominant monoterpenes are at all times  $\alpha$ -pinene and  $\Delta^3$ -carene. The inorganic contribution together with the contribution from directly emitted monoterpenes account for 96% of the total instan-
- taneous reactivity. Oxidised Known oxidised BVOCs are therefore insignificant in the our simulations of the NO<sub>3</sub>-reactivity, suggesting that we would not expect a similarly large missing. Organic atmospheric chemistry involving reactions with the NO<sub>3</sub> radical has been much less studied than the chemistry of OH, but recent studies suggests its importance

(e.g. Browne and Cohen, 2012; Browne et al., 2014). Due to this unexplored chemistry, it is therefore expected that the  $NO_3$ -reactivity as the missing OH-reactivity due to reactions with oxidised VOCs is significantly larger than simulated here.

The vertical profile of the NO<sub>3</sub>-reactivity covering from the ground to approximately 10 m
 <sup>5</sup> above the canopy is presented in Fig. 9c as a daily average for the campaign period. The pattern of the vertical NO<sub>3</sub>-reactivity is somewhat similar to the vertical OH-reactivity, since the main sink of NO<sub>3</sub> is the monoterpenes that are also emitted during the warm nights. As also seen in the vertical profile for the OH-reactivity, the NO<sub>3</sub>-reactivity peaks in the canopy crown, close to the emission source. Since the only significant organic source is the primary
 <sup>10</sup> emitted monoterpenes, the difference between daytime and night time reactivity is larger for NO<sub>3</sub> than OH.

The concentration of NO<sub>3</sub> was measured (Fig. 10c) on 18 nights during the HUMPPA-COPEC-10 campaign. The low NO<sub>X</sub> levels and large biogenic emissions (mainly monoterpenes) resulted in NO<sub>3</sub> mixing ratios which were below the instrumental detection limit (< 1 ppt in 10 min averaging). On average, the model predicted NO<sub>3</sub> night time concen-

- <sup>15</sup> (< 1 ppt in 10 min averaging). On average, the model predicted NO<sub>3</sub> night time concentrations of 0.8 ppt. In order to calculate the steady state reactivity ( $R_{ss}$ ) of NO<sub>3</sub> during the HUMPPA campaign, we have taken an upper limit of 0.5 ppt NO<sub>3</sub> for the whole campaign and divided it by the production term ( $P_{NO_3} = k_6[NO_2][O_3]$ , Fig. 10b), resulting in a lower limit to the  $R_{ss}$ . The results are shown in Fig. 10a. In order to make this result comparable
- <sup>20</sup> to the instantaneous reactivity, which the model generates, we have also added a term that accounts for the reactions of NO<sub>3</sub> with NO<sub>2</sub> (red line in Fig. 10a). The red line is thus  $R_{ss} + k_{NO_2+NO_3}$  [NO<sub>2</sub>]. We call this the corrected steady state reactivity,  $R_{ss}$  (cor). The variability in the calculated steady state reactivity of NO<sub>3</sub> is due to the production term (Fig. 10b). In Fig. 10a we show both the instantaneous reactivity of NO<sub>3</sub> modelled
- <sup>25</sup> using the SMEAR II obtained NO<sub>X</sub> concentrations (inst) and the NO<sub>X</sub> concentrations measured by MPI (inst MPI, which is our default). The figure reveals that the instantaneous (modelled) reactivity of In general, the model over-predicted the measured (and corrected) NO<sub>3</sub>is always larger -reactivity (on average by a factor 4–5) than the corrected steady state reactivity but on some occasions reasonable agreement was obtained (e.g. on day 08/03).

On average, the instantaneous NO<sub>3</sub>-reactivity was  $0.069 \text{ s}^{-1}$  (lifetime of 14 s) when using SMEAR II NO<sub>X</sub> concentrations and 0.058 s<sup>-1</sup> (lifetime of 17 s) when using MPI NO<sub>X</sub> concentrations, while the steady state reactivity was  $0.0089 \, \mathrm{s}^{-1}$  (lifetime of 113 s), and the corrected steady state reactivity was found to be  $0.015 \,\mathrm{s}^{-1}$  (lifetime of 68 s). There are several possible explanations for the difference between the modelled reactivity ( $R_{inst}$ ) and that based 5 on measurements of NO<sub>3</sub> concentrations ( $R_{ss}$  (cor)). Though the averaged modelled night time  $NO_3$  concentration was 0.8 ppt, the concentration was simulated to be significantly lower than the 0.5 ppt taken as the upper limit for the calculations of  $R_{ss}$  (cor) on several nights. Alternatively, the steady-state analysis is only valid when production and loss terms are balanced. For NO<sub>3</sub>, achieving steady-state can take several hours after sunset, depend-10 ing on the size of its sink reactions. In this campaign, where the NO<sub>3</sub> sinks are clearly quite large, this should, however, not be an issue. A further explanation is that the trace gases that act as sinks for NO<sub>3</sub> are overestimated in the model. These sinks are largely terpenes and their concentrations, which are based on an emission model, can contribute to the discrepancy, though in which direction the model bias might go, is unclear. Further, we can consider 15 the effects of recycling of  $NO_3$ , or of unknown  $NO_3$  sources. So far we consider only the reaction of NO<sub>2</sub> with O<sub>3</sub> as source of NO<sub>3</sub> in the calculation of its steady state lifetime. Any other reaction that forms NO<sub>3</sub> would result in an underestimation of the NO<sub>3</sub> reactivity for a given steady-state concentration. Similarly, if there are routes to NO<sub>3</sub> reformation from the organic nitrates formed in the initial reactions with terpenes, this will have the ef-20 fect of enhancing the modelled, instantaneous reactivity compared to that obtained from a steady state analysis. Further measurements of NO<sub>3</sub> steady state concentrations (above the detection limit) and reactivity and comparison with modelled instantaneous reactivity in the boreal forest would be useful in order to resolve this issue. Direct measurement of the NO<sub>3</sub> lifetime in this environment would be most informative and is the subject of ongoing 25 instrument development with a summer campaign at this site planned for the near future.

# 7.4.4 O<sub>3</sub>-reactivity

The daily averaged profile of the reactivity of  $O_3$  at 18 m is presented in Fig. 7d (right *y* axis). The  $O_3$ -reactivity shows an early morning peak (sharp build-up from 5 a.m. until ~ 8 a.m.) and the reactivity is generally higher during daytime. This is due to the fact that the known

<sup>5</sup> O<sub>3</sub> sink mainly consists of inorganic compounds (see below) and their concentration is largest at the beginning of the day. The largest difference in the O<sub>3</sub>-reactivity throughout the day is found between ~ 8 a.m. (~  $2.5 \times 10^{-5} s^{-1}$ ) and 8 p.m.–5 a.m. (~  $2 \times 10^{-6} s^{-1}$ ). The O<sub>3</sub>-reactivity is approximately 5 orders of magnitude less than the modelled OH-reactivity, which of course informs us that O<sub>3</sub> is much less reactive than OH, however, we also need to take the concentration of our respective oxidants into consideration when evaluating their relative importance (Sect. 7.4.5).

The contributions to the O<sub>3</sub>-reactivity together with the total reactivity of O<sub>3</sub> are presented in Table 3. For the list of specific inorganic compounds, and total amount of compounds that O<sub>3</sub> reacts with, we refer to Sect. 7.4. Independent of time, the controlling O<sub>3</sub> sink is by far the inorganic compounds (> 90% of the total sink). The resisting remaining O<sub>3</sub>-reactivity is made up by reactions with monoterpenes (< 2% at noon, ~ 2% during night) and sesquiterpenes (~ 7% at noon and < 2% at night). As in the case of the NO<sub>3</sub>-reactivity, known oxidised BVOCs are also insignificant for our simulations of the O<sub>3</sub>-reactivity. However, the chemistry of O<sub>3</sub> has also received much less attention than the

- 20 chemistry of OH, and we therefore expect that O<sub>3</sub> undergoes many important reactions in the atmosphere (e.g. Ehn et al., 2014), that are still to be discovered. We therefore expect that the O<sub>3</sub>-reactivity due to reactions with oxidised VOCs is significantly larger than simulated here. The contribution from the individual inorganic compounds to the total inorganic O<sub>3</sub>-reactivity is shown in Fig. 8b, and their absolute reactivities are presented in
- Fig. 13b. At all times, the main fraction of the inorganic  $O_3$ -reactivity is due to reaction with NO. During daytime, NO accounts for ~ 98% of the total inorganic  $O_3$ -reactivity. During night time NO<sub>2</sub>, however, also plays a role, since its contribution to the total inorganic re-

activity is  $\sim$  30 %. The inorganic O<sub>3</sub>-reactivity due to reaction with OH is at all times small (> 0.5 %).

The vertical profile of the reactivity of O<sub>3</sub> covering from the ground to approximately 10 m above the canopy is presented in Fig. 9b as a daily average for the campaign period. The vertical profile of the O<sub>3</sub>-reactivity is opposite of that of the two other oxidant reactivities, due to the main sink of O<sub>3</sub>, which consists of inorganic compounds. As shown in Fig. 8b O<sub>3</sub> reacts with NO<sub>X</sub> and these are mostly transported to the site.

Since the OH-reactivity is highly underestimated due to missing sinks, it is also possible that our modelled O<sub>3</sub> and NO<sub>3</sub> reactivities are underestimated due to potentially missing sinks (Wolfe et al., 2011, and references therein).

#### 7.4.5 Relative oxidative strength

 $O_3$ - and  $NO_3$ -reactivities have not received nearly as much attention as the OH-reactivity. To our knowledge, direct total  $NO_3$ -reactivity has never been measured, but the steady state  $NO_3$ -reactivity has been calculated, but mostly in environments very different to SMEAR II

- (Brown et al., 2011, and references therein). Crowley et al. (2010b) measured at a mountain site surrounded by spruce forest and reported steady state NO<sub>3</sub>-reactivities that were about an order of magnitude lower than ours. Ozone has been, and still is, a hot topic, due to its unresolved canopy flux. The non-stomatal ozone flux usually makes up more than half of the total ozone flux, but it seems that gas phase chemical reactions can only account for
- <sup>20</sup> a few percentages of the flux (e.g. Rannik et al., 2012; Wolfe et al., 2011). Until now there exists only one publication about direct measurements of O<sub>3</sub>-reactivity, where the author measured the reactivity in the lab (Matsumoto, 2014). Unfortunately, the detection limit of that instrument is so high that ambient measurements are impossible. Park et al. (2013) has developed a new method called ORMS (Ozone Reactivity Measurement System) and
- tested this in ambient conditions during the SOAS (Southeast Oxidant and Aerosol Study) campaign in summer 2013.

When considering the importance and strength of an oxidant, one should not only focus on its reactivity, but also consider its concentration. We evaluate the oxidation strength

(R13)

(OS, or rate of removal) of the oxidant (OX) by multiplying its concentration ([OX]) with its reactivity ( $R_{OX}$ towards organic compounds ( $R_{OX,org}$ );

 $OS_{OX} = R_{OX,OX,Org} \times [OX]$ 

The time dependent oxidant strength of each of the oxidants considered is illustrated in Fig. 11. It is seen that is the oxidant that is capable of removing compounds from the 5 atmosphere fastest during daytime, while during night time and, and the 24 hours integrated oxidation strength is  $9.90 \times 10^{+10}$  molecule/cm<sup>3</sup> for OH,  $4.35 \times 10^{+10}$  molecule/cm<sup>3</sup> for NO<sub>3</sub> are competing. This is so, even though the reactivity of is order of magnitudes less than that of the other two oxidants. The concentration does not have a distinctive daily pattern at the SMEAR II station, though when averaged, we observe a minima around 10 6a.m. and a maxima around 6p and  $8.55 \times 10^{+10}$  molecule/cm<sup>3</sup> for O<sub>3</sub>. During daytime, OH is capable of removing compounds much more than the two other oxidants. From around midnight till about 4.30 a.m. (not shown here). This is opposite to the daytime -reactivity slope (see Fig. 7d). Therefore, the oxidative strength of NO<sub>3</sub> is the dominant remover of organic compounds, whereas  $O_3$  is rather constant during daytime (7 slightly prevails for 15 less than an hour around 5 a.m. - 5p.m.). The strength of as an oxidant is least during night, since the concentration of and for a few hours in the early evening. O<sub>3</sub> reactive compounds decreases by itself not the fastest oxidant at any time, however, even then the oxidative strength of is much larger than that of (even when the missing OH-reactivity is considered). During daytime, the oxidative strength of at times, O<sub>3</sub> is almost 3 times larger than that of 20 the radical, and during night time about 5 times stronger. Since the concentration peaks during daytime (due to its photolytic source) and since the reactivity of does not show significant variability, its oxidative strength is by far greatest during daytime. Oppositely, the concentration peak of is found during night time due to the absence of the photolytic sink reaction of, and since the reactivity of is also slightly higher during night time, these two 25 effects strengthen each other, which is why the strength of as an oxidant is largest during night and exceeds that of removes reactants more than other oxidants, since it is much more

abundant in concentration at the site. The daily patterns of the radical (the radical is circa

seven times as efficient an oxidant as the radical). The day time oxidant strength of is similar to the night time oxidant strength of . oxidant strength of all oxidants are mainly controlled by the daily pattern of the oxidant concentration. The campaign averaged  $O_3$  concentration is depicted in Fig. 15 and we expect that the major night time removal process of  $O_3$  is by deposition (Rannik et al., 2012).

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When evaluating this relative oxidative strength or rate of removal, we should keep a few things in mind. Firstly, we know that we are underestimating the OH-reactivity with  $\sim 65$  %, while it is uncertain how large a fraction of the NO<sub>3</sub>- and O<sub>3</sub>-reactivity we are underestimating. However, according to our analysis of the compound specific contribution to their reactivity, we found that the contribution due to the included oxidised VOCs were insignificant. Including the missing OH-reactivity would not change the relative oxidative strengthAs mentioned previously, the chemistry involving NO<sub>3</sub> and O<sub>3</sub> has been much

less studied than the OH chemistry, thus the missing reactivities of NO<sub>3</sub> and O<sub>3</sub> have the potential to be large. Secondly, we have to evaluate the concentration of the oxidants. The concentration of O<sub>3</sub> is taken from measurements. As seen from the intercomparison in Sect. 7.2, the difference was  $\sim 10$  %. This propagates linearly into the uncertainty in the oxidative strength. The concentration of NO<sub>3</sub> is mostly determined by NO<sub>2</sub> (source of NO<sub>3</sub>) which is from measurements, O<sub>3</sub> (source of NO<sub>3</sub>) which is also from measurements, and

- finally the monoterpenes (sink of NO<sub>3</sub>) which are predicted. It is difficult to evaluate the correctness of the predicted NO<sub>3</sub> concentration, since the measured concentration was mostly below detection limit. Further, one should remember that while and are reformed, is not. Lastly, we have only considered the *strength* of the respective oxidants, which basically means how fast can the oxidant remove pollutants at what rate the oxidant is capable of removing organic compounds from the atmosphere, but we also have to consider the variety of compounds that the oxidants are reacting with. Though we show that posses
- variety of compounds that the oxidants are reacting with. Though we show that posses the largest oxidative strength, it only reacts with 44 compounds in total (of those 38 are of organic origin and the organic reactivity makes up only ~<10). In comparison In our chemistry scheme, that includes known chemical reactions, OH reacts with 1082 organic compounds, whereas NO<sub>3</sub> reacts with 1095 compounds in total (of those 1082 are 448

and O<sub>3</sub> only with 38 species of organic origin). When considering known chemistry, OH therefore has the capacity to clean the atmosphere of much more compounds though it is only capable of doing it at a slow rate than the other oxidants. Further, we have to consider what kind of organic compounds it is that our oxidants are reacting with. Since O<sub>3</sub> almost exclusively reacts with inorganic compounds, the main role of only participate in 5 the first oxidation step of primary emitted organic compounds (especially sesquiterpenes), though O<sub>3</sub> in the lower troposphere is therefore to keep the inorganic chemistry chain alive also reacts with some second or higher generation products from primary emitted compounds (e.g. by production of and). Otherwise, methacrolein and methyl vinyl ketone). Ehn et al. (2014) recently showed that O<sub>3</sub> almost only participate in the first oxidation step 10 of primary emitted organic compounds (especially sesquiterpenes), however, participates in the production of ELVOCs (extremely low volatility compounds) which, due to their extremely low volatility, condense immediately unto aerosol particles, which are later lost from the atmosphere via deposition.  $O_3$  is by itself not thereby capable of removing car-

- <sup>15</sup> bon from the atmosphere. The induced oxidation of inorganic compounds (and ) impacts mainly on the partitioning between and at night. From an organic point of view, the primary strength\_primary\_role of NO<sub>3</sub> is to oxidise directly emitted monoterpenes (first oxidation step). Though reacts with many organic compounds (> 400), the oxidation is not fast and cannot compete with. The main path for NO<sub>3</sub> to remove carbon from the atmosphere is
- <sup>20</sup> by oxidation of terpenes to soluble nitrates which can be washed out. OH has the capacity to remove carbon, since it has the capability of oxidising compounds until the compounds have such a low vapour pressure that they go into the particle phase and then later can deposit out of the atmosphere. We will therefore as a final remark emphasis that the oxidative strength is not equal to the oxidative importance.

#### 25 8 Conclusions

Using a 1D chemistry-transport model we have performed the following:

- Validation of the full vertical profile with sonde observations showed a tendency to underestimate the depth of the mixed layer, and consequently also the depth of the night time residual layer. The absolute humidity in the model was lower than measured. The largest discrepancies of surface energy balance were with the sensible and latent heat fluxes, reflecting the challenge of modelling turbulent fluxes. Evaluating the momentum flux showed satisfactory agreement, and we can conclude the meteorology module to work well.
- We discussed the model uncertainty due to use of measured inorganic gases by intercomparison of the gas concentrations obtained by different measurement techniques. Mostly the gas concentrations were within measurement uncertainty. The largest problem seems to arise due to the high detection limit and low concentration of NO<sub>X</sub>.
- We aimed and managed to successfully create a simple conversion for measured spectral irradiance to actinic flux only based on measurements of photolysis frequency of NO<sub>2</sub> and O<sub>3</sub> (to form O<sup>1</sup>D). We showed that the modelled rates compared well with the measured (with index of agreement of 0.93 and 0.98).
- For the first time we have modelled the reactivity of O<sub>3</sub> and NO<sub>3</sub> and compared those to the reactivity of OH. We conclude that OH is the main cleaning agent of organic compounds in the atmosphere. We find that OH is approximately one order of magnitude more reactive than NO<sub>3</sub> and five orders of magnitude more reactive then O<sub>3</sub> when considering the total reactivity.

We introduced a term that we call *oxidative strength* that takes both the reactivity and towards organic compounds and the concentration of an oxidant into account. It describes how fast the rate at which a given oxidant is capable of removing organic compounds from the atmosphere. We show that OH is the strongest oxidant at our boreal site during day time, but is equally strong as while NO<sub>3</sub> is strongest during night time. O<sub>3</sub> competes with OH and NO<sub>3</sub> during short periods in the early morning and evening.

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We observed little difference between in-canopy and above-canopy reactivity. The largest difference in reactivity when considering the full day and canopy was  $\sim 15$ % in case of OH,  $\sim 50$ % for NO<sub>3</sub> and about a factor of three in case of O<sub>3</sub>.

In the model, about 50% of the OH-reactivity was due to inorganic compounds and methane, ~ 14% due to reactions with primary emitted monoterpenes, while about 44% was due to oxidised biogenic volatile organic compounds. When comparing the modelled OH-reactivity to the measured, we find a large discrepancy (~ 65%) which is very common in this type of environment. Most probably the actual main sink of OH is therefore not the modelled inorganic compounds, but instead unaccounted hydrocarbons. Almost the entire reactivity of O<sub>3</sub> was due to inorganic compounds. In case of NO<sub>3</sub>, ~ 37% of the reactivity was accounted for by inorganic compounds, while the resisting remaining reactivity was mostly due to first order reactions with monoterpenes. NO<sub>2</sub>, which was included in the inorganic sink term, is, however, an instantaneous sink of NO<sub>3</sub> and it does therefore not control the boreal NO<sub>3</sub> concentrations.

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– Furthermore, we performed the first steady-state lifetime calculations of NO<sub>3</sub> in a boreal forest. We obtained a summertime steady state reactivity of NO<sub>3</sub> in the order of  $\sim 0.009 \, \text{s}^{-1}$  (campaign average), which corresponds to a steady state lifetime of 113 s or 68 s if loss due to reaction with NO<sub>2</sub> is considered. For comparison, the averaged instantaneous NO<sub>3</sub> lifetime was calculated to be 14–17 s.

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**Table 1.** Measurement uncertainty and estimates for quality of fit for the measured input gas concentrations. H = height, MES and MEC are the estimated total accuracies calculated as a combination of precision and relative the accuracy of reading for the SMEAR II (MES) and campaign (MEC) instrumentation. DP = amount of measured data points considered,  $\overline{S}$  and  $\overline{C}$  are the SMEAR II measured (S) and campaign measured (C) means, SD<sub>S</sub> and SD<sub>C</sub> are the corresponding SD, r = Pearson's product–moment correlation coefficient which describes colinearity between measured and modelled parameteres,  $r^2 =$  the coefficient of determination which describes the proportion of the total variance explained by the model, b is the slope and a the intercept of linear least-square regression, MSE = mean square error, RMSE<sub>s</sub> = systematic RMSE, RMSE<sub>u</sub> = unsystematic RMSE, RMSE = total root mean square error, Bias is the difference between  $\overline{C}$  and  $\overline{S}$ , while d = index of agreement.

	[NO]	[NO <sub>2</sub> ]	[O <sub>3</sub> ]	[CO]
<i>H</i> [m]	24	24	24	24
MES [ppb]	$\pm 0.05$	$\pm 0.09$	$\pm 1$	±25
MEC [ppb]	$\pm 0.01$	$\pm 0.03$	$\pm 4$	$\pm 10$
DP	1066	1066	1066	833
$\overline{S}$ [ppb]	2.32E-02	3.64E-01	3.70E+01	1.20E+02
$SD_S$ [ppb]	3.35E-02	3.03E-01	9.89E+00	2.53E+01
$\overline{C}$ [ppb]	2.90E-02	3.38E-01	3.99E+01	9.82E+01
$SD_C$ [ppb]	3.28E-02	2.14E-01	9.69E+00	1.32E+01
r	6.84E-01	9.27E-01	9.94E-01	6.23E-01
$r^2$	4.68E-01	8.60E-01	9.89E-01	3.88E-01
b	6.98E-01	1.31E+00	1.02E+00	1.19E+00
a [ppb]	2.89E-03	-7.94E-02	-3.51E+00	2.89E+00
MSE [ppb <sup>2</sup> ]	3.29E-02	6.72E-01	8.04E+03	3.48E+05
RMSE <sub>s</sub> [ppb]	1.20E-02	6.24E-02	2.96E+00	2.23E+01
RMSE <sub>u</sub> [ppb]	1.81E-01	8.17E-01	8.96E+01	5.89E+02
RMSE [ppb]	1.81E-01	8.20E-01	8.97E+01	5.90E+02
Bias [ppb]	-5.89E-03	2.66E-02	-2.90E+00	2.16E+01
d	8.18E-01	9.30E-01	9.76E-01	6.21E-01

Table 2. Measurement uncertainty and estimates for quality of fit for photolysis rates $(J(NO_2))$ and
$J(O^{1}D)$ ) and the reactivity of OH ( $R_{OH}$ ). ME = reported measurement uncertainty, $\overline{O}$ and $\overline{P}$ are the
measured ( $O$ ) and modelled ( $P$ ) means, SD <sub>O</sub> and SD <sub>P</sub> are the corresponding SDs, Bias is the
difference between the mean measured and mean modelled parameter. For the meaining of the
remaining symbols, we refer to the description in the Table 1. $* =$ only noon value.

	$J(NO_2)$	$J(O^1D)$	$R_{OH}$	$R_{OH}$
<i>H</i> [m]	24	24	18	24
ME [%]	$\sim$ 5–8	> 8	16	16
DP	1019	1019	357	320
$\overline{O}\left[s^{-1} ight]$	6.41E-03*	1.55E-05*	1.26E+01	1.05E+01
$SD_O\left[s^{-1} ight]$	1.80E-03*	4.76E-06*	1.34E+01	9.79E+00
$\overline{P}\left[s^{-1} ight]$	5.37E-03*	1.55E-05*	2.59E+00	2.52e+00
$SD_P  [s^{-1}]$	1.88E-03*	4.99E-06*	4.96E-01	4.47E-01
r	9.00E-01	9.28E-01	3.17E-01	3.49E-01
$r^2$	8.10E-01	8.62E-01	1.01E-01	1.22E-01
b	1.31E+00	1.02E+00	1.17E-02	1.59E-02
$a  [s^{-1}]$	-7.94E-02	-3.51E+00	2.44E+00	2.35E+00
MSE [s <sup>-2</sup> ]	6.72E-01	8.04E+03	3.59E+04	2.05E+04
RMSE <sub>s</sub> [s <sup>-1</sup> ]	6.24E-02	2.96E+00	1.66E+01	1.25E+01
$RMSE_{u}\left[s^{-1}\right]$	8.17E-01	8.96E+01	1.89E+02	1.43E+02
$RMSE\left[s^{-1} ight]$	8.20E-01	8.97E+01	1.90E+02	1.43E+02
Bias [s $^{-1}$ ]	2.66E-02	-2.90E+00	1.00E+01	8.01E+00
d	9.30E-01	9.76E-01	4.33E-01	4.43E-01

**Table 3.** Time dependent contribution to the investigated instantaneous reactivities. The contribution distributions and total reactivities are given as means for 18 m at noon and at night (2 a.m.) for the OH-,  $O_3$ - and  $NO_3$ -reactivity. The contributions are given with respect to inorganic coumpounds (see Sect. 7.4 for which compounds are included), methane (CH<sub>4</sub>), isoprene (C<sub>5</sub>H<sub>8</sub>), total and individual monoterpenes (C<sub>10</sub>H<sub>16</sub>) and sesquiterpenes (C<sub>15</sub>H<sub>24</sub>) (see Sect. 5.4) together with the resisting organic compounds that the three oxidants are reacting with (see Sect. 7.4 for how many compounds this includes).

	OH-reactivity Noon	Night	O <sub>3</sub> -reactivity Noon	Night	NO <sub>3</sub> -reactivity Noon	Night
Total [s <sup>-1</sup> ]	2.79	3.00	1.58E-05	1.67E-05	6.07E-02	6.45E-02
Inorganics [s <sup>-1</sup> ]	1.18	1.20	1.44E-05	9.17E-07	2.68E-02	1.29E-02
CH <sub>4</sub> [s <sup>-1</sup> ]	2.71E-01	2.45E-01	0	0	0	0
C <sub>5</sub> H <sub>8</sub> [s <sup>-1</sup> ]	4.39E-02	7.18E-03	5.67E-09	7.45E-10	3.07E-04	4.65E-05
$\alpha$ -pinene [s <sup>-1</sup> ]	1.02E-01	1.47E-01	1.76E-07	2.32E-07	1.22E-02	1.75E-02
$eta$ -pinene [s $^{-1}$ ]	3.56E-02	7.87E-02	6.86E-09	1.47E-08	1.10E-03	2.40E-03
$\Delta^3$ -carene [s <sup>-1</sup> ]	1.44E-01	2.59E-01	6.29E-08	1.08E-07	1.53E-02	2.63E-02
Limonene [s <sup>-1</sup> ]	1.00E-02	1.38E-02	1.30E-08	1.63E-08	7.44E-04	9.89E-04
Cineol [s <sup>-1</sup> ]	3.40E-04	4.34E-04	4.68E-12	5.93E-12	5.24E-09	6.67E-09
Other C <sub>10</sub> H <sub>16</sub> [s <sup>-1</sup> ]	1.25E-02	1.82E-02	2.06E-08	2.73E-08	1.50E-03	2.20E-03
Total $C_{10}H_{16}$ [s <sup>-1</sup> ]	3.05E-01	5.16E-01	2.79E-07	3.98E-07	3.08E-02	4.94E-02
$\beta$ -caryophyllene [s <sup>-1</sup> ]	1.50E-02	4.20E-03	8.76E-07	2.46E-07	1.40E-03	4.04E-04
Farnescene [s <sup>-1</sup> ]	3.40E-03	9.59E-04	1.96E-07	5.50E-08	3.22E-04	9.02E-05
Other $C_{15}H_{24}$ [s <sup>-1</sup> ]	1.00E-03	2.90E-04	5.85E-08	1.67E-08	9.63E-05	2.73E-05
Total $C_{15}H_{24}$ [s <sup>-1</sup> ]	1.94E-02	5.42E-03	1.13E-06	3.18E-07	1.86E-03	5.21E-04
Other VOCs [s <sup>-1</sup> ]	1.25	1.26	2.86E-08	3.14E-08	9.33E-04	1.65E-03



**Figure 1.** The model structure of SOSAA: SCADIS describes the meteorological evolution of the vertical domain, followed by either MEGAN or SIMBIM that provide emissions of VOCs from the individual levels of the canopy. Chemical reactions are chosen from the MCM and processed by the KPP whereafter aerosol dynamical processes are calculated by UHMA.



**Figure 2.** Examples of modelled and observed vertical profiles at 12 p.m. on 12 July (top) and 3 a.m. on 11 July (bottom). Solid lines are data obtained from radiosonde observations, and the dots are 30 min averages from the SMEAR II tower. The model values are representing the 30 min during which the soundings were made.


**Figure 3.** Diurnal averages of the components of the surface energy balance. Net radiation: sum of all radiation components in the model (the direct and diffuse global radiation, atmospheric thermal radiation, PAR and NIR reflected and emitted by the vegetative canopy, and the thermal radiation by the soil surface) compared to the net radiation measured for 300–40 000 nm above the canopy. Heat flux and storage in the soil is the average of four heat plates, and observed values were used as model input. Turbulent fluxes of sensible and latent heat measured with an eddy covariance system at 23.3 m. The shaded areas represents the uncertainty on the measurements which are estimated to be  $\pm 20$ % for the heat fluxes and  $\pm 10$ % for the net radiation.



**Figure 4.** Average wind speed profile  $\pm$ SD at 7–81–2 a.m. and p.m. (a). Red line and blue lines and area are simulated values for day and night (3 m/s added for clarity), respectively, black from measurements. Simulated diurnal mean friction velocity ( $u^*$ ) (b). The top of the canopy is shown with a solid line and the measurement heights of the eddy covariance systems with dash lines. Observed and simulated mean friction velocity in (d) and above the canopy (c). The shaded areas in the (c and d) represents the estimated uncertainty of  $\pm$ 20% (c) and  $\pm$ 50% (d), respectively.



**Figure 5.** Difference in measured gas concentration of (a) NO, (b)  $NO_2$ , and (c)  $O_3$  (blue, left hand side) and CO (green, right hand side). The difference is calculated by subtracting the campaign measured concentrations by the SMEAR II obtained concentrations.

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**Figure 6.** Above-canopy measured (black dots) and SOSAA modelled (red line) photolysis rate for (a)  $NO_2 \rightarrow NO + O$ , and (b)  $O_3 \rightarrow O(^1D) + O_2$ . For comparison, also the TUV (Tropospheric Ultraviolet and Visible Radiation Model) predicted rates are included.



**Figure 7.** Daily averaged measured and modelled total OH-reactivity together with daily averaged modelled total  $O_3$ - and  $NO_3$ -reactivity. (a) indicates the amount of measured half hour data points that has been used for the averaging of the measured reactivity, (b) measured OH-reactivity at 18 (solid red line) and 24 m (dashed blue line), where the shaded areas are the 75 and 25 percentiles, (c) modelled OH-reactivity at 18 m (solid red line) and at 24 m (dashed red line), and (d) modelled reactivities of  $NO_3$  (blue line, left sided *y* axis) and  $O_3$  (green line, right sided *y* axis).

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**Figure 8.** The daily averaged fractional contribution of individual inorganic compounds to the total inorganic reactivity of OH (a),  $O_3$  (b) and  $NO_3$  (c) at 18 m.



Figure 9. Daily averaged vertical total reactivity of OH (a),  $O_3$  (b), and  $NO_3$  (c). The top of the canopy is indicated by a black solid line.

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**Figure 10. (a)** The steady state (ss, in black) and instantaneous (inst, in dashed blue, when using SMEAR II NO<sub>X</sub> concentrations, inst MPI, in dashed green, when using MPI NO<sub>X</sub> concentrations) NO<sub>3</sub>-reactivity ( $R_{NO_3}$ ) together with the the corrected steady state reactivity where also the reactions of NO<sub>3</sub> with NO<sub>2</sub> have been taken into account (NO<sub>3</sub>-NO<sub>2</sub>, in red), **(b)** the production term ( $P_{NO_3} = k_6[NO_2][O_3]$ ) of NO<sub>3</sub>, and **(c)** the measured concentration of NO<sub>3</sub> ([NO<sub>3</sub>]). Please note the log scale in the a section.

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**Figure 11.** The daily averaged oxidation strength (see Sect. 7.4.5 for definition) of OH (blue line),  $O_3$  (green line) and  $NO_3$  (blue line with  $\cdot$ ) at 18 m. Please note the log scale on the *y* axis.

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**Figure 12.** Scatter plots of the measured versus the modelled reactivity of OH at 18 (a) and 24 m (b). The solid lines indicate the 1:1 reference line, whereas the broken lines represent the least-squares line.

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Figure 13. The daily averaged reactivity of OH (a),  $O_3$  (b) and  $NO_3$  (c) at 18 m due to reactions with specific individual inorganic compounds. Please note the log scale on the y axis.

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**Figure 14.** Scatter plots of the measured versus the SOSAA modelled (red dots) and the TUV (Tropospheric Ultraviolet and Visible Radiation Model, blue dots) predicted above-canopy photolysis rates for (a)  $NO_2 \rightarrow NO + O$ , and (b)  $O_3 \rightarrow O(^1D) + O_2$ . The solid lines indicate the 1:1 reference line, whereas the broken lines represent the least-squares line.

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Figure 15. The daily averaged measured concentration of (a) NO, (b) NO<sub>2</sub>, (c) O<sub>3</sub>, (d) CO, and (e) SO<sub>2</sub> during the campaign. The SMEAR II mast data is shown in black, while the extra measurements by MPI are shown in magenta.