

Interactive comment on “The oxidation capacity of the boreal forest: first simulated reactivities of O₃ and NO₃” by D. Mogensen

Anonymous Referee #1

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This paper describes the use of a 1D chemistry transport model to estimate reactivity in a boreal forest presenting the first vertically resolved model simulations of NO₃ and O₃ reactivities. 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. Significant improvements are required to the manuscript before it is suitable for publication in either journal, however. The methodologies and discussions are often difficult to follow and the style of writing is unscientific at times. My major concerns and specific comments are provided below:

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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 photolyzes 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.

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

C11460

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.

Specific comments

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

Pg 30948, line 17: 'conditions of the campaign' mention temperature specifically here.

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.

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.

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.

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.

Pg 30953, line 3: 'campaign' is spelt incorrectly

Section 3.2: were either O₃ instruments calibrated against an ozone standard?

Page 30954: lines 2 – 4 are not necessary.

Pg 30954, line 21: 'poorer' – please state by how much?

C11461

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.

Section 5.3.1 – unclear what exactly has been done here and why analysis of this type was needed?

Section 5.3.2 – What is the impact of adding these additional photolysis reactions?

Pg 30960, line 18: 'This includes information..' It is not clear what is being referred to here? The reference?

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.

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

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?

Pg 30966, lines 16-18: The specific pollution event times are not necessary.

Pg 30968, line 9: add 'with' after 'coincides'

Pg 30968, line 19: replace 'with' with 'by'

Section 7.1.1: A brief discussion on the impact of underestimating the [H₂O] should be provided

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'

C11462

Pg 30971, line 4: please state the albedo used in the TUV calculations

Pg 30971, line 7: remove ' as required'

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

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.

Pg 30973, line 27: 'the largest fraction' please give this fraction.

Pg 30974, line 6: 'with a bit more than 2/5..' this sentence needs improving.

Pg 30974, line 12: 'partly due to..' what else is contributing to the differences?

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.

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

Pg 30979, line 15: 'resisting' to 'remaining'

Pg 30981, line 7: 'least' to 'lowest'

Pg 30983, line 15: It is unclear why a conversion of spectral irradiance to actinic flux from measurements of $j(\text{NO}_2)$ and $j(\text{O}^1\text{D})$ is useful? If measurements of $j(\text{O}^1\text{D})$ and $j(\text{NO}_2)$ are available, it would be straightforward to estimate other photolysis rates directly from these.

Pg 30984, line 14: 'resisting' to 'remaining'

Tables 2: A correlation plot of OH reactivity modelled vs measurements would be more informative than the information provide in Table 2 alone.

C11463

Table 3: I suggest replacing this table with either pie-charts or a figure equivalent to figure 8.

Figure 1: isn't necessary

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.

Figure 11: should be updated to reflect oxidative strength relating to the removal of organic compounds only.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30947, 2014.

C11464