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Interactive comment on "The oxidation capacity of the boreal forest: first simulated reactivities of O_3 and NO_3" *by* D. Mogensen

Anonymous Referee #2

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This manuscript by Mogensen et al. describes first simulation to evaluate oxidation strength by O3 and NO3 in a boreal forest using 1D atmospheric chemistry transport model (SOSAA; model to Simulate Organic vapours, Sulphuric Acid and Aerosols). The authors concluded that OH is the most reactive and followed by NO3 and O3, while O3 is the fastest remover for pollutants when considering ambient levels of each oxidant. I do not agree with this though, as specifically commented below. They also found some missing OH reactivity due to unknown BVOCs and their oxidation products.

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. Otherwise, this cannot be published in ACP. My comments and suggestions are below.

General Comments:

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. In addition, reacitivities of each oxidant by reacting with organics are poorly explained despite of their importance in the forest area. 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. As the referee #1 pointed out, I agree that discrepancy of modeled vs observed OH reactivity needs to be thoroughly discussed. 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. Moreover, the lifetime of oxidant is equivalent to the inverse of reactivity, thus lifetime of O3 is estimated ~13 hours based on the result in the abstract. This is considerably slow and not plausible in the forest environment if trees emit BVOCs. Further, when considering NO+O3 reaction as null cycle, the O3 lifetime is going to be even much slower. This is also required to discuss in the MS.

Specific comments:

Abstract: Overall, this part should be rewritten after revision of the MS.

- 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.

-P.30949 L18-19: What do you mean by 'the measurement is tricky'? Be specific here

and need good references.

-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.

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

-P.30955 L6-8: Explain what method you used to calculate uncertainty or add a reference.

-Section 4.4: What was the measurement uncertainties for NO3 and N2O5?

-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?

-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).

-P.30960 L13: 'MCM v3.2' is mentioned first here, so give the full name here than in

the section 5.4.

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

-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.

-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.

-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.

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

-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 $\sim$11 hours during daytime and $\sim$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 reacitivies.

-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.

-P.30982 L4-5: Explain in detail how OH and NO3 are reformed and why not for O3?

-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.

-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.

-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 iso- prene 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 rea- son 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.

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

-Section 8: This part needs to be rewritten after revision.

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

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.

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 MODEL with red triangles.)

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.

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