MODELLING ATMOSPHERIC OH-REACTIVITY

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INTRODUCTION

As the focus on climate, air quality, visibility and public health has increased, so has the research on secondary organic aerosol (SOA) formation. SOAs are formed from atmospheric oxidation of volatile organic compounds (VOCs). The hydroxyl radical (OH) is the most important oxidant of the atmosphere, and knowledge of the atmospheric concentration and lifetime of OH is necessary to further the understanding of the SOA formation. However, the overall OH sink term is currently poorly constrained in models due to a still high missing fraction of unknown organic molecules contributing.

We have modelled the atmospheric OH-reactivity in a boreal forest and investigated the contributions from atmospheric inorganic species, methane, isoprene, monoterpens and other important VOCs. We have used SBSA; a one-dimensional vertical chemistry-transport model (Boy et al., 2010) together with measured data from Hyytiälä, SMEAR II station, Southern Finland, August 2008.

In order to ascertain how well we understand the OH initiated photochemical processes, we have compared our calculated OH-reactivity with measured ambient OH-reactivity from the BFORM (Boreal Forest OH Reactivity Measurements) campaign, August 2008. Here the total atmospheric OH-reactivity was measured using the Comparative Reactivity Method. (Sinha et al., 2008)

METHODS

Model simulations. The one-dimensional chemistry-transport model SBSA (Model to Simulate the concentrations of Organic vapours and Sulphuric Acid) was used in the calculations of the OH-reactivity. (Boy et al., 2010) The chemistry was calculated using the Kinetic PreProcessor (KPP), (Damian et al., 2002) while emissions of the most important organic vapours were predicted by the MEGAN model (Guenther et al., 2006). SBSA also includes measured meteorologic data and needed gas concentrations from Hyytiälä, SMEAR II station, Southern Finland.

The OH-reactivity is calculated as

\[ R_{OH} = \sum_{\text{Reactions}} k_{OH+X} \times [X] \]

where \( R_{OH} \) is the OH-reactivity, and \( k_{OH+X} \) is the rate constant for the chemical reaction between the OH radical and the chemical species X, were the concentration of X is given by [X]. The OH-reactivity is given as an average over 30 minutes periods of 60 seconds time step.
**Measurements.** The simulated OH-reactivities have also been compared with measurements. The traditional approach to OH-reactivity has been to measure the individual OH reactive components (e.g. NMHCs, CO, CH$_4$, NO$_x$). (Holzinger *et al.*, 2005; Maris *et al.*, 2003; Roberts *et al.*, 1998) However, this is a very limited approach since sticky and short lived reactive species get lost while sampling. In this study the total OH-reactivity has been measured using the Comparative Reactivity Method where a reactive molecule X, not normally present in air, is passed through a glass reactor and its concentration is monitored. OH radicals are then introduced in the glass reactor at a constant rate to react with X, first in the presence of zero air and then in the presence of ambient air containing VOCs and other OH reactive species. Comparing the amount of X exiting the reactor with and without the ambient air allows the air reactivity to be determined. (Sinha *et al.*, 2008)

**RESULTS AND DISCUSSION**

In Figure 1, measured and calculated OH-reactivities are presented for a two week period. The OH-reactivity has been measured in the height of 12-14 meters and calculated in the height of 14.2 meters. Also the different contributions as mentioned earlier are visualized here. On average we are underestimating the total OH-reactivity by $\sim 40\%$, but for large periods of time we are within the uncertainties of the measurements. In some periods we are overestimating the measurements, which can be explained by the uncertainties withing the measurements and model. The fluctuation in the measured OH-reactivity could be due to the meteorological turbulence that is not present in the model. According to our simulations the largest OH sinks originate from the following: inorganics $>\text{CH}_4 >$ other VOCs $>\text{monoterpenes} \geq \text{isoprene}$. In the near future we will investigate the altitude dependency of the OH-reactivity.

**CONCLUSIONS**

We have modelled the total OH-reactivity over a boreal forest. We found that we are currently unable to simulate $\sim 40\%$ of the total OH sink term, but we have reason to believe that this arise from the many unknown organic compounds not included in the model.
Figure 1: Measured and calculated OH-reactivity. See text for details.
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REFERENCES


