

Interactive comment on “

Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010” by A. C. Nölscher et al.

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The authors are grateful for the interesting and constructive comments of the referee. After addressing the main issues, important points in the manuscript will be revised and improved based on the referee's remarks, as detailed below.

Comment 1) It would be useful to show the NO concentrations measured during each regime in Figure 4 for comparison between the regimes and with other studies. Were there significant differences in the observed NO concentration between “normal boreal”

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and “transported pollution” periods that could impact the expected oxidation products?

Ambient NO levels are known to control oxidation regimes that produce different kinds of products. Therefore it is valuable to search for significant differences of NO levels in the regimes, which were defined for the HUMPPA-COPEC campaign. Similarly to the compounds presented in Figure 5, NO measurements have been used to create diel median profiles which are shown in Figure 1.

NO diel trends did not change throughout the campaign. A maximum was reached in the morning hours, followed by decreasing values throughout the day. Mean NO values for stressed boreal, transported pollution and normal boreal conditions were 30 pptV, 27 pptV, and 31 pptV respectively. The fact, that NO levels were that consistently low during the campaign is relevant and will be clarified in the manuscript.

Comment 2) Figure 2 shows the measured reactivity above and below canopy as well as the deviation from equal OH reactivity. It appears that there are several occasions where the deviation from equal OH reactivity suggests that the above canopy reactivity is 3-4 times greater than the below canopy reactivity. Yet the absolute values of the reactivity shown below do not appear to reflect this. What are the reactivity values that led to values greater than 2?

The comparison between in and above canopy total OH reactivity Γ shows for several occasions short duration spikes. These generally last only for a couple of measurement points and are caused by various factors: e.g. fast mixing after breakup in the morning of the nocturnal boundary layer, enhanced tree emissions during daytime, influence of burned biomass (especially in the transported pollution regime), local pollution (predominantly in the normal boreal conditions), and impact by transported emissions of nearby anthropogenic sources. The average Γ shows significant differences between the three defined regimes, which can be seen in Table 3.

Comment 3, 4) The authors state that higher rates of emissions during “stressed boreal” conditions are likely responsible for the significant missing reactivity, as the diurnal

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OH reactivity profile is similar to the monoterpene profile. However, is there a significant correlation between the measured monoterpene concentration and the missing reactivity fraction that would provide additional quantitative evidence that the missing reactivity is related to monoterpene emissions? Similarly the authors suggest that the missing reactivity during the “transported pollution” regime may be due to reactive unmeasured oxidation products, as the measured concentration of PAN and pinic acid is higher during this period. However, it also appears that there may be a correlation of the fraction of missing reactivity with pinic acid concentrations based on the data shown in Figures 5 and 6, which would provide additional evidence to support their conclusions. Are there correlations with other possible oxidation products, such as formaldehyde?

Thanks to comments number 3 and 4 we would like to add some important explanatory aspects to the manuscript. The calculated missing OH reactivity has been correlated to almost all variables that have been monitored during the HUMPPA-COPEC campaign. For most of these no significant correlation could be found (that's why previously the authors did not include it in the manuscript). When separating the correlations for the three defined regimes, we find the following interesting dependencies: During the stressed boreal regime missing OH reactivity was not correlated to monoterpene mixing ratios, but weakly dependent on wind direction and solar zenith angle. To clarify: we see similar diurnal pattern in biogenic emissions, such as monoterpenes, and in the measured total OH reactivity. Additionally, the in and above canopy comparison suggests a strong flux from inside the canopy. Also, high emissions of sesquiterpenes could be observed from enclosure measurements which showed a much broader variety of different species under the heat stress conditions. Combining this evidence we conclude that the origin of the missing total OH reactivity is biogenic and effected by the extreme heat stress. Known stress released compounds such as sesquiterpenes, aldehydes and methyl salicylate and their oxidation products were not measured during HUMPPA-COPEC 2010. The strongest correlation of missing total OH reactivity to another compound occurred during the transported pollution regime. Here H₂O₂ and

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the measurements of total organic peroxides, agree well with the missing total OH reactivity, which supports the hypothesis that the secondary products play an important role in this regime. A weak correlation between missing total OH reactivity and ozone could be found in the normal boreal regime. Here pollutants, including ozone from nearby cities, were advected occasionally to the site which enhances the probability for ozonolysis products.

These additional points will be added to the revised manuscript and we thank the reviewer again for the insightful questions.

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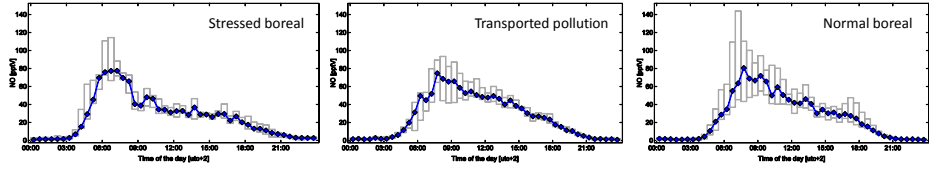


Fig. 1. NO diel median profiles for the three characteristic regimes during HUMPPA-COPEC 2010

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