**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

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 wish to thank the reviewer for the clear and interesting remarks on our manuscript. The manuscript will be revised according to these comments as described in detail below. In the following we address each remark and emphasize the changes that will be applied to the current version of the paper.

Comment: The main flaw in the data analysis is that the mid-day temperature during the "pollution" period is actually higher than "stress" period according to the daily ambient

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temperature variation in the figures. Based on the descriptions about "stress" in the manuscript,it was all about the heat stress so during the "pollution" period, the forest environment may actually experience a stress both from pollution and heat. Therefore, I urge the authors to regroup the dataset for better data analysis.

Reply: The three regimes delineated in the HUMPPA-COPEC campaign 2010 based on several factors: 1) Meteorologically a distinct signature could be found not only in temperature but also in other typical variables such as wind direction and speed, convection, turbulence, advection etc. (Williams et al, ACP 2011) 2) The chemical composition of the site air changed in the course of the campaign, most significantly through the impact of the advected pollution of the biomass burning 3) Total OH reactivity showed different patterns in both temporal evolution and vertical gradients (as can be seen in Figure 2 and 4). The authors are aware of the fact that the high temperatures extended into the "transported pollution" regime and even national temperature records were reached in this time. As can be seen from Figure 2 during midday, when high temperatures were reached in combination with maximum radiation, the in canopy total OH reactivity measurement showed higher levels than above the canopy. These high levels are clearly of biogenic origin. Interestingly the referee proposed a reaction of the vegetation to pollution stress.

For the manuscript we prefer to maintain the present segregation of the data. The referee is correct that the term "heat stress" needs to be further clarified as the temperature during the second "pollution transport" section is indeed higher. We will clarify in the text that the heat stress section is defined not terms of the ambient temperature but rather because of the extended period of high temperatures and low rainfall preceding the campaign.

Comment: The other aspect that can make the manuscript clear is about monoterpene speciation analysis. Although PTR-MS was deployed in the field campaign (Table 2), it is appeared that the authors only applied the GC-MS measured monoterpene concentrations for the calculated OH reactivity estimations. There is an anecdotal evi-

dence that GC techniques may not be able to detect significant portions of very reactive monoterpenes (∼30 %) that on the other hand can be detected by the PTR-MS technique (Lee et al., 2005 ACP). I recommend authors to include the PTR-MS measured monoterpene dataset if available.

Reply: Indeed there are PTR-MS monoterpene measurements available which have been considered within total OH reactivity calculations. The reasons we choose not to include the total PTR-MS monoterpene signal were: 1) The PTR-MS signal was calibrated with a-pinene. It is unclear if the PTR-MS is equally sensitive to all monoterpenes, meaning it could distort the true amount of monoterpenes present. 2) For total OH reactivity calculations a rate coefficient has to be considered. This differs greatly for different monoterpenes between e.g. (b-myrcene) 3.34x10-10 cm3molecules-1s-1 and (a-pinene) 5.3x10-11 cm3molecules-1s-1. 3) During the influence of the biomass burning plume all PTR-MS measured masses showed the same signature which indicates possible interferences. Nevertheless a calculation including the total monoterpenes measured by PTR-MS using a weighted rate coefficient (based on the GC-MS speciation: 4.24x10-11 cm3molecules-1s-1) has been made. The average missing OH reactivity could be improved by this approach of about 2 %. This result will also be added to the revised manuscript text. In addition the signal of total organic peroxides and the total organic acids could be used with estimated rate coefficients to re-calculate the total OH reactivity. The largest improvement could be found during the transported pollution regime and was about 5 %. Accordingly, including budgets of monoterpenes, organic peroxides and acids does not improve the calculations of total OH reactivity significantly. These points will be added to the text to further strengthen the conclusion and the reviewer is thanked for this suggestion.

Comment: Further discussion is also recommended that how much of reactive monoterpenes or sesquiterpenes is required to explain the observed missing OH reactivity. My expectation is if that much of unmeasured reactive species existed inside of the canopy, you should be able to see significant differences in secondary photochemi-

cal oxidation product distributions such as ozone and SOA between the "stressed" and "normal" boreal environments. I would like to see the discussions on this aspect also.

Reply: Assuming that the measured total OH reactivity is significantly influenced by substances that cannot be detected in ambient air because they are below the limit of detection (approx. 5 pptV) and have the moderate reaction velocity of k=5x10-11 cm3molecules-1s-1 (which is slowly in comparison to isoprene and terpenes, and fast in comparison to many secondary products), we would need about 1000 of these not-detectable, quite reactive compounds to explain the average missing OH reactivity of 9 s-1. This is consistent with current literature from e.g. Dudavera et al (2004), who states that there are more than 1000 unknown compounds emitted by the biosphere, or Goldstein and Galbally (2007), who talk about more than 10.000 unknown species in the atmosphere. Additionally, substances might exist, which are more abundant but not detectable by current measurement techniques. This very interesting and important aspect will be included into the manuscript.

Differences between the regimes "stressed boreal" and "normal boreal" in terms of secondary photochemical product distribution are difficult to examine, since only very little data for those are available. Indicators for different oxidation regimes can be NO and Ozone. As described in Answer 1 (Comment 1), NO mean values do not change throughout the campaign. Ozone mean values are 38.5 ppbV, 46.8 ppbV and 42.6 ppbV for the regimes "stressed boreal", "normal boreal" and "transported pollution" respectively, with similar diel median profiles which can be seen in Figure 5. For "normal boreal" forest conditions a weak correlation between missing OH reactivity and Ozone was observed, which is also discussed in Answer 1 (Comment 3,4) and will be added to the manuscript. Additionally, we are hoping to get some more insights from further studies dealing with secondary organic aerosol which was measured during HUMPPA-COPEC 2010 as well and is part of future publications.

Comment: Minor Points - Add the statistics (e.g avgs, and S.D.) of ambient temperatures in the text. - Table 2. I am not familiar with the Smear II method for SO2 analysis.

describe it or put a reference about it. - Figure 4 and 5 It is very hard to read axis labels. Use a bigger font size - Figure 5. Add error bars that indicate standard deviations.

Reply: These minor changes will be incorporated into the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 7419, 2012.