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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds" *by* R. Holzinger et al.

Anonymous Referee #1

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General comment:

The manuscript presents interesting and novel results on biogenic emissions of reactive carbon from a pine plantation using PTR-MS technology. Investigating the fate and magnitude of biogenic emissions has a high priority for improving our understanding of atmospheric chemistry and climate. One of the main conclusions of this manuscript is that the release of reactive compounds could play a role in determining the direct chemical loss of ozone. In principle I recommend publication in ACP, however the authors need address some key content issues raised below.

Specific comments:

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Introduction:

Forest thinning is a very different scenario compared to the undisturbed forest investigated in the present case. During and after forest thinning it is expected that not only terpene emissions / concentrations increase dramatically, but also a wide range of very reactive compounds due to damaged plant material. A myriad of different compounds related to wounding are produced while vegetation dries out or is significantly damaged. While the chemical loss of ozone might be explained by the wide suite of compounds released during and after forest thinning, the ozone deposition above the undisturbed forest could be caused by a combination of different compounds and mechanisms. Comparison between these two scenarios (disturbed vs undisturbed ecosystem) is certainly instructive, however it also needs to be pointed out that there are fundamental physiochemical differences leading to the emission of VOCs between the heavily disturbed and the undisturbed case.

It is argued that ozonolysis of biogenic precursor compounds plays the major role in determining the lifetime and reactivity of what is termed VR-BVOCs. Previous papers from the same group have argued that reactive terpenes could account for most of the chemical ozone deposition above this plantation. While it is conceivable that these compounds can potentially influence the lifetime of ozone, the authors need to consider other mechanisms in more detail:

Experimental: It is mentioned that 2 um Teflon filters were used in front of each sample line. How often were these filters replaced? Considering the fact that any of the oxidation products of the proposed reactive terpenes are probably very low volatile species with multifunctional groups, these compounds could also origin from aerosols collected on the Teflon filters. It is conceivable that these compounds condense on filters during nighttime and reevaporate during the day. Effects of UV radiation with aerosols on the filters could possibly also lead to the production of various species that were observed in the higher mass range. Any quantitative conclusion drawn from the gradient measurements should assess the systematic bias due to in-situ production of these compounds on the Teflon filters or state the possibility of artifact formation.

Section on reactivity and conclusions: It is argued that the oxidation via ozone is the main mechanism producing compounds plotted in figure 2 (d). If this was the case I would expect a concentration gradient throughout the canopy that is much less pronounced. The ozone concentration probably varies by less than 30% throughout the canopy. If these compounds were entirely produced due to alkene+O3 type reactions, they should also accumulate in the lower part of the canopy: Instead the plotted diurnal profiles (e.g. figure 2d) for compounds termed as OX01-OX13 seem to suggest that these species are either produced by oxidation via HO, which can be substantially lower (e.g. a factor of 5-10) in the lower part of the canopy, or are directly emitted from the vegetation. Assuming that these compounds are emitted proportionally to the leaf area index and react with ozone as fast as proposed (order of minutes) the gradient of these compounds would look very similar to examples shown in figure 2(d). In addition deposition to the ground could also be an important loss term which has not been addressed in this manuscript. Considering that these compounds are probably very low volatile, I would expect that they can rapidly deposit on surfaces, conceivable with deposition velocities close to ammonia. Assuming deposition velocities (vd) on the order of 2-5 cm/s and deposition to the ground, the lifetime due to dry deposition in the canopy (height h) could be on the order of 120 -300 seconds (h/vd). This could be comparable to chemical loss rates calculated due to ozonolysis. I would therefore argue that dry deposition of directly emitted reactive terpenes can not be completely ignored and that the gradients of OX01-OX13 in turn could potentially be explained by either of the above arguments.

The authors convey the picture that emissions of reactive terpenes are the only cause for the unaccounted ozone deposition flux reported by Kurpius and Goldstein (2003). If this was the case one would expect significant aerosol production. The oxidation products of ozone+sesquitperene reactions for example have almost unity yield. Assuming a conservative yield of 0.5 and taking the reported ozone flux of 20 umol/m2/h,

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the local secondary organic aerosol production would be on the order of 10 umol/m2/h or ˜1.500 mg/m2/h, taking an average molecular weight of 150 amu. Typical average daytime diffusion coefficients (K) in the surface layer are in the range of 5-10 m2/s. The average organic aerosol concentration difference (K x dC/dz = F) throughout the surface layer assuming dz ˜ 200 m would then equate to 8 - 16 ug/m3. This seems to be an extremely large concentration range compared to typical organic and total aerosol loadings above forests. For comparison the total fine particulate mass (PM2.5) measured at similar ecosystems (e.g. BIOFOR 3) is on the order of 2-20 ug/m3. Is there any evidence of exceptionally high aerosol concentrations above Blodgett Forest?

According to this manuscript and a paper by Kurpius and Goldstein (2003), the uncertainty of the chemical term for ozone deposition is estimated to be ˜ 20 +/- 16 umol/m2/h. In the limit the chemical term could then also be explained by the reaction of NO+O3, which was reported to be in the range of 0.4-4 umol/m2/h. This inherent uncertainty needs to be considered when discussing potential reactions affecting the ozone deposition flux.

In summary the presented observations highlight that our understanding of the release of biogenic VOCs is still limited and would therefore present a very valuable contribution to this journal. Considering the uncertainties of the reported chemical term for ozone deposition, it seems highly speculative to argue that one process can be singled out and entirely explain the discrepancy between measured and estimated ozone deposition fluxes at this point. I would argue that the present VOC observations provide a necessary but not sufficient constraint for this assumption. For example other studies at sites with comparably low VOC emissions [Fowler et al., 2001] also showed that a significant fraction of ozone deposition does not occur through stomatal uptake. It should be pointed out that there are a number of different poorly constrained factors controlling the ozone deposition above forests. In order to constrain their magnitude it appears that an intensive atmospheric chemistry study above a reasonably homogenous forest is required to quantitatively constrain the fate of oxidants and reconcile re-

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cent observations above densely forested ecosystems. So far most studies were only able to address a few aspects of the complex interplay between emissions, deposition, chemistry and transport.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5345, 2004.

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