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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variation in vertical volatile compounds air concentrations within a remote hemiboreal mixed forest" *by* S. M. Noe et al.

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It is interesting to note that the hemiboreal mixed forest showed similar isoprene but higher monoterpene concentrations than the boreal forest, as one would expect that the monoterpene mixing ratios are smaller due to a generally lower fraction of conifers. However, this interpretation of course depends on the specific site characteristics (tree species distribution), and the significance of the statement and/or generalization of this finding is vague. Likewise, this also depends on which boreal forest data are used for comparison. A site intercomparison (table?) would help the reader to judge the robustness of respective statements. In the text the authors mention 2-5 μg m-3 for

isoprene and 10-18 μg m-3 for monoterpenes in boreal forest ecosystems (Hakola et al., 2000; Rinne et al., 2000; Räisänen et al., 2009), compared to 1-7 μg m-3 for isoprene and 10-40 μg m-3 of monoterpenes from their own data, if the extreme values measured in July 2010 were excluded; and the authors also state that their data well reflect the boreal data of Hakola et al. (2009). So, differences are obviously small, and let assume that the field site VOC concentrations are not far from those in boreal conditions. As the focus is mainly on observed concentration (profiles) of the hemiboreal forest ecosystem, I would propose (though not mandatory) including a table that compare the observed data with earlier literature data on similar (boreal) ecosystems. A well elaborated classification in that comparison would be what tips the scale. For example, one argument for higher monoterpene mixing ratios found here might also be a higher temperature regime of this site compared to real boreal forests, with emissions being strongly dependent on temperature. A compilation of boreal VOC data would also ramp up the citation rate of the manuscript.

A small site intercomparison table might be provided in a revised version of the manuscript, however, boreal ambient BVOC data are still quite limited to few places. We do not agree to the reviewers viewpoint that we can compare the hemiboreal forest ecosystem to the boreal ecosystem just because the differences in ambient concentrations seem to be small. As the reviewer rightly mention before, the species contribution is different (up to 50% deciduous as example) and the site characteristic play as well a role. Therefore, it is quite remarkable that, let's say, half of the conifers manage to feed the same or more ambient monoterpene concentration. That is even more remarkable if taken into account that the indeed higher temperature regime should lead to a higher chemical loss rate, at least during summer and above the canopy. But the canopy is also much more dense due to the share of deciduous trees. We agree with the reviewer that compiling VOC data (boreal and other) would be a well appreciated task, but that would be best done as a full fledged review paper and not as a minor bit of a paper reporting on concentration profiles of a specific forest ecosystem.

As mentioned by the authors, eddy covariance (EC) measurements have been applied at the site. Is there any chance using these data of physiological activity to link their conclusions on the seasonal pattern (refer to Noe et al. 2011, Forest Ecology and Management 262, 2, 71-81)?

Yet, we have unfortunately no eddy covariance data that is covering the whole season of the presented measurements. The systems have been working in 2008 and 2009 only during campaigns in summer and autumn. The 20 m system started to work year round in July 2010, the 2 m system still only during summer and autumn because of other experiments where the equipment is needed.

Do the authors have an idea on the seasonal pattern of phenology at the measurement site, i.e., dates of bud break, or start of net photosynthesis of deciduous trees on the one hand and leaf senescence on the other hand (i.e., specify dates in lines 15-17 on page 14618)?

Yes, of course. Typically bud break of main deciduous species is about end of April. The foliation about mid May and leaf senescence about mid October, these dates may fluctuate depending on the given yearly situation with $\pm$ 14 days. We will include such data in a revised version.

What was the outcome of the resin samples that are described in the section 2.3? Is it "We know that 3-carene is the main compound emitted from P. abies (Noe et al., 2010) at our site and it shared up to 14% of the spruce resin monoterpene content"? The latter rather seems to me to be a citation, and hence the description can well be omitted in the section 2.3 (or better present and discuss respective resin results).

As we analyzed the resins in summer only once assuming that they will not change the monoterpene fractions fast as the resin was already exuded from the stem, we decided to give as percentage of the total monoterpene content. As we focused on ambient BVOC concentrations, the resin qualitative result gives some hints on possible trunk space and also litter emissions and the main monoterpene compounds to be expected. We will set that more clear in a revised version of the manuscript. A good quantitative analysis would need many different samplings and extractions to our opinion, that was not possible to achieve. We have limitations in human resources and not all analysis were possible to conduct during that seasonal campaign.

Supplement: as the focus of the manuscript is mainly on concentrations, I would suggest having the concentration data (merge tables S1 and S2) in the main body of the paper, rather than in the supplement. Add sesquiterpene data mentioned in section 3.2 (if available). The creation of such kind of data base is very labour-intensive, and inclusion of sesquiterpenes would strengthen the impact of the manuscript. Sesquiterpenes are much more reactive than isoprene and monoterpenes and could play an important role in atmospheric chemistry and particle nucleation, which is why information on these compounds is highly appreciated within the scientific community.

Yes, we agree to move them into the main text in a revised version. The sesquiterpenes will also be given in a table. (see also answer to reviewer #1 comment).

Page 14619, line 27: concerning the sentence "Furthermore, Eerdekens et al. (2009) reported larger terpene concentrations at night time indicating the loss of activity in the chemical sink when there is no or low light.": Given similar source strength, increased nighttime concentrations are generally explained by a cease of turbulent mixing, and decoupling of canopy air with the air aloft (stratification of air above the canopy) and/or the built-up of a shallow nocturnal boundary layer, where VOC are released in a confined volume of air. I think Eerdekens et al. (2009) is

going the same way of reasoning ("Higher monoterpene mixing ratios at night is likely due to the formation of a shallow nocturnal inversion layer at night over the continuously emitting vegetation."), rather than reduced chemical degradation. To judge the statement on dependence of the chemical sink of these monoterpenes on light availability, one would have to compare the chemical lifetime versus the transport time within the canopy.

That is right, we will revise that section. As we did measure during day, the night time changes are not really relevant in that focus but should be set clear anyway.

Page 14620, line 3: concerning the sentence "This indicates, that the change in the oxidative state due to lack of light may influence substantially the accumulation of monoterpenes within the canopy." Omit comma after "This indicates". Else: Did the authors come to this conclusion due to the intercomparison of chemical lifetime of isoprene (no vertical gradient) versus those of monoterpenes (steep vertical gradient)? The shorter the chemical lifetime (reaction rate coefficients) of a compound, the higher would be the expected impact on the vertical gradient (if the oxidative state would really play a major role). An alternative reasoning would be to just have a different source attribution of isoprene versus monoterpenes (with the soil being a main source for monoterpenes, as described elsewhere in the text).

Well, the chemical lifetimes should be one reason, the different sources another one. We can not prove that by the current measurements but the shape of the profiles tell something about the impact of both factors. As isoprene should have a lifetime in the range of hours while monoterpenes in the range of minutes the shapes are fitting to that picture. Given also large monoterpene sources from the soil (under normal conditions) plus lower chemical degradation (no light, lower O3 and NOX) inside the canopy and lower wind speed, that might lead to the accumulation of monoterpenes inside the canopy, even during daytime. There will be also the mixing as continuous factor of di-

lution take part and that all together will finally be responsible for the measured profiles.

Page 14621, line 12: I can't yet see the point in the sentence "Above the canopy the chemical loss of limonene should be larger than for a-pinene", as in the following only limonene is being discussed.

We will revise that section as there has to be given a clearer point on the pattern we found and what we expected by a previous study.

Fig. 1, legend: Give the respective (day)time interval of the measurements used for averaging (also in Fig. 2). Are these daytime averages or averaged for the VOC sampling periods? Measured simultaneously or sequentially? Else: In section 2.5 the authors claim that PPFD measurements were carried out in sunny and shaded conditions: "On each height, PPFD was measured in shade conditions and in full sunlight, if available." Which data were used for this figure? Were the data averaged above all? Else: Do the authors have any idea why the temperature showed highest variation directly above the forest floor? Reduced mixing of in-canopy air during summer months, and low variation in horizontal wind speed (Fig. 2) would led assume rather low variability in temperature close to the ground.

Averaged over the VOC sampling periods. Temperature was measured sequentially, each time the tubes have been placed for VOC sampling. We will include a more detailed description as this is also recommended by the other reviewers. For the graph we used both, light and shade measurements taken over the period of VOC sampling. It is clear, that on top of the canopy, we have no shade measurement and over ground only spots of sunlight for short time so basically no full sunlight. The variations match that situation very nicely. The variation in the temperature directly above the forest floor did astonished us as well. We can not give a conclusive answer but the forest floor is as written in the site description influenced by the high water table and there is a peat

layer which can be very different in it's humidity on small spatial scales. Maybe that together with the forest floor vegetation at the site is leading to a variation of 2° Celsius.

We thank the reviewer for the suggestions and corrections and will consider them in a evised version.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14607, 2011.