

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

**Anonymous Referee #2**

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Until now only few studies have reported about VOC concentrations in the hemiboreal forest zone. The manuscript represents a substantial contribution to ACP in terms of a yet underrepresented VOC data base on this type of forest ecosystems, especially concerning seasonal patterns of in-canopy mixing ratios, which can be used for modelling exercises.

Data evaluation and discussion/reasoning is restricted to fairly qualitative statements. The authors nicely bring up the issue of within-canopy reactions (chemistry and depositing losses) in section 1, but unfortunately fail to systematically discuss it based on their own findings in the following (see below). The manuscript is within the scope of

C5103

ACP, and I recommend publication after consideration of the comments below.

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  $\mu\text{g m}^{-3}$  for isoprene and 10–18  $\mu\text{g m}^{-3}$  for monoterpenes in boreal forest ecosystems (Hakola et al., 2000; Rinne et al., 2000; Räisänen et al., 2009), compared to 1–7  $\mu\text{g m}^{-3}$  for isoprene and 10–40  $\mu\text{g m}^{-3}$  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.

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)? 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 photo-

C5104

synthesis 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)? It is reasonable that isoprene production/emission only started in June in this latitude, with a time lag between the onset of net photosynthesis and the isoprene emission, being dependent on the temperature regime of the habitat (see, e.g., Harley et al. 1994, Monson et al. 1994; Kuhn et al. 2004).

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).

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.

Minor corrections / comments:

Title: instead of “vertical . . . concentrations” I would suggest changing the title in something like: “Seasonal variation in vertical in-canopy profiles of volatile organic compounds within a remote hemiboreal mixed forest”

Page 14608, line 8: “were found to be . . .”

Page 14608, line 9: “. . . the vertical profile suggests . . .” or “. . . the vertical profiles suggest . . .”

C5105

Page 14608, line 13: suggest: “During summer months, dominance of  $\alpha$ -pinene in the lower and of limonene in the upper part of the canopy was observed, both accounting for up to 70% of the total monoterpene concentration. During wintertime, 3-carene was the dominant species, accounting for 60% of total monoterpene concentration in January.”

Page 14610, line 27: replace “asses” by “assess”

Page 14613, line 1: replace “are dissolved” by “was dissolved”

Page 14615, line 12: replace “The latter both are likely originated from . . .” by “The latter both likely originated from . . .”

Page 14616, line 6: suggest “For isoprene, we can clearly distinct differences in observed concentration ranges in the summer months . . .”

Page 14617. line 1-3: add comma after “. . . monoterpene species emitted . . .”. Could also be rephrased to something like: “In Fig. 5, the spatial and temporal relative contribution of each individual monoterpene species to the total monoterpene concentration is shown.”

Page 14617. line 14-19: There is no specific statement linked to the manuscript data in the sentence “Further ambient terpene concentrations were reported for Greece (Harrison et al., 2001), the Amazon (Rinne et al., 2002), Duke Forest and Oak Ridge in USA (Stroud et al., 2005; Fuentes et al., 2007), where Oak Ridge employed the highest isoprene mixing ratios among the sites noted here.” If this is meant to reflect all ambient VOC data in all other ecosystems, I am sure there are more . . .

Page 14616, line 6: replace “While in June the highest concentrations was found . . .” by “While in June the highest concentrations were found . . .”

Page 14617, line 7: suggest “. . ., indicative of different sources contributing to individual monoterpene species.”

C5106

Page 14617, line 9: omit one "of"

Page 14618, line 3: add "tree" in front of "species" to omit mix-up with monoterpene species.

Page 14618, line 7: suggest "The seasonal variability of both isoprene and monoterpene concentrations in the canopy is high, as expected from variability of plant physiological activity". As mentioned above, observed CO<sub>2</sub> fluxes might help here to support that.

Page 14618, line 9: suggest to replace "...the relative contribution of different biogenic sources to ambient terpene concentrations is changing substantially." by "... the biogenic source attribution of individual monoterpene compounds changes substantially."

Page 14618, line 13: omit comma after "even though"

Page 14618, line 19: omit "the" in "... during the most time of the year"

Page 14619, line 2: please briefly explain here what is meant by "an asymmetric seasonal variation".

Page 14619, line 17: add comma after "to do so"

Page 14619, line 18: suggest to replace "source location" by "source attribution"

Page 14619, line 27: concerning the sentence "Furthermore, Eerdeken 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 Eerdeken 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

C5107

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.

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).

Page 14620, line 24: replace "the biogenic source" by "plant foliage source" or something similar, as the soil can also be attributed "biogenic".

Page 14621, line 2: replace "on the top ..." by "at the top ..."

Page 14621, line 3: the "exception" is not the 3-carene, but rather the month of January: Suggest "An exception of this pattern was the month of January, when the 3-carene contribution dominated at all heights"

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  $\alpha$ -pinene", as in the following only limonene is being discussed.

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

C5108

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 lead to assume rather low variability in temperature close to the ground.

Fig. 2: add a blank between “m” and “s-1” in the y-axis annotation

cited literature:

Monson R.K., Harley P.C., Litvak M.E., Wildermuth M., Guenther A.B., Zimmerman P.R. & Fall R. (1994) Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves. *Oecologia* 99, 260–270.

Harley P.C., Litvak M.E., Sharkey T.D. and Monson R.K. (1994) Isoprene emission from velvet bean leaves – interactions among nitrogen availability, growth photon flux-density, and leaf development. *Plant Physiology* 105, 279–285.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., and Kesselmeier, J. (2004) Strong correlation between isoprene emission and gross photosynthetic capacity during leaf phenology of the tropical tree species *Hymenaea courbaril* with fundamental changes in VOC emission composition during early leaf development, *Plant Cell & Environ.*, 27(12)

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