

Interactive comment on “Day-time concentrations of biogenic volatile organic compounds in a boreal forest canopy and their relation to environmental and biological factors” by H. K. Lappalainen et al.

Anonymous Referee #1

Received and published: 7 May 2009

1.General comments The data presented in this paper show very well the seasonal behavior of isoprenoids and some oxygenated VOCs in the canopy of a Scots pine forest. It is very interesting to observe the link of these emissions with micrometeorological parameters (Temperature, PAR, Precipitation) and physiological parameters (GPP, photosynthetic capacity S, Total ecosystem respiration, Stem growth, Budburst). I found the explanation of the results and the discussion in general correct, but in some cases the discussion is very difficult to understand. Sometimes I found nonsensical explanations (see specific comments). There are several references that do not correspond with the discussion. In a few cases the English is not correct and some sentences are almost impossible to understand. Verbs are missing and there are several

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spelling errors, which is inexcusable given modern spell-checking technology. From the scientific point of view it would be very interesting for the next work to be combined with enclosure measurements in tree branches and in the soil to understand better the sources of BVOCs that reach the canopy.

2.Specific comments

The discussion should be revised more carefully at several points. For example in page 6257 line 17-20, the explanation given for the lower seasonal concentration levels at your site in comparison with those reported in Karl et al., 2003 could be correct, but what is the link between monoterpene emissions and methanol emissions? Why should be methanol emissions of Scots pine lower than those of aspen species? Please discuss again this point with reference to the literature, if possible.

First you mention that it is difficult to distinguish between the effects of the onset of photosynthetic activity and snowmelt in the measured concentrations (page 6259 line 6-8) and in the conclusion (page 6266, line 5-6) you assume that you found a soil emission produced from snowmelt. You should formulate it carefully!

Did you measure only m/z 137 for the monoterpene quantification? Is it known that monoterpenes are mainly detected at m/z 81 and m/z 137 (de Gouw 2003; Holzinger et al. 2000; Tani et al. 2003). m/z 81 can yield 67 % of the monoterpene signal at 130 Td (Holzinger et al. 2000). Other E/N values have been described by Tani et al., 2003.

I do not agree with the discussion in section 3.3 “Factor effecting BVOC concentrations in a boreal forest”. You mention that air temperature influences the BVOC emissions by effecting photosynthetic capacity and thereby the biosynthesis of isoprenoids. This could be the case, but as you said, all BVOC correlates mainly with air temperature and not with GPP. For me, it seems to be an emission mainly derived from the volatility of the compounds from storage pools. But you explain that the reason for the lower correlation between monoterpene emissions and air temperature in comparison with other compounds, are due to emissions coming from storage pools. I do not understand your

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discussion.

Sometimes sentences are not clear (English!) and citations were not correct (see technical corrections).

3. Technical corrections

You should numerate all the lines in the paper continuously and not start by 1 in every page. This would avoid confusion at the time of correction.

Page 6248 Line 9: Repetition of “during”

Page 6249 Line 12: I would not mention stomatal closure/opening. Stomatal closure/opening does not affect emissions of all BVOC. I would mention PAR. Line 15-17: The second point that you mention is not correct. Emissions of biological sources also affect concentrations in the air! You should rephrase the sentence. Line 28-31: The citation of Jardine et al., 2008 is not correct. In this paper acetone is not mentioned and the metabolic route of acetaldehyde is not explained. Jardine et al., 2008 explains that the metabolism of Acetaldehyde in plants is unclear and explains only the case of flooding, but other routes are not mentioned. The example that you mention in line 29 of page 6249 and line 1 of page 6250 about the production during light-dark transitions is from Fall et al., 2003. The second production way that you mention during root anoxia is explained in Kreuzwieser et al., 2004. The last production way that you mention is correctly cited. You have to correct the citations.

Page 6250 Line 7: You say: “these emissions”. Which emissions are you talking about? All BVOC? You should specify. Line 11: It is not clear what do you mean with “these factors”. Are you talking about the environmental changes? Please specify. Line 17: I do not understand very well why you cite Fall et al., 2003 at this point. Fall et al., 2003 describe the metabolism of acetaldehyde, acetone and methanol, but has nothing to do with the description of the PTR-MS method. You should put the citation of Lindinger et al., 1998 in line 16 after compounds. Line 17-19: References are missing.

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Page 6252 Line 8: Is the year of publication for Ruuskanen 2009 or did you forget to mention Ruuskanen 2008 in the references?

Page 6255: Line 19-20: Which parameter value do you mean? TT or TT and S? Please specify. Line 22: Spelling: “at” instead of “a”

Page 6256 Line 14-15: What do you mean with this sentence? It is not clear enough! Why do you cite Seco et al., 2007? If I understood well, you mean that Methanol may be produced in the atmosphere through atmospheric secondary production. But in Seco et al., 2007 I do not see any comments on this topic. Line 17: Spelling: The sentence has no meaning, “Our measurements were made at the top canopy level where atmospheric mixing in high during day time. . .”? Do you mean “mixing is high”? English!

Page 6257 Line 21-23: The dates between 26th of February and the 31st of May are discussed, but in the figure 4 the data showed are from 15th of March to August 2007. Where are the data between the 26th of February and the 15th of March? When you said correlated; is it a linear correlation? Please mention it. You should also show the line in the figure 4.

Line 25: How can you talk about high emissions in spring time? As I read above, except from the winter values, you report the lowest emissions in spring and if you compare with literature they are quite low. I would skip the word “high” and I would just say “measured concentrations” or “increasing concentrations during spring” if you want to enhance the increasing trend.

Page 6258 Line 9: Spelling: beginning Line 17: I do not agree with the citation of Seco et al., 2007 in this case. I think for example Schade and Goldstein 2001 would be more adequate.

Page 6259 Line 4: Citation of Loreto et al., 2008 is not correct. In the paper of Loreto et al, 2008 there is no mention of soil emissions after the end of the snow. Please revise

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again the literature cited.

Page 6260 Line 28: 0.8 ... 0.2 ppbv. I do not think that ... is correct.

Page 6262 Line 3: Spelling: "then" is not correct. You should write "than"

Page 6263: Line 5: Why do you cite Seco et al., 2007? Seco et al., 2007 report oxygenated VOCs and you are discussing monoterpenes.

Line 7: You should mention that the suggestion of Fischbach et al., 2002 was for *Quercus ilex*.

Line 9-11: Sentence not clear. You mixed two different things and it is difficult to understand what you mean. I would write: "The decrease of concentrations could also be quicker at high temperatures or due to chemical reactions with..."

Line 28: Citation is not correct. The paper that you mean is not Penuelas and Lucia 2006 but Penuelas and Llusia, 2004. Or is there a paper from 2006 that you did not mention? Be careful with the spelling!

Page 6264 Line 1-2: I would change "intermediate" for "product". If you use intermediate it could create confusion.

Line 8: Spelling: concentrations

Line 13-15: Rephrase this sentence. Not clear! Line 15: Please specify which compound are you talking about, VOCs or which VOCs?

Page 6265 Line 3: "was 24 and XX percent" a number is missing!

Line 16: Again citation is not correct. The paper that you mean is not Penuelas and Lucia 2006 but Penuelas and Llusia, 2004. Or is there a paper from 2006 that you did not mention? Be careful with the spelling!

Line 19: Please note that the citation should be in brackets.

Page 6266: References are not in alphabetical order and I found spelling errors as I
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mentioned above.

Table 3: Are these data also day-time medians? Please specify!

Figure 1: What do you mean with fields? Agricultural fields or pasture? A "field" can refer to many different things.

Figure 3: Did you make the monthly mean of the day-time medians? I did not see the standard deviation of the means for each month; that would give a better view of the real difference between the months.

Figure 4: Where is the regression line you talk about?

Figure 5: The uncertainty in the analytical determination of the concentration of each compound is missing.

Figure 6: Specify which the first temperature is. Is it air temperature?

Figure 7: Spelling on the y-axis: Monoterpene

Literature:

de Gouw, J. A., et al. (2003). Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002. *Journal of Geophysical Research*. 108: 4682, doi:4610.1029/2003JD003863

Holzinger, R., Sandoval-Soto, L., Rottenberger, S., Crutzen, P. J. and Kesselmeier, J. (2000). Emissions of volatile organic compounds from *Quercus ilex* L. measured by Proton Transfer Reaction Mass Spectrometry under different environmental conditions 2. *Journal of Geophysical Research-Atmospheres*. 105: 20573-20579

Tani, A., Hayward, S. and Hewitta, C. N. (2003). Measurement of monoterpenes and related compounds by proton transfer reaction-mass spectrometry (PTR-MS). *International Journal of Mass Spectrometry*. 223: 561-578

