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Atmospheric Chemistry and Physics Discussions

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.

H. K. Lappalainen

hanna.k.lappalainen@helsinki.fi

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Author Comments on behalf of all co-authors.

We thank the two anonymous referees for their constructive comments and suggestions. In the revised version we have tried to take care of the technical and language issues and to clarify the text. We have also corrected the figures and tables as suggested. Below are our responses to the specific suggestions and comments.

Anonymous Referee #1

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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 that those of aspen species? Please discuss again this point with reference to the literature, if possible.

We have removed the earlier sentence concerning a link between monoterpene emissions and methanol emissions. We added one reference (Karl et al 2005), where emissions from a conifer stand with deciduous understorey vegetation (Duke Forest) were studied. Also there the methanol emissions were 5-10 times higher than at our site. We have clarified the reasons for the difference between our site and the two other sites: the difference in methanol concentrations (and emissions) may originate from species-specific differences in canopy methanol production, and/or lower methanol production from decaying plant material in boreal conditions.

Reformulated: "In the autumn, the median monthly day-time methanol concentrations were around 1 ppbv, in spring 0.5 ppbv and in summer around 2 ppbv (Fig. 3). These concentrations were clearly lower than those reported for a mixed hardwood forest in the US (4, 8, 10 ppbv, respectively; Karl et al., 2003) or in the Duke forest in a loblolly pine plantation (5.8 ppbv) (Karl et al., 2005). The lower seasonal concentration levels at our site are most likely related to the species composition and other site-specific factors. Hyytiälä observation site is dominated by Scots pine, while the mixed hardwood forest was dominated by aspen species, and the Duke stand also had some sweetgum as understorey growth. Significant differences may exist among plant species in their methanol emission capacity, due to e.g. differences in the fraction of cell walls and pectin content of leaves (Galbally & Kirsten 2002). Also, in a temperate ecosystem the

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emissions from decaying plant material (Warneke et al. 1999) may be larger than in a relatively cool boreal coniferous stand."

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!

These two incidents are occurring at the same time, and therefore their separation is rather difficult, unfortunately. We have removed the conclusions related to soil from page 6266, line 5-6.

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.

True, monoterpene fragmentation has to be taken into account in concentration calculation. As described by Taipale et al. (2008), we calibrated the PTR-MS for monoterpenes using both M81 and M137 separately. We chose to use M137 because the effect of interfering compounds and fragments on M81 tend to be higher. However, the hourly average concentrations derived from the M81 signal agreed well with those calculated from M137 (see Taipale et al., 2008).

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

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We suggest that the variation in correlations between temperature and concentrations of e.g. monoterpene or isoprene may reflect the complex relationship between VOC synthesis and storage. The storage pool turnover rates depend on the physicochemical nature of the compound and on the structural factors of the storage. If the storage is located in the leaf liquid compartments (such as for example methanol), then the emission may be more directly related to temperature than in the case when the storage is in lipid phase and/or in structurally isolated compartments (such as many monoterpenes) (Copolovici & Niinemets 2005). This may be reflected in the temperature correlation coefficients of concentrations. This has been clarified and the Chapter 3.3. has been revised.

3.3 is reformulated:

"Of the environmental factors (air temperature (T_{air}), soil temperature (T_{soil}), radiation (PPFD), photosynthesis (GPP) and total ecosystem respiration (TER) (Fig. 6), all the studied BVOC concentrations correlated best with day-time air temperature (Table 3). Also the correlations between BVOCs and biological factors (GPP and TER) were always weaker than the correlation with T_{air}. Soil temperature failed in explaining the concentrations especially in spring (frost) and during the summer drought (low soil water content). Weaker correlations between BVOC concentrations and GPP were particularly evident during the summer drought.

The terpenoid emissions are often presented as a function of temperature alone (monoterpenes) or temperature together with light intensity (isoprene) (e.g. Monson et al., 1995; Guenther et al., 1995). We found that if the BVOC concentrations in our boreal pine forest stand are explained by one environmental factor, air temperature (t) was the best. The concentrations were best described by an exponent function $y=ae^{(bt)}$ (Fig. 7). In general the temperature dependence functions of terpenoids and other compounds were quite similar. This was not a surprise because their concentrations were significantly correlated with each other. The temperature relationship could explain 65–67 percent of the variation in methanol, acetone and isoprene concentra-

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tions (see Fig.7). For acetaldehyde and monoterpenes the degree of explanation was 24 and 29 percent, respectively. This low value may result from the different biosynthesis and emission pathways of these compounds. Acetaldehyde emissions are in many cases related to stress responses (Fall, 2003), which implies other regulatory factors besides temperature. In our case e.g. the periodic drought could have been stimulating the emission of acetaldehyde.

Monoterpene concentrations had several distinct peaks, which did not follow the temperature response pattern of the rest of the monoterpene data. Monoterpene emissions from the coniferous foliage may originate from both de novo synthesis and permanent storage pools (Shao et al 2001, Ghirardo et al 2009). Therefore, the emissions are probably regulated by several factors. In a short term, temperature has an effect on the diffusion and the equilibrium coefficients between storage pools (Copolovici & Niinemets 2005). However, the storage pool turnover rates depend also on the physical location and structure of the storage. If the storage is located in the liquid compartments (such as for example methanol or acetone), then the liberation of molecules from the storage may be more directly related to temperature than in the case when the storage is in lipid compartments or in specialized storage structures (such as most of the monoterpenes).

Air temperature is the driving factor behind biological activity in a long time scale (Hari and Kulmala, 2008). In addition to its direct effects through volatility, air temperature influences the BVOC emissions indirectly, by affecting leaf development and photosynthetic capacity and thereby also the biosynthesis of volatile compounds. Gray et al. (2006) used a variable describing thermal history to model the emissions of methyl butenol (MBO) from ponderosa pine foliage, in order to correct for seasonal changes in the standard emission capacity. This approach proved useful for MBO, but for other compounds it has not been properly tested. Our data suggest that also for methanol, acetone and monoterpenes some longer term temperature influence could be important. The specific role of temperature history and foliage development in the unfore-

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seen high BVOC emissions during springtime warrants further studies, which are only possible with this kind of long time series of data. “

Technical corrections

You should numerate all the lines in the paper continuously and not start by 1 in every page.

The line numbering was generated by the Editor’s Office.

Page 6248 Line 9: Repetition of “during”

Corrected.

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.

“stomatal closure/opening, stress, temperature etc” is replaced by “PAR, temperature, stress”

Page 6249 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.

The aim of this paragraph is introduce the multiple aspects affecting the BVOC air concentrations: biological source (=The first), atmospheric chemistry and long-range transport (=The second). This is also an argument for using the wind rose analysis.

Revision: “Second, there are the factors affecting the measured concentrations in the air such as the chemical reactivity of a substance, the long range transport and the mixing of the atmosphere” is replaced by “Second, the air concentrations are also affected by the chemical reactivity of a substance, the long range transport and the mixing of the atmosphere”.

Page 6249 Line 28-31: The citation of Jardine et al., 2008 is not correct. In this paper

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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.

The citations are corrected as suggested. Jardine et al., 2008 deleted and replaced by Fall 2003, Kreuzwieser et al. 2004 added.

Page 6250 Line 7: You say: "these emissions". Which emissions are you talking about? All BVOC? You should specify.

Corrected: "these emissions" -> "the isoprene, monoterpene and methanol emissions"

Page 6250 Line 11: It is not clear what do you mean with "these factors". Are you talking about the environmental changes? Please specify.

Corrected: "these factors" -> "environmental factors together with plant physiological status"

Page 6250 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.

Lindinger et al., 1998 corrected as suggested. In the end of Fall 2003 paper he discusses new possibilities of long-term PTR-MS measurements.

Page 6250 Line 17-19: References are missing.

Fall 2003 is a correct reference here.

Page 6252 Line 8: Is the year of publication for Ruuskanen 2009 or did you forget to

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mention Ruuskanen 2008 in the references?

The correct year is 2009. This is corrected.

Page 6255: Line 19-20: Which parameter value do you mean? TT or TT and S? Please specify.

"Parameter values" corrected as "Parameter values (onset date for the temperature sum accumulation, critical temperature sum threshold)"

Page 6255: Line 22: Spelling: "at" instead of "a"

Corrected.

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.

Seco et al., 2007 removed and replaced by Legreida et al. 2007: Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zurich (Europe): Seasonal variation and source allocation, Atmospheric Environment 41, 8409–8423.

Page 6256 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"?

Corrected in -> is.

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.

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"26th of February" is corrected "15th May". The correlation coefficients (linear) are removed from the Fig. 4. and added to the text.

Page 6257 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.

This is corrected as suggested "increasing concentrations during spring".

Page 6258 Line 9: Spelling: beginning

Corrected.

Page 6258 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.

Corrected. Seco et al., 2007 replaced by Schade and Goldstein 2001.

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 again the literature cited.

Line 4 removed.

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

Corrected: 0.8.-2.2 ppbv (in the manuscipt it is 0.8. . . 2.2 ppbv?)

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

Corrected.

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

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Corrected as: 'The high concentrations during the drought could also result from emissions from the soil and litter (Asensio et al., 2007; Leff & Fierer 2008)

Leff, J.W. & Fierer, N. 2008: Volatile organic compound (VOC) emissions from soil and litter samples. Soil Biology & Biochemistry 40: 1629–1636.

Page 6263 Line 7: You should mention that the suggestion of Fischbach et al., 2002 was for Quercus ilex.

Quercus ilex is added.

Page 6263 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: : :."

Sentence is reformulated as following "The decrease of concentrations could also be enhanced by high temperatures and the chemical reactions with O_3, OH and NO_3 in the air (Atkinson and Arey, 2003)."

Page 6263 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!

Corrected as follows: Penuelas, J. and Llusià, J.: Plant VOC emissions: making use of the unavoidable, TRENDS in Ecology and Evolution, 19, 402-404, 2004.

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

Corrected: "intermediate" -> "product"

Page 6264 Line 8: Spelling: concnetrations

Corrected: - > concentrations

Page 6264 Line 13-15: Rephrase this sentence. Not clear! Line 15: Please specify

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which compound are you talking about, VOCs or which VOCs?

Chapter 3.3. is rewritten.

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

Chapter 3.3. is rewritten. (XX=29)

Page 6265 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!

Chapter 3.3. is rewritten incl. references.

Page 6265 Line 19: Please note that the citation should be in brackets.

Corrected.

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

Reference List is corrected.

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

Day-time added.

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

"field" replaced by "agricultural field"

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.

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Corrected. Standard deviation of the means for each month added.

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

The figure text is edited and the correlation coefficients are removed. The Fig.4 demonstrates that in the spring the S is related to the BVOC concentration (running mean) but in summer it does not correlate anymore.

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

Here we refer to Taipale et al 2008. The following detection limits were added to the text (Material and methods, BVOC measurements): M33 300 pptv, M45 76 pptv, M59 74 pptv, M69 53 pptv and M137 46 pptv.

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

"Air" added.

Figure 7: Spelling on the y-axis: Monoterpene

Spelling corrected.

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Anonymous Referee #2

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Comments

P6252 Did you only use M137 to calculate monoterpenes? If so, discuss why you did not also use M81 and the related uncertainty (e.g., Rinne et al., 2007).

This has been clarified in the text. As described by Taipale et al. (2008), we calibrated the PTR-MS for monoterpenes using both M81 and M137 separately. We chose to use M137 since the effect of interfering compounds and fragments on M81 is probably higher. However, the hourly average concentrations derived from the M81 signal agreed well with those calculated from M137 (see Taipale et al., 2008).

P6258. The budburst of birch does not seem to be a likely explanation for the peak in methanol given that birch accounts for less than 1% of the trees in the area.

P6261. Again how relevant is the leaf area of deciduous trees when they represent a very small fraction of the trees?

The budburst of birch is used here as a proxy for the vegetation growth period. It correlates well with the overall progress of the growing season at the stand.

The atmospheric lifetime of methanol is several days. The measured methanol concentrations in a pine stand may include the transported concentration from the nearby mixed forest areas.

We have also added a new reference: "Hannu Ilvesniemi, Janne Levula, Risto Ojansuu, Pasi Kolari, Liisa Kulmala, Jukka Pumpanen, Samuli Launiainen ,Timo Vesala and Eero Nikinmaa 2009. Long-term measurements of the carbon balance of a boreal Scots pine dominated forest ecosystem. Boreal Env. Res. 14: xx-xx, in print." In this paper the stand characteristic is evaluated and new information on the species distribution is

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provided. The share of broadleaved trees is unexpectedly high. In the class “trees with DBH<5 cm” the broadleaves are the most common, but in the “class with DBH>=5 cm” pine and spruce species are dominant.

P6261, L11. What is the correlation between isoprene and S as reported for methanol and acetone?

The correlation was weak for the growing season (spring-summer) period but was high during the spring. The text was modified.

P6261-6262 I am not convinced by the discussed relationship between tree-stem diameter and isoprene. There are other periods where they appear almost anti-correlated.

The apparent anti correlation between isoprene concentration and stem diameter in July-August is due to the drought induced stem shrinkage. This was clarified in the text.

P6263. Have such high monoterpene concentrations in March been reported previously? This is an important time for particle formation at this site so deserves more discussion.

Tarvainen et al. 2005 and Hakola et al. 2006 report high monoterpene emission rates in March and April at the same site. Text and citations added to the page.

P6266. The evidence for a soil source of VOCs is limited. Either provide more evidence or remove from the conclusion.

“Some evidence of contributions of rarely studied soil emissions on atmospheric concentrations of VOCs were detected, in particular during springtime when the compounds accumulated into or below snow pack were released.” Removed from the conclusions.

Minor comments

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P6252 What is the status of the Ruuskanen et al., ACPD paper?

Ruuskanen et al., 2009 has been published Atmos. Chem. Phys. Discuss., 9, 81-134, 2009 www.atmos-chem-phys-discuss.net/9/81/2009/ and will be corrected for ACP by 31.5.2009.

P6253, Line 21. Define TDR

The time domain reflectometry (TDR) is added.

P6265, L3 Missing number

The chapter 3.3. is rewritten.

Editorial corrections:

P6253, L27-28 corrected: exchanges -> exchange, end - > in the end,

the significant - > a significant

P6255, L22 corrected: a -> at

P6256, L17 corrected: in -> is

P6256, L26 corrected: According to information from local forestry authorities, several forest fells and other harvesting operations

P6258, L29 High concentrations of methanol -> High concentration peaks of methanol

P6260, L19 a mix -> a mixed

P6260, L28 line is removed (Ref #1 comments)

P6263, L10 fasten - > be enhanced

P6264, L8 corrected: concentration- > concentrations

Table 1. Are these local time?

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Yes these are local time. This is added to Table heading text.

Fig. 5: Missing "-" in caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 6247, 2009.