**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "BVOC ecosystem flux measurements at a high latitude wetland site" *by* T. Holst et al.

T. Holst et al.

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Please find now our responses to the referees and their comments. We would like to thank all referees for their constructive criticism and the detailed suggestions they have made. We have revised the manuscript accordingly. In addition, we have restructured the text substantially, since reviewer 2 was correct about the lack of clarity in some parts of the text. This affected mainly the (former) sections 3.3 and 3.4, and we describe the chief structural changes in our response to reviewer 2, below.

1) J. Vila (Referee) Abstract - Line 20: What do they mean by some nocturnal deposition? Please clarify it. It is also mentioned loosely at page 21145 (line 28).

We rewrite the sentence in the abstract as "...and during most nights small negative fluxes directed from the atmosphere to the surface were observed. " Later on in sec-

tion 3.4.2 we revise as "While night-time fluxes of isoprene were virtually zero, fluxes of methanol at night reached ca. -30 μg C m-2 h-1 (Figs. 7D, 9B), thus indicating a flux directed to the surface. As methanol is water soluble, one could speculate if condensation and deposition on dew-wetted surfaces or water patches at the wetland site could, besides oxidation processes, explain this behaviour (Seco et al., 2007)." As discussed, there is the possibility of interactions between moist surfaces and methanol but since methanol fluxes at night were small overall we hesitate to draw definite conclusions. Finally, the statement in the conclusion section was changed into "...and negative fluxes directed to the surface layer appeared to occur at night."

Introduction -Line 15-20: The authors stressed the dependence of BVOC emission to biological and chemistry. In my opinion, the influence of meteorological factors, for instance boundary layer development, clouds, turbulence-canopy interaction, etc; on the BVOC emission is also not well studied and it exerts a strong influence on the emission levels. Could the authors comment on this effect?

The reviewer is in principle correct in that boundary layer height and within-canopy re-actions are important aspects for BVOC-atmosphere interactions. But in our view these are not crucial in context of our analysis. In case of isoprene and methanol, the within-canopy reactions are not important since their atmospheric reactions times are many times longer than the turbulence transport time. Thus the measurements made above the canopy are in principle representative for the surface emissions (by contrast, for instance, to sesquiterpenes, and some monoterpenes which react so rapidly after emission that they can only be detected with difficulties by above-canopy measurements). We have discussed this and added a paragraph about the reaction times in section 3.1 to the source area discussion (last paragraph; see also reviewers comments to the result-section later). As for boundary layer development, clouds, etc; Clouds, of course, affect emissions, particularly in case of the light-dependent production rate of isoprene. Boundary layer development as such should not have a direct effect on the canopy production and emissions (other than by affecting the local micro-climate). The

truly crucial aspect (and indeed poorly understood) in BVOC-CBL interactions is in atmospheric chemistry modelling, when the emissions from the surface need to be mixed correctly into the near-surface layer to obtain proper values of concentration. And for this the growth rate and height (or volume) of the CBL indeed becomes critical. In our analysis, we deal, however, mostly with the controls on emissions on the canopy scale. Therefore, we prefer not elaborate on these additional aspects in the manuscript to avoid it loosing its focus. However, to clarify some of the points we introduced changes to the Introduction and later in the text we have also add some discussion about CBL development and its feedback to the BVOC concentrations measured (section 3.5).

Methods Experimental site - Line 1-15. I will include here information on the canopy height (it is included at page 21144) and the roughness length of the site. Is the roughness length equal for all the wind directions?

We have done as the reviewer suggested and added a paragraph with a short explanation on canopy height, leaf area index, roughness length and canopy development to the site description in section 2.1.

- Page 21137. Line 15. The flux measurements are averaged over a period of 30 minutes. Is this period adequate? What about the contributions of low frequencies to the fluxes? At section 3.2.3., it is mentioned the use of Ogives. From this spectral analysis, it is possible to retrieve the averaging time to calculate the fluxes depending on the turbulence and atmospheric characteristics.

Ogives are difficult to be using with disjunct data sets since spectra need to be calculated from a continuous time-series (see also the comment on page 21142, l. 3-5, section 3.2.3: " However, as a spectrum can not be calculated from a disjunct time series, this technique could not be used in our study to estimate damping effects."). To elucidate the possible influence of integration periods, we tested effects of varying the averaging periods on the calculated fluxes, using 15min, 60min and 120 min integration periods. Effects were only small and we therefore decide to keep the 30minute period

as one of the "standard" periods used in eddy covariance, and added a new paragraph (in section 2.3) to report about these tests.

Results and discussion - Page 21138. Line 21-25. Could the authors specify quantitatively the time scales of turbulence and chemistry for the different reactants?

We specify example lifetimes for oxidation in the atmosphere and compare it to the time scales of turbulence, and add a paragraph on this to section 3.1: "The time scale for vertical mixing above the canopy after emission at the surface, $t_{mix} = z/u*$ (Rinne et al. 2007) was less than 10 seconds in most cases for the data presented in this study. Rinne et al. (2007) concluded for measurements above a Scots pine forest and based on a transport model with chemical degradation, that isoprene had a lifetime of at least 27 minutes during day and about 5 hours during nights while methanol had a lifetime of 2 days. According to their results, the effect of chemical degradation on the fluxes measured was about 10% for monoterpenes, which have lifetimes comparable to isoprene, and much less for methanol."

- Section 3.2. As mentioned previously, I miss here some comments on the role of low frequencies on the flux calculations.

See our response above, response to the averaging period of 30minutes (added paragraph at end of section 2.3).

- Section 3.3. Were clouds observed during the measurement period?

Days with intermitted cloud, or mostly overcast weather can be identified from Figure 6. We revised beginning of section 3.3 to refer to the presence of cloud conditions.

- Page 21146. Line 1-25. It will be very enlightening to show a comparison of the daily evolution of the measured fluxes against the flux calculations. Figure 11 shows BVOC measurements at four different periods. How did the flux algorithms with the three different assumptions compared with the observed fluxes?

The primary purpose of this paper is to report on the measured fluxes from an envi-

ronment where this kind of information is scarce/non-existent, and to demonstrate the general performance of the disjunct EC flux technology as used in our set-up (see last sentences of the Introduction). The simple model analysis in this paper provides an initial investigation whether widely used algorithms also hold in this extreme northern environment from where only very limited information on canopy BVOC fluxes is available. To do so, the entire data set was used to fit the models. The inset in Figure 9A, shows comparison between measured and modeled fluxes obtained by the non-linear fitting routine. A forward model run, as suggested here by the reviewer for model evaluation, but would have -at the very least- required to split the data set into a "fitting" and an "evaluation" data set. Due to the limited period covered, and the inherent statistical scatter in half-hourly flux measurements this would have been difficult. Moreover, a visualization as suggested by the reviewer would involve 4 periods X 3 model assumptions = 12 lines and can not be included by simply adding another panel to the Figure, it would require an additional Figure to be included, and to also lengthen the Discussion on the modelling results considerably. We agree with the reviewer that the simulation of isoprene flux time-course over the season is an interesting objective in itself, but we feel that it pushes the scope of this current paper too far from its initial purpose; it will be included it for latter analysis in a follow-up manuscript.

- Page 21148. Line 21148. I will include at figure 11, the daily evolution of the sensible heat flux and latent heat flux. By so doing, the data set will be more complete allowing future studies of the role of surface and boundary layer dynamics on BVOC compounds. At least, I will be personally interested (see de Arellano et al, ACPD 9, 4159-4193, 2009).

According to the comments of the reviewer we have included a figure (fig. 7, panel E) showing the diurnal course of the sensible flux H. However, latent heat fluxes are unfortunately not available for now to be included in this ms, as the latent heat flux was not measured by our set-up. However, we hope to be able to include it in the forthcoming paper, as a second EC system was installed at the site, but these data sets need to

be combined first using i.e detailed footprint analysis before drawing any conclusions. The PTR-MS is able to measure a water cluster ion, which is fragmentated within the reaction tube of the instrument. The count rate of the water cluster ion is known to be closely related with ambient humidity (see last paragraph of section 2.2.; Ammann et al. 2006, de Gouw & Warneke 2007) and potentially could be used to derive the latent heat flux as well. But as this relation is dependent on the performance and the specific settings of the instrument, it will need to be analysed and compared first using data of latent heat flux of a different system. Otherwise, the calculated latent heat flux would be highly speculative, and we prefer not to use this information now.

- Figure 12. The discussion here can be more elaborated. For instance, I see that for the same period I, different values of the isoprene flux are observed for the same range of sensible heat flux values (between 100-150 W/m2). Is there any explanation?
- In view of the discussion at page 21146 (lines 5-10), would it be more interesting to include and to discuss a figure of PAR versus the isoprene emissions at the different periods?

A plot of PAR vs. isoprene (and methanol) for example periods is shown in Figure 8, showing two of the four periods described in detail. We don't think that an extra figure is needed to show the other periods as well, as in the latter period IV almost no fluxes could be measured at all. But the reviewer is correct about the possibility to discuss the results plotted in a figure (the former Fig. 12, now Fig. 11) in more detail, also in light of the criticism raised by reviewer 2. So we added the last paragraph of section 3.4.2: " The fact that both isoprene and methanol increase linearly with H is at first perhaps surprising since the relationship with weather variables like temperature differed distinctly for these two compounds. While sensible heat flux and temperature are naturally related, the diurnal cycle of the two is dissimilar with maximum temperatures normally reached in the afternoon, when H is already past its daytime peak rates. The better correlation of H and isoprene or methanol, compared to using temperature and/or light is thus not indicative of a distinct process related to their production, but much rather to

the similarity of turbulent transport patterns. The variation in the slope, however likely reflects variation in the BVOC production rates. Since measurements of sensible heat fluxes are much more easy to conduct on an annual basis these kind of empirical linear relationships could be used for gap filling of BVOC time series, at least over short periods (hours to days) if the sensible heat-and BVOC flux data is sufficient to represent the seasonal variation that obviously exist in the slope of the relationship. In absence of more complex model analyses this would allow a simple means of extrapolating from seasonal BVOC flux measurement campaigns to growing-season budgets."

2) J. Rinne It is true that the generally used normalization conditions of T=30 _C and PPFD=1000 μmol m-2 s-1 are warmer than the conditions usual in high latitudes. However, use of another temperature, as T=20_C in this paper, makes comparison of different datasets difficult. Therefore I would recommend also presenting emission potentials normalized to T=30_C and PPFD=1000 μmol m-2 s-1.

We have included in the revised version a brief tabular overview (Table 1) over I_s at two temperatures, which should facilitate comparison with measurements at other sites. We would like to emphasize, however, that this is purely for comparison, since to do so the relationships have to be extrapolated vastly outside the temperature range encountered in this study. We have added a new paragraph to the restructured section 3.6, which also draws attention to this issue.

3) Anonymous referee 2: From a scientific point of view, I generally do not like it when Results and Discussion are mixed, but I can still accept it as long as the contents are arranged in a clear systematic way. Especially in Sections 3.4, this is not really the case.

We have rearranged large parts of the text, see our description below.

(1) The presentation and discussion of winddirections and footprints (Sect. 3.1) is not of any use here as long as no vegetation map or other spatial information about the surroundings of the measurement site are shown (or if the surrounding area is

homogeneous). So this part should be either omitted or completed with a map showing the vegetation pattern around the measurement site.

We have updated the Figure (now Figure 1) with an indication of the "palsa" (dry) vs. wetter parts of the mire.

(2) It makes not much sense to me to discuss the BVOC concentration (especially for isoprene and methanol) before the respective fluxes are presented. Obviously there is a very strong relation between the observed concentration and fluxes of isoprene (maybe also methanol?) that should be discussed. For this purpose I also suggest to combine Figs. 6, 7, and 8 to one stacked figure. This would also facilitate the comparison of the seasonal changes in the fluxes and the environmental parameters.

In the restructured manuscript, we have moved the section with flux measurement results directly after 3.3 "Meteorol. Conditions" (Section 3.4 "BVOC fluxes"). The former figures 6-8 have been combined into one new Fig. 6, as suggested by the reviewer. The discussion of concentrations (now section 3.5) includes reference to measured fluxes (e.g., 2nd paragraph section 3.5.; 3rd paragraph section 3.5), as well as to atmospheric conditions (2nd paragraph section 3.5). We also added a Figure showing averaged diel concentrations (for all 4 compounds) for the select sub-periods (new Figure 11), similar to what was done for fluxes (Figure 7).

(3) In section 3.4, the description of seasonal and diurnal flux variation, analysis of dependencies on environmental parameters (T, T48, PAR, and H) and fitting of emission algorithms are strongly mixed. I suggest to re-arrange Section 3.4 into the following two sub-sections: 1. Seasonal and diurnal variation of BVOC fluxes, descriptive analysis (with Figs.8 and 11a-d) 2. Dependence of BVOC fluxes on environmental parameters (with Figs.9, 10, 11e/f, 12) For the second part, it is important to clearly distinguish and compare analyses of the full dataset and of selected sub-periods. I do not understand, why a standard emission factor (isoprene) for the entire period was determined but not for the sub-periods, which obviously represent different development stages of the

vegetation. It would also be helpful to mark the selected sub-periods in Fig. 6/7/8.

We agree that the first ms was a bit unfocussed in the former section 3.4. We have now, as suggested by the reviewer, divided this section into section 3.4. "BVOC fluxes" with subsections 3.4.1 "seasonal and diurnal flux variation", and 3.4.2. "dependence on environmental parameters", 3.5 "BVOC concentrations" followed by the section about the emission algorithms (section 3.6). The former figures 6-8 have been merged, to give the new figure 6 (a-f), and the sub-periods I-IV specifically analyzed in the ms have been highlighted in Fig. 6a. We also clearly marked results that have been based on analyses of the sub-periods in the text and in the figures. However, although we tried to determine a standard emission factor not only for the whole data set but specifically for the sub-periods, the non-linear curve-fitting algorithm did not show any reliable result and varied significantly as the data base for the rather short sub-periods unfortunately was too small to draw any conclusions. We agree with the reviewer that the different development stages might lead to different emission factors, and that more attention should be paid to the seasonality of emissions. However, long-term measurements are still lacking for this, but we are currently analyzing more data from subsequent years that could contribute to this problem.

(4) The site description in Section 2.1 should be improved. Some important information is missing or introduced only in the discussion (which is not adequate). - wet, semi-wet and dry areas are mentioned but it is not shown of what size and in what distance to the measurement location they are (cf. comment 1). - typical or average values of canopy height and LAI should be given - describe development of vegetation during the measurement period (growth,senescence)

We add more detail to the site description, including LAI, canopy height and vegetation development, (see also response to reviewer 1) and added a new paragraph to section 2.1 (see comment to J. Vila, above). We also changed (former) Figure 2 (now Fig. 1) which now includes more information about the general surface structure together with the footprint and main wind direction analyses.

SPECIFIC COMMENTS p.34 line 15: Explain what "palsas" are.

A palsa is the raised mound of peat typically found in areas with discontinuous permafrost. The explanation is now provided in the site description (section 2.1): "...with slightly elevated drier areas that are underlain by permafrost (called palsas) and wet, fen-like areas lacking permafrost."

p.36 line 11: I suggest to move the important information about the measurement period to the beginning of the Section.

As suggested by the reviewer, we moved the information about the measurement period to a more prominent position. It is now located at the beginning of the Methods-section (2.1).

p.37 line 10: Is the noise level at the analogue output of the PTR-MS similar or worse compared to the digital output?

The 2004 built PTR-MS used in this study normally is connected with a recording PC via RS232-output (which is analogue). Different to that, we used the analogue output directly provided at the PTR-MS electronics to synchronize mass identifier and ion counts with the sonic anemometer. However, no difference in noise level has been observed.

p.38 line 4: What fraction of data had to be rejected due to this criterion?

Less than 20%, we added this information to section 2.3 where the flux calculation scheme is described.

p.39 line 1: The meaning of this sentence is not clear. ("...60% of the measured fluxes were emitted..."?) -and- p.39 line 3: In the text, the footprint calculation is refered to "Wilson and Swaters (1991)", but in Fig. 2 to "Schuepp et al. (1990)". Which one is right? Why was the footprint calculation based on a quite old method and not a newer one? As far as I remember, the simple model by Schuepp et al. does only consider neutral conditions.

Based on the comments of the reviewer, we now referred to a "newer" footprint tool (Neftel et al. 2008) which is based on the Kormann and Meixner (2001) analytical model and changed the (new) Figure 1 (former Fig. 2) accordingly. However, the results of the footprint analysis remained the same.

p.40 line 10f. "larger eddies" and "lower frequency range" is very unspecific here. Give typical limits.

We have revised the sentence as: "...with the major part of the flux being transported with larger eddies in the lower frequency range (ca. 0.1 to 1 Hz; Foken, 2003; Grabmer et al., 2004). "

p.40 line 14f. When comparing the damping effect with literature results, it has to be considered that it strongly depends on the measurement height and the windspeed.

We added numbers taken from Spirig et al. (2005) and Lee et al. (2005) papers (section 3.2.1) to cover that issue and to compare with our set-up.

p.40 Section 3.2.2: The effect of reduced sample number in the DEC approach had been (theoretically) assessed already by Lenschow et al. (1994, "How long is long enough...", J.Atmos.Oceanic Techn.,11,661-673). It would be interesting to compare the results to this original work.

Yes, this is a very valid suggestion. We analysed our data accordingly, and a new paragraph has been added to section 3.2.2 to report on the results.

p.40 line 25f. Why are the effects for w'T' and std(w)/u* mixed here? I doubt if the analysis of std(w)/u* (this is not a flux!) can be considered as representative for the behaviour of scalar BVOC fluxes. I suggest to show instead the results for w'T' in Fig. 5!

Good point, and we use normalised w'T' in Figure 5 in the revised version of the manuscript. The results remain unchanged.

p.41 line 17-20: The quantitative contributions to the damping effect strongly depend on the instrumental setup (e.g. measurement height, tube dimensions and flow rate) and might deviate from the cited studies. At least the physical tube damping effect (by mixing in the tube flow) could be easily estimated for the present setup using theoretical transfer functions e.g. by Lenschow and Raupach (JGR, 1991).

We have done as the reviewer suggested, and add the results of this test to the text (section 3.2.3). We have also supplied a note on the influence of the instrumental setup on the damping effect before comparing with other studies.

p.42 line 18: Did the authors also look for other BVOC compounds at the site beside the mentioned 4 species (e.g. monoterpenes)? If yes, it would be useful for the community also to report on masses/compounds not found at the site.

No we did not include other compounds since we wanted to ensure that the dwell-time would be sufficiently long to capture the measured compounds sufficiently well.

p.43 line 12f. While I see the advantage of using carbon mass related units for BVOC fluxes, I do not see it for concentrations.

We prefer to use C units throughout the manuscript, for reasons of consistency, and to have the same base for between-compound comparison. In the manuscript text we refer to both C and ppb units for readers who prefer thinking in ppb.

p.43 line 14: replace "comparably" by a more specific expression.

The sentence has been revised as: "...was observed on a comparably hot (maximum temperature of 23.2°C) and sunny day (2 August), when also fluxes were highest."

p.45 line 26-29: The discussion of the relationship between methanol fluxes (deposition) and sensible heat flux is scattered in different pieces (additionally occuring on p.48 line 11f. and on p.49 line 20f.). These pieces should be combined to one focused discussion paragraph (see also general comments above).

We have clarified this issue by focusing on one paragraph in the new section 3.4.2 where we discuss the negative methanol fluxes observed.

p.46 line 16f.: Since the temperature response function CT1 is an important issue in the present study, its definition (formula of original and modified emission algorithm) should be shown here.

We added equations (2)-(4) presenting the Guenther algorithms to the restructured/new section 3.6 which contains the focused emission algorithm analyses.

p.46 line 26: How exactly is the standard emission factor "Is" defined when the dependence on T48 is included. Obviously this new standard emission factor is not comparable to the original one. I also doubt whether the dependence on T48 is a mechanistic effect or a spurious correlation here. Obviously there was a development (senescence of the vegetation during the observation period in parallel to the generally decreasing average temperatures. In my view it would be elucidating to see how the common standard emission factor (according to Guenther et al.) varies with time when fitted to different sub-periods (e.g. the four sub-periods described in the text)

The reviewer strikes an important point here - it is also in our view a principle weakness of BVOC flux modelling when done in the typical multiplicative way: how many multipliers should be added that reach the value of unity under some set of standard conditions? Still, in the absence of process-understanding we cannot offer a better emission model, and the primary aim of this manuscript in any case lies with the presentation of the methodology, rather than new model development. However, the effect of short-term weather history has been identified in a number of studies, although there is as yet no uniformly accepted parameterization in the modelling community. Guenther et al. (2006) in MEGAN, for instance, apply a very complex formula that accounts for both light and temperature and over the past 24 and the past 240h. We opt here for a simpler formulation, excluding the "long" (for instance 10-days as in MEGAN) time influence. We agree with the reviewer that in that case effects of vegetation development

could easily be confused with effects of temperature. For shorter periods, fluctuations in standard emission rates, however, can be interpreted as the short-term adaptation of enzymatic capacity to a changing environment. The T48 function we apply here was derived from repeated leaf measurements at the same field location (Ekberg et al., 2009) performed over two years, with each leaf-measurement campaign encountering warm and cool days (see their Figure 1). Therefore the shape of the function is not influenced by spurious correlation due to T48 varying with senescence. Obviously, the brevity of the text in the discussion leaves room for misunderstanding and we added a new paragraph (now in the new section 3.6) to clarify this.

p.47 line 14: rephrase to "The estimate for Is (at 20_C) obtained using the Guenther et al. algorithm..."

Done.

p.47 line 14-28: I suggest to compile the various values for the standard emission factors (both for 20_C and 30_C) in a Table. Listing the values for both standard temperature would also satisfy the short comment by J.Rinne.

We have included the tabular overview (new Table 1); see also our response to Janne Rinne, above.

p.48 line 2: "...the correlation with these ..."

Done.

p.48 line 3-5: I do not understand the meaning of this sentence. Isoprene emission is also strongly correlated with assimilation whithout being limited by stomatal conductance!

The reviewer is correct, this statement was phrased in an unclear way. We have revised as (new, restructured section 3.4.2): "It remains to be tested whether at our flux site surface- or canopy conductance, or canopy assimilation rate can aid to explain short-term variation of methanol emissions (Nemecek-Marshall et al., 1995; Niinemets et al.,

2004; Hüve et al., 2007), or (in the case of assimilation rate) those of isoprene."

p.49 line 7: explain this statement in more detail. Presumably the light distribution in the canopy depends on the LAI profile of the vegetation, for which no information is given here.

What we meant was that at the relatively low solar angle and maximum instantaneous irradiance there periods when isoprene production on canopy scale (which is what's measured) is light limited will be short. This likely is the cause for the relatively linear increase of emissions with light, by contrast to the typically observed hyperbolic saturation at high light levels. We clarified this in the text.

p.49 line 20/21: What is the possible reason (and potential use) of this linear relationship. Please discuss.

Please see our response to J. Vila, above.

p.50 line 18: "...rather than to ..."

Done.

p.50 line 21: specify: "BVOC emission responses that had been found already by ..."

Done.

Fig. 4: It is not clear, for which quantity the spectral analysis was calculated here (is it the sensible heat flux?) Explain the meaning of std(u) in the y-axis title. Is this the horizontal windspeed like in the x-axis titel?

Yes, u stands for horizontal windspeed, we have revised the Figure caption accordingly.

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