Anonymous Referee #1

Received and published: 21 June 2017

The paper by Schallhart et al. describes NMVOC flux measurements above a forested site in Finland using two PTR instruments. They calculate fluxes based on the direct eddy covariance and the indirect gradient method.

1) It is interesting that a much smaller number of actively exchanged VOCs were observed during this study than by Park et al., 2013, using similar methods for analyzing the entire mass spectrum. Is there an explanation? Was it a problem of the analysis (e.g. shifting time synchronization) or are Boreal forest generally just low (or not very active) BVOC emitting ecosystems? It appears that the measured net-fluxes are generally quite low when comparing with similar measurements from temperate and tropical forests.

A good question, we do not suspect the analysis being the cause of the discrepancy in the number of actively exchanged VOCs. The analysis was same as in Schallhart et al., 2016, where VOC fluxes with constant lag time (2.6 s) were measured above a very active (24 h net flux: 9.78 nmol m^{-2} s^{-1}) oak forest. Still in the oak forest, only 29 compounds were actively exchanged. Schallhart et al. (2016) also gives a more detailed explanation of automated method and compares this method with a manual method.

Therefore, the reason in the huge difference between 494 (Park et al., 2013), 29 (Schallhart et al., 2016) and 17 (for 21 days in June; this study) exchanged compounds must be primarily caused by the behavior of the orange yard, which seems to be a unique ecosystem. The measurement setup, e.g. shorter inlet lines as used by Park et al. (2013), can reduce the losses for heavier, stickier and/or more reactive VOCs, but cannot explain an order of magnitude difference in number of exchanged compounds. Additionally, the meteorological circumstances (PAR, T) can lead to stress responses in plants and higher photochemistry could lead to additional oxidation products.

Overall, a comparison between different ecosystems is very challenging. The flux of individual compounds are similar as in previous boreal forest measurements indicating that the measurements of ecosystem fluxes worked well.

If the oak forest and the boreal forest are compared, the difference in number of actively exchanged compounds should be mainly caused by the lower emissions in the boreal forest and fewer compounds are released in detectable amounts. The shift in lag time should have a minor effect (after the described corrections).

2) No flux footprint analysis is presented. Why? It would seem important for the interpretation of the results, especially for a site which is largely comprised of a managed forest (with clearings). I also see there is a nearby lake. Knowing the footprint might also be a very relevant issue for the comparison between the two flux methods. The analysis would also seem to be crucial for the interpretation of butanol contamination from aerosol measurements (section 3.4). The plotted wind rose suggests that a large proportion of the wind-direction is from the S-W sector, where the buildings of the research station are situated.

Thank you for your comment, we agree that footprints would be important for interpreting the results. Therefore, we added average cumulative footprints (50% and 80%) for both the EC and the SLP measurements. The average footprints were calculated from the measurement period using daytime

values (07:00 – 19:00). During night, the flux footprint would be generally larger due to stronger stable conditions, but the VOC emissions are, on the other hand, usually low.

Cumulative footprints were estimated using an analytical function by Kormann and Meixner (2001). The algorithm uses horizontal wind speed, Obukhov length, standard deviation of a lateral wind, roughness length (estimated to be ca. 1.5 m), measurement height and zero displacement height (we used a value 13 m) to determine the footprint function. According to Horst (1999), footprints are similar for both the EC and the SLP methods if the measurement heights are equal. Therefore, we used the same algorithm also for the SLP fluxes.

Determined footprints have error sources and thus the results should be taken as estimates. The nominal measurement height of the SLP fluxes was 36 m (for unstable stratification). However, we used the height 33 m because horizontal wind measurements were available from that level. This underestimates slightly the footprints. On the other hand, Kormann & Meixner algorithm excludes an effect of roughness sublayer which leads to an underestimation of the turbulent transport and thus overestimates the cumulative footprints.

3) m/z 93: While this mass is commonly shown to be associated with toluene using PTR ionization, there is evidence that a fragment from cymene can exhibit some interference (e.g. 20-30%) above evergreen forests. Have the authors verified that this is not the case – e.g. by correlating fluxes or concentrations of the corresponding ions? I also wonder whether benzene fluxes were detectable, and whether benzene to toluene (concentrations and/or fluxes) ratios could indicate local pollution.

We agree that para-cymene can influence the signal and stated it in the end of Sect. 2.2. With the E/N used in this study, over 80% of the para-cymene signal should fragment to 93.0699 Da (Tani et al., 2003). Our intention was to name each signal depending on the mass where it was measured and discuss the possible compounds in Sect. 2.2. However, we realize that this can lead to misinterpretations and therefore will rename all signals measured at mass 93.0699 from toluene to toluene & p-cymene.

The correlation between the p-cymene (135.1168 Da) and toluene & p-cymene (93.0699 Da) concentration was 0.79. Due to the small fluxes of p-cymene (135.1168 Da), the 30 min files (used for the correlation) were influenced by noise, leading to a correlation with toluene & p-cymene (93.0699 Da) beneath 0.3.

Benzene fluxes were not detected and the average toluene & p-cymene/ benzene concentration ratio in June was 1.26 (standard deviation: 0.51). . The toluene/benzene ratio from fresh anthropogenic plume is 4.25 (Warneke et al., 2007) and in the order of 2 for fresh traffic and the ratio goes down as the air mass is oxidized during transported from the source (Gelencsér et al., 2007) indicating that the source is not dominated by local anthropogenic or traffic sources.

4) Section 3.2. While being a valuable section, a number of studies are missing here – it would benefit the manuscript to conduct a more thorough literature review.

We thank the reviewer for this comment. The aim in this paper is to give an overview over the relative new and few already published studies, where no preselection of VOCs had to be made and, therefore, all VOCs with a flux above the detection limit (excluding instrument related signals) are reported. Thus the literature of VOC fluxes was focused on comparing EC fluxes measured with PTR-TOF that can scan the full range of VOCs emitted, instead of studies with a preselected set of studied compounds, typically 10-20 masses with the DEC fluxes using the PTR-Quad. Furthermore, we omitted publications which use less than four days of data (e.g. Ruuskanen et al., 2011) as fluxes would be prone to statistical variation and, therefore, be not representative of the ecosystem. Also studies which concentrate on specific VOCs are disregarded (e.g. Fares et al., 2013; Su et al., 2016).

Thus, as stated, we would like just to include EC fluxes (measured with PTR-TOF), as a comparison with DEC fluxes (measured by PTR-Quad) would be out of the scope of this study and would need, due to the large amount of studies, an individual review paper.
We added Juráň et al. (2017), where approximately five days of VOC fluxes were measured using EC with a PTR-TOF. However, we added the fraction of the assimilated carbon released from VOCs from Misztal et al. (2011) and Seco et al. (2017).

5) Table 2: 24 h flux average are chosen quite randomly and are often problematic, because most of the studies do not apply corrections to night time fluxes (e.g. storage and advection). A couple of clarifications would be important. Which (if any) corrections were applied to night time fluxes? Also why compare a 24h average with an 8h average – this does not make much sense. One should average the current dataset over the same period as each of the referenced datasets to be a meaningful comparison.

We agree that 24 h flux values are problematic, as the night time fluxes are more prone to errors. As suggested we added 8 h average flux values from this study, to compare to the values of Kaser et al. (2013) and clearly marked them as 8 h averages.
However, especially when measuring in northern countries, where emission are low but continue longer than in mid latitude areas, 8 h fluxes can lead to an underestimation. In high latitudes the sun sets only for a few hours in the night in summertime and temperature as well as light and temperature dependent emissions continue to midnight (maximum length of daytime light in this study: 19.5 h) and using midday 8 h flux averages would further decrease the cumulative emissions . We clarified in Sect. 2.3 that no additional corrections were applied to the measured fluxes (in addition to the high frequency attenuation correction).

6) Page 10 Line 32: So if you conclude that the SMEAR station generally suffers from widespread butanol contamination from aerosol instrumentation, why talk about a 'butene flux' in this paper?

Similarly as discussed in question 3, the initial idea was to always use the compound name of the measured mass and discuss the identification of the compound in Sect. 2.2. We agree that this can lead to misinterpretations and changed all butene references to butene & butanol. We would like to keep butene in the name, as a separation of the $C_4H_9^+$ signal into butene and butanol fragment is, with our measurements setup, not possible. However, we clarify at several points that the butene & butanol emissions are anthropogenic and refer to Sect. 3.4.

There are a large number of grammatical errors or confusing statements– I suggest copy-editing if this cannot be easily resolved by the authors. A small number of examples is listed below.

We thank the reviewer for this comment the manuscript was checked carefully for mistakes after all reviewer comments were implemented.

Page 5 Line 28: Overall 22 compounds with flux – change to "with a flux"
Page 5 Line 29: "C1" is an odd way to present a sum formula – I suggest to change it to "C" throughout the manuscript
Page 6 Line 4: measured in mid-afternoon – change to "during mid-afternoon"
Page 6 Line 6: methane is typically not considered a VOC – I suggest changing VOC to NMVOC throughout the manuscript as this is a more commonly used expression
We agree with the reviewer, however, we would like to stay with the term VOC. Therefore the sentence was rewritten and any reference to methane was omitted.

Page 6 Line 6: The entire sentence here is confusing – I suggest to rephrase it.
Page 6 line 9: "for all months"
Page 6 line 10: "detectable fluxes"
Page 6 line 20: The heaviest measured compounds with detectable flux was - > "were"
Page 9 line 4: using surface layer profile method - > using "THE" surface layer method
Page 9 line 7: "ON" the same order
Page 9 line 8 : between the two measurements ?
Was changed to: The discrepancy between the results of the two measurements is mainly […]
Page 9 Line 12: "by" both methods
Page 11: "air chemistry"
Table 1 and 2, Figure 3, 6, 7: change "C1, O1, N1, etc." in the elemental composition column to "C, O, N"
All above mentioned examples were corrected.

Note: The unit of mass was changed from amu to Da, to ensure that the reader knows that the mass units used are based on the ^{12}C atom.

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Anonymous Referee #2

The paper written by Schallhart et al. describes VOCs fluxes above a boreal forest by using PTR-TOF and PTR-Quad instruments coupled with eddy covariance technique and indirect gradient method, respectively.

1) The fluxes are measured during 9 days in April and May and 21 days during June. I doubt, if only 9 days of months are enough to represent the whole month.

We agree that the labeling of the months could give the impression that the measurements covered the whole month. We therefore rephrased the sentence (P5 L21) and exchanged "represent" to "give insight to". We also renamed the periods from April to snowmelt, May to start of growing season and June to summer, as the periods should give insight into the development of the temporal variations of VOC fluxes. In some cases we still refer to the months, but then as measurement period in April (May or June).

2) Page 2 line 34: Surroundings are described in paper published in 2005 and 2010. Please add at least current (2013) leaf area index, tree density, when the trees were planted or how old are the trees.

Sadly, we were not able to add the mentioned values from 2013. Therefore, we added the parameters closest to the measurement time. The LAI is quite stable over the recent years, which can be explained by the closed canopy and the constant light availability over the years.

3) Page 2 line 35: I would not use "climatological mean temperature" but rather mean annual air temperature. From which years is the mean computed should be added. Similarly for precipitation. Additionally the mean should cover the measured period. As there is (page 2 line 36) Pirinen et al., (2012 cited), it seems that the mean is only until 2012. However you measured in 2013.

The used values are cited from Pirinen et al. (2012) and are calculated using for the climatological normal period 1981–2010 that represents typical temperature and precipitation of the area. The instruments and data analysis follow the criteria of the WMO. As the data from the same instruments used in Pirinen et al. (2012) is not accessible, we refrain from adding more years to the average. However, we added the information about the measurement period to the description.

4) Page 3 Line 9: There should be: data "were" analysed

Changed as requested.

5) Page 3 Line 28: Since here the rest should be in discussion section. It has no relationship to the measurement setup.

We agree and moved the section to the start of the Results and Discussion chapter (Sect. 3).

6) Page 4 Line 40: When your lines were heated and the effect was negligible, why to write about that? I would omit those sentences on lines 37-40.

We agree and neglected the sentence.

7) Page 5 Lines 5-6: It is clear that the response time cannot be used in other studies. Do not need to be mentioned.

Sentence deleted.

8) Page 5 Line 15 and afterwards: How could butane emissions dominated the flux, when the emissions are possibly originating artificially nearby the tower? This is a big problem and you should omit all the measured butane flux in here and in all the tables and graphs, since it is not product of the forest, as you conclude at page 10 line 31.
Similarly, how you could calculate the C release caused by BVOCs, when you count artificial butane in there? Please recalculate all the values, where butane was used and all the graphs (figure 3, 4, 6, 7) and tables (table 1). The discussion section and results should be rephrased based on the new data without the butane flux.

We published all exchange from the SMEAR II station, without focusing just on the biogenic VOC fluxes. However, we agree with the reviewer, that this can be confusing and the information about the anthropogenic nature of the butene & butanol flux is lost, if just parts of the manuscript are read. Therefore, we will omit the artificial butene & butanol flux in the total emission (Table 1 and 2) and in Fig. 7. Still, the individual values will be presented in Table 1 and 2 as well as in Figs. 3, 4 and 6 as we would like to inform the reader that these fluxes do exist. All values connected with butene & butanol will be labelled as anthropogenic. Please see also Reviewer 3, P10 section 3.4.

9) Page 7 Line 30: Check supplement of M. Müller et al. (2015), doi:10.5194/acpd-15-31501-2015-supplement. The 99.0201 amu could be C4H3O3.

We thank the reviewer for this good comment. In Müller et al. (2016) a PTR-TOF 1000 (Ionicon Analytic GmbH) was used, which has different characteristics than the PTR-TOF 8000 used in this study. The crucial difference of the two instruments is the mass resolution ($^{m}/_{\Delta m}$ at full-width half maximum) and mass accuracy. The PTR-TOF 1000 has a mass resolution of 1000 to 1500 (Müller et al., 2016) and the PTR-TOF 8000 has a mass resolution of 3000 to 4500. Therefore, mass peaks are slimmer. This is one reason that leads to a better mass accuracy (MA) of the PTR-TOF 8000:

$$MA = \left| \frac{^{m}/_{z_{literature}} - ^{m}/_{z_{measurement}}}{^{m}/_{z_{literature}}} \right|$$

The PTR-TOF 8000 using the tofTools software has a MA of maximum 20 ppm (for non-saturated single peaks). The literature mass for $C_4H_3O_3^+$ is 99.0077 Da and our measured signal was at 99.0201 Da, giving a MA of 125 ppm. Therefore, we disregarded $C_4H_3O_3^+$ as a possible compound for 99.0201 Da.

10) Page 7 Line 32: 89.0386 amu could be C3H5O3.

The literature mass for $C_3H_5O_3^+$ is 89.0233 Da and our measured signal was a single peak at 89.0386 Da, giving a MA of 171 ppm. Therefore, we disregarded $C_3H_5O_3^+$ as a possible compound for 89.0386 Da.

11) Page 8 Line 8: I do not see sense in comparing 24 h flux, measured in different periods of year at different plant ecosystems. Authors conclude that 8 hours flux by Kaser et al. (2013a) could not be compared to the 24 h net fluxes. Then why to put 8 h flux in Table 2?

We agree with the reviewer and added 8 h values to the table (see Reviewer 1 Q5).

12) Page 8 Line 21: Toluene fragment contribute to the carbon flux. That would mean, that toluene is produced by vegetation, however that is no longer discussed in all manuscript. Authors should bring more convincing results about toluene being released by Scots pine forest or give explanation how can be toluene emitted being anthropogenic. Check also figure 4, where is toluene emission and recalculate that.

Thank you for the valuable comment, we have clarified the observations on the toluene mass. In the ACPD version all compounds were named after the mass where the signal was measured (Sect. 2.2). We discussed in this section also, that a p-cymene is fragmenting on the toluene mass (93.0699 Da) and thereby, the signals cannot be separated. P-cymene has been measured in the forest in Hyytiälä before (Hakola et al., 2012). Also, the concentration of p-cymene and toluene had a correlation factor above 0.75 (see Reviewer 1 Q3).
To clarify that, all measured toluene signals have been renamed to toluene & p-cymene.

13) Page 8 Line 22-25: I would add the study conducted by Juran et al. (2017), doi:10.1016/j.agrformet.2016.10.005, since they identified portion of carbon released by BVOC to GPP on Norway spruce forest. I find that more close to forest in Finland than the mentioned papers here dealing with other ecosystems covered by very different trees.

We thank the reviewer for that comment. The Study was added.

14) Page 9 Line 9: Why there is such vertical difference between the two inlets? The footprints are very different than and thus the results are not comparable.

The difference of the measurement height is caused by the used methods. When using the surface layer profile method, the difference in concentration between the different heights is crucial and both measurements should be above the canopy, whereas for EC the measurements are done from one height above the canopy. Especially, when sampling from several heights, the calculated measurement height increases. In our case the measurement heights of the different inlets for the SLP were 16.8 m, 33.6 m, 50.4 m and 67.2 m. These are long term measurements, which are ongoing since 2010.
In eddy covariance, fast measurements at one height are made, and, in order to capture also smll scale turbulent fluctuations, the inlet is normally placed just above the canopy to keep the tubing as short as possible and a high flowrate is used. In our case, no 3D sonic anemometer was available at the main tower (used for SLP) at 36 m and the closest cottage is 15 m away. Therefore we had to use the scaffolding tower for the EC measurements, which is located about 28 m from the main tower, and the inlet was located at 23 m above ground (which is the highest point at this tower). We agree that for the comparison similar measurement heights would have been better and we stated in the manuscript, that the footprint is different (Fig. 8 in the revised manuscript), which affects the results (see also Reviewer 1, Q2).

15) Page 9 Line 18: How is possible, that PTR-TOF has not detected those three compounds and less sensitive PTR-Quad has?

The classification, if a compound has a measurable flux is very different between the two methods. While classification for the EC fluxes is stated in Sect. 2.3, the classification of SLP fluxes is described in Rantala et al. (2015). In the latter study, data between May 2010 and December 2013 were distributed in 12 monthly bins. Using the positive and negative flux values inside a bin, it was determined if the binomial distribution with a confidence level of 99.9937% (4σ, Clopper-Pearson

method) could be generated from a random process, or if there was a real positive or negative flux. This was done for night (02:00 – 08:00) and daytime (11:00 – 17:00) values.

Therefore, the data for the classification if compounds were exchanged or not, differed between the two datasets. The SLP used a longer period, including June data from previous years with higher temperature, but the SLP fluxes were measured every third hour only. The EC fluxes were measured just in 2013, but continuously. This difference was necessary, as the SLP fluxes would otherwise have too little data for a classification (<120 data points; see Table 3).

The flux values stated in the manuscript were calculated when both instruments were measuring.

16) Page 9 Line 22: The correlation between monoterpene and methanol fluxes with each other at Fig 9 is rather bad than good. Similarly, R2 in Table 3 for acetonitrile, acetaldehyde, acetone and toluene suggests that there is no correlation at all. I doubt that the data were post-processed correctly or the instrument was working fine. Could you give explanation about that?

Thank you for the comment and valid questions, we corrected the text and removed the statement that the correlations were good (see also Reviewer 3 P9L22):

One should note that the measured VOC fluxes had quite high uncertainties that reduces the correlation. In addition, the compared fluxes were measured by different methods and instruments and had different inlets (length, position, measurement height) and footprints (revised manuscript, Fig. 8). Therefore, we think that the linear correlations for methanol and monoterpene fluxes were reasonable, with around 0.6. However, we agree that for rest of the compounds, the correlations were poor, probably due to small flux values connected with relatively large uncertainties. This can already be seen in Fig. 9, where the scatter of compounds with the highest flux, is considerable. Similarly, the uncertainties of the fitting parameters in Table 3 show the large uncertainties of the presented fluxes.

The poor correlation of acetonitrile, acetaldehyde and toluene follows the reasoning above, but also the comparison is based on less than 60 data points and the mean fluxes (for at least one instrument) are below 0.03 nmol m^{-2} s^{-1}.

As discussed in the manuscript, it is suspected that the flux from toluene (in the revised version toluene & p-cymene) is most likely caused by the fragmentation of p-cymene, which was measured in the forest in Hyytiälä before (Hakola et al., 2012). As p-cymene was not calibrated and a separation of toluene and p-cymene was not possible with the used setup, the toluene sensitivity was used. The fragmentation pattern of the two instruments, is sadly not known and could differ significantly and therefore, the uncertainties of the toluene & p-cymene fluxes are very high.

The low correlation of acetone was surprising, as the mean fluxes of both instruments agreed very well and also the amount of data was largest. Both values were comparable with the monoterpene data. However, the scatter of the data was increased, when compared to the monoterpenes. This can be seen in the large discrepancy of the median, as well as the high intercept (75% of the mean flux) and the high uncertainties of the fitted parameters.

We checked the data as suggested and did not find any errors in the post processing.

17) Page 9 Line 9: It might be useful to show transmission curve to check how certain is to calculate the sensitivities.

A description how the sensitivities were calculated for the PTR-TOF is in Sect. 2.2. The PTR-TOF 8000 is using an Einzel-lens system to guide the ions in the transfer region which does not show a mass dependent discrimination (unlike e.g. PTR-QiTOFs). Therefore, the transmission is similar to the duty cycle of the instrument (Graus et al., 2012). The duty cycle of the instrument (with used settings) can be described as:

$$duty\ cycle(^m/_z) = 0.29 \sqrt{\frac{^m/_z}{322\ Th}}$$

The transmission curve for the PTR-Quad was calculated according to Taipale et al., 2008. In Fig. Z1 a typical transmission curve from the measurement period, as well as the scatter plot from calculated and measured sensitivities is shown. We refrain from adding Fig. Z8 to the manuscript as the SLP data is already published and described in Rantala et al., (2015), while in this manuscript the focus was on the PTR-TOF EC measurements.

18) Table 3: Rephrase "educated guesses"

We deleted this reference, as the compound names are discussed in Sect. 3.

Note: The unit of mass was changed from amu to Da, to ensure that the reader knows that the mass units used are based on the ^{12}C atom.

References:

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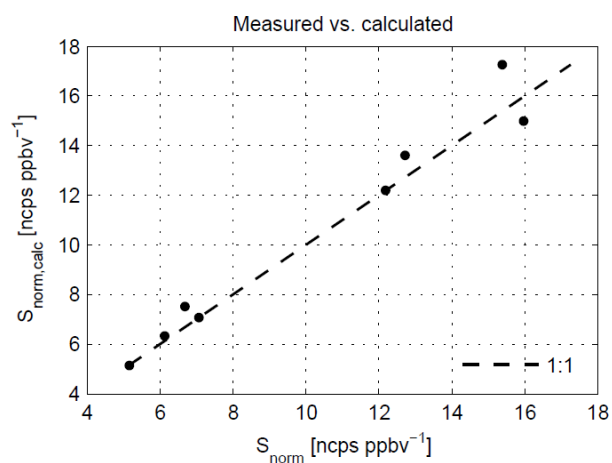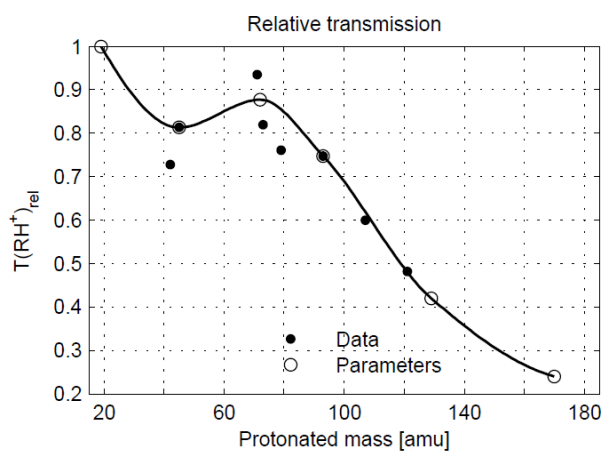
Figure Z1: Mass dependency of the transmission of the PTR-Quad (left) and scatter of the measured and calculated normalized sensitivity.

Anonymous Referee #3

Schallhart and colleagues present VOC flux measurements at the SMEAR II station in Southern Finland. The measurements reported are interesting to the biogenic VOC flux community, however, some more work needs to be done to be able to accept this manuscript for publication. In addition, the language should be edited throughout the manuscript in order to improve sentence structure and thus text readability. Some issues that deserve attention are shown in the list below.

P1L13 Correct 'only a three' to 'only three'

changed

P1L1-2 This sentence needs some English editing

We rephrased the sentence to: "The VOC exchange followed a seasonal trend and the emissions increased from spring to summer"

P2L5 "seems" should be "seem"

changed

P3L37-39 rephrase

We rephrased the section.

P4L17-25 It is not clear to me what is the advantage of the second step, because the second and third steps seem almost the same thing. Please clarify the reason why those steps were taken.

We thank the reviewer for this comment. After the first step, all lag times are similar than the lag time of the monoterpenes. The second step is used to correct compound specific lag times, e.g. if certain compounds would have on average a shorter or longer lag time, e.g. due to interaction with RH or tube walls (similar to the response time). This correction is constant over all the measurement period and ensures that the next step (three) uses a +- 10 s time window around the maximum.
In step 3 every 30 min flux point individually is corrected. This corrects small fluctuations in the lag time, e.g. when the linear regression fit was not precise enough.
We added a sentence explaining step 2 to the revised manuscript.

P5L6 Can the authors list the values of average correction factors for day and night separately?

Yes, we added the average daytime value of 16% (between 09:00 and 17:00) and nighttime value 23% (between 20:00 and 04:00).

P5L19 why the period of 21 days from 04 to 24 May is shown when only a period of 9 days was used?

During May we had technical problems with the 3d-sonic anemometer, which stopped recording data during several occasions during the period of 04 May 2013 to 24 May 2013. Therefore, only 423 30 min files (equals 211.5 h, approximately 9 days of data) of fluxes could be calculated in this period. We clarified this section in the manuscript.

P6L25-26 confusing sentence

We rewrote the sentence and improved the readability.

P6L24-P7L34 Sections 3.1.2 and 3.1.3 should be rewritten to emphasize readability

We rewrote the mentioned sections and improved the readability.

P7L10 does this "highest total emission" refer to the maximum "average daytime emission"? Please clarify since it is difficult to discern from the (higher) 9.69 nmol/m2s shown on P7L13.

We changed the "highest total emission" to "highest 24 h total emission". We did not use "average daytime emission", as the mentioned value includes also nighttime emissions.

P7L36-P8L38 There are many other recent studies that, either with PTR-TOF or PTRQuad, reported VOC fluxes that would give a more complete view to your discussion. Some of these studies report what fraction of the assimilated carbon was released as VOCs. In addition, some studies report VOC fluxes from monoterpene-emitting conifer species, which may be more relevant to your study. Some examples:
- McKinney et al (2011) https://doi.org/10.5194/acp-11-4807-2011
- Misztal et al (2011) https://doi.org/10.5194/acp-11-8995-2011
- Kalogridis et al (2014) https://doi.org/10.5194/acp-14-10085-2014
- Seco et al (2015) https://doi.org/10.1111/gcb.12980
- Juráˇn et al (2017) https://doi.org/10.1016/j.agrformet.2016.10.005
- Seco et al (2017) https://doi.org/10.1016/j.agrformet.2017.02.007

We thank the reviewer for the suggested literature and also refer to Reviewer 1 Q4:
As stated we would like to include just EC fluxes (measured with PTR-TOF), as a comparison with DEC fluxes (measured by PTR-Quad) would be out of the scope of this study and would need, due to the amount of studies, an individual review paper.
The aim in this paper was to give an overview over the relative new and few already published studies, where no preselection of VOCs had to be made and, therefore, all VOCs with a flux above the detection limit (excluding instrument related signals) are reported.
Furthermore, we omitted publications which use less than four days of data (e.g. Ruuskanen et al., 2011) as fluxes would be prone to statistical variation and, therefore, be not representative of the ecosystem. Also studies which concentrate on specific VOCs are disregarded (e.g. Fares et al., 2013; Su et al., 2016).
We added Juráň et al. (2017), where approximately five days of VOC fluxes were measured using EC with a PTR-TOF. However, as 24 h flux values were not stated for all measured compounds, the study was not added in Table 2. We also we added the fraction of the assimilated carbon released from VOCs from Misztal et al. (2011) and Seco et al. (2017).
McKinney et al. (2011) and Kalogridis et al. (2014) were not added, as no VOC/NEE carbon fraction was stated. Seco et al. (2015) was not used, as just the daytime fraction is stated.

P9L5 Should the text "12 more compounds" be interpreted as 12 compounds exhibiting SLP fluxes not found with the TOF-only EC analysis?

No, the opposite, there were 12 more compounds measured with the EC method that were not found with the SLP method. We clarified this in the text.

P9L22 Figure 8 shows indeed that fluxes for monoterpenes, isoprene and acetone were comparable. However, Table 3 lists the slope of the fit between the fluxes calculated with both methods and the slopes for all compounds (including monoterpenes) except acetone are far away from 1. The authors should further discuss this discrepancy, in addition to what is already discussed in P10L4-10. Also please rephrase the last sentence because from the text it seems that monoterpene and methanol were correlated with each other, when Fig 9 shows that what was correlated were the fluxes calculated with EC and SLP.

The mentioned major discrepancy is caused by the high intercept of the fitting. In the case of the monoterpenes, the intercept is around 50% of the mean flux, explaining the flat slope of 0.5. When we forced the offset to be zero, the slope increase to 0.7. The still existing discrepancy from unity can be partly explained by the outliers (Fig. 9), which are far off the 1:1 line and thereby decrease the slope (with their high influence on the explained sum of squares).
A similar case is the slope of isoprene. Here, the offset is about 30% of the mean flux and again, by forcing a zero intercept the slope increased. Furthermore, a close look at Fig. 8 shows, that there is clearly a smaller flux measured by the EC method, when compared with the SLP method and thereby the slope should be less than one.
Acetone has the highest intercept compared to the mean flux (> 60%) and also higher uncertainty of the slope (0.276 ±0.191) with respect to the compounds mentioned above.
When the offset was forced to be zero, the R^2 values decreased for all compounds.
Overall, the discrepancy from unity can be explained by the scatter of the measured fluxes, which is shown in the uncertainties of the fitting parameters. The scatter is caused, as discussed in the paper, by variation in turbulence measurements, noise of the VOC measurements, different inlet heights (36 m, 23 m), methods (SLP, EC), instruments (PTR-Quad, PTR-TOF) and footprints (see revised manuscript Fig. 8). The comparison also lacked high flux periods, as can be seen when comparing the values of the monoterpene EC flux in Fig 8 (right side; 3 values above 1 nmol m^{-2} s^{-1}) and Fig. 4 (bottom panel), where in the 9 day period already 44 values were above 1 nmol m^{-2} s^{-1} (maximum emission 2.44 nmol m^{-2} s^{-1}).
We added a discussion about the discrepancy of the fitted slopes from unity to the manuscript.

P10 section 3.4 the contamination from butanol used in CPCs is a major problem for the attempt to report butene fluxes. Since the authors have concluded that most of the signal of CH4H9+ is from butanol, the results and discussion section relating to butene should be omitted. I would recommend still having part of the manuscript dedicated to explaining what happened with butanol so other researchers can keep this contamination in mind for future experiments. Also, have the authors quantified the capacity of the forest (e.g. the fluxes measured on the eastern side of the forest) to take up butanol?

See also the answer to Reviewer 2 Q8:
We agree with the reviewer, that the anthropogenic nature of the butene & butanol flux is lost, if just parts of the manuscript are read. Therefore we will omit the artificial butene & butanol flux in the total emission (Table 1 and 2), mentioned net fluxes and in Fig. 7. Still, the individual values will be presented in Table 1 and 2 as well as in Figs. 3, 4 and 6 as we would like to inform the reader that these fluxes do exist. All values connected with butene & butanol were labelled as anthropogenic to clarify that the flux does not come from the same biogenic source as other VOCs.
In the Fig. 10 left panel a small deposition of butene & butanol has been found with -0.04 nmol m^{-2} s^{-1} (0°-30° sector, NNE) and < 0.01 nmol m^{-2} s^{-1} (30°-60°, NE) sector. However, if this is active up-take of the forest or dry deposition we cannot answer with our measurement setup.

P10L28 How many compounds showed fluxes? Here and in section 3.2 the authors say 25, but in section 3.1 they say 22. Please be consistent.

We thank the reviewer for the comment and clarified the text. Overall, 25 compounds with fluxes have been discovered, 17 during the 21 day measurements in June, and 22 during the 3 periods in April, May and June. We rephrased the sentence in Sect. 3.1.

P11L6-8 A good reference for this final sentence is Rinne et al 2016
https://doi.org/10.1016/j.atmosenv.2016.02.005

We added the reference.

Fig 10 caption: "butanol using aerosol instruments" is confusing

Was changed to "[…] aerosol instruments, which use butanol."

Note: The unit of mass was changed from amu to Da, to ensure that the reader knows that the mass units used are based on the ^{12}C atom.

Temporal variation of VOC fluxes measured with PTR-TOF above a boreal forest

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Abstract. Between April and June 2013 fluxes of volatile organic compounds (VOCs) were measured in a Scots pine and Norway spruce forest using the eddy covariance (EC) method with a proton transfer reaction time of flight (PTR-TOF) mass spectrometer. The observations were performed above a boreal forest at the SMEAR II site in s~~S~~outhern Finland. We found a total of 25 different compounds with exchange and investigated their seasonal variations from spring to summer. The majority of the net VOC flux was comprised of methanol, monoterpenes, acetone and butene & butanol. The butene and butanol emissions were concluded to not originate from the forest and, therefore, be anthropogenic. The VOC exchange followed a seasonal trend and the emissions increased from spring to summer~~The VOC emissions followed a seasonal trend, the released amount increased from spring to summer~~. Only ~~a~~ three compounds were emitted ~~in~~during the snow melt ~~April~~ while in ~~June~~summer emissions of some 19 VOCs were observed. During the measurement~~s~~ period in April, the emissions were dominated by butene & butanol, while during the start of the growing season and in summer,~~in May and June~~ methanol was the most emitted compound. The main source of methanol ~~i~~was likely the growth of new biomass. During a 21-day period in June, the net VOC flux was 2.1~~3~~ nmol m^{-2} s^{-1}. This is on the lower end of PTR-TOF flux measurements from other ecosystems, which range from 2 to 10 nmol m^{-2} s^{-1}. The EC flux results were compared with surface layer profile measurements~~, an indirect method,~~ using a proton transfer reaction quadrupole mass spectrometer, which is permanently installed at the SMEAR II site~~ was used~~. For the major compounds, the~~most of the compounds the~~ fluxes~~,~~ measured with the two different methods~~,~~ agreed well.

1. Introduction

Boreal forests, covering approximately 12.2·10^6 km^2 of the earth's surface, which is 30% of the world's forest area (Keenan et al., 2015), emit volatile organic compounds (VOCs), which have an important impact on the chemistry and composition of the atmosphere. These emitted compounds can react with O_3, NO_3 or OH and form a multitude of new VOCs, which can contribute to the formation and growth of aerosol particles and thereby affect climate change (Tunved et al., 2006; Spracklen et al., 2008). An understanding of these emissions and their quantity is necessary for numerical assessments of future climate and air quality (Guenther et al., 2012; Makkonen et al., 2012). The direct measurement of VOC fluxes above the canopy is one key element in this process. Eddy covariance has become a reference method for measuring canopy exchange (Baldocchi, 2014).

The ecosystem scale VOC fluxes result from emissions caused by biological activity and chemistry, which, take place in soil, forest floor and understory vegetation, trees and within the canopy airspace. The prevalent ability to synthesize and release VOCs to the atmosphere varies between species and often changes with seasons and during the lifecycle of a plant (Karl et al., 2003, Hakola et al., 2006, Holzke et al., 2006). The more heterogeneous a habitat, the more potential sources of variation as regards VOC fluxes exist. Although managed boreal forests are commonly considered to be relatively

homogeneous habitats, they are still relatively heterogeneous when compared to grasslands or other agricultural areas (Newbold et al., 2015). In addition to the array of tree species, the understory and forest floor vegetation vary significantly in terms of species selection, luxuriance and coverage as a result of soil properties, orientation, canopy coverage and water availability. Even a single species, as exemplified for Scots pine, may express considerable intra-species variation in terms of emission composition (Bäck et al., 2012) and capacity (Aalto et al., 2014, 2015). Soils and forest floors are very complex but as yet poorly understood sources of VOCs (Aaltonen et al., 2011, 2013); however, the diverse forms of microbial activity seems to play a central role in VOC emissions from the soil (Bäck et al., 2010). In this context, above canopy VOC flux measurements represent a vast array of signals from biogenic activity, which largely complicates drawing conclusions on the effects of biological and ecophysiological phenomena on VOC emissions from forests. However, the above canopy VOC flux method is a crucial tool in studying VOC emission in a continuum from the sub-cellular scale up to the effects of VOCs on atmospheric composition and processes on local, regional and global scales. VOC concentrations and emissions have been measured during campaigns since 1998 at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations). The VOC flux measurements at the station have consisted of different instruments and techniques: disjunct eddy covariance (DEC; e.g. Rinne et al., 2007), the surface layer profile (SLP) method (e.g. Rantala et al., 2014) using a Proton Transfer Reaction-Quadrupole (PTR-Quad) mass spectrometry and a gas chromatograph mass spectrometry using the gradient method (e.g. Rinne et al., 2000). In recent years, proton transfer reaction-time of flight (PTR-TOF) mass spectrometers have been used to measure eddy covariance fluxes (Ruuskanen et al., 2011; Kaser et al., 2013a; Park et al., 2013; Brilli et al., 2015; Schallhart et al., 2016), but the number of these studies is still low. With this new measurement setup, it is possible to identify the elemental composition of the compounds with detectable fluxes. Furthermore, the preselection of the measured compounds is no longer necessary, as the PTR-TOF measures full mass spectra. Its ability to measure all VOCs with 10 Hz time resolution leads to noise reduction compared to the DEC method using PTR-Quad, which uses a lower measurement frequency (typically 0.05 to 1 Hz; e.g. Rinne and Amman, 2012).

This study used a PTR-TOF to measure VOC fluxes during April the snow melt (9 days), May start of the growing season (9 days) and June summer (21 days) 2013 and these are the first results from EC measurements of VOCs above a boreal forest. The main objective was to investigate how the fluxes and compounds with flux behavior set of compounds with detectable fluxes and their flux magnitude change during the transition from winter to summer. A second objective was to compare these PTR-TOF EC measurements with the long-term PTR-Quad measurements of SLP fluxes. Finally, the results from the 21 days of flux measurements in June were compared with other VOC flux studies using EC and PTR-TOF.

2. Methods

2.1. Site description

The measurements were carried out from April until the end of June 2013 at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, southern Finland. The station is 180 m above sea level and located in the middle of a *Pinus sylvestris* (Scots pine) dominated stand, while *Picea abies* (Norway spruce) covers 15% of the forest. In addition to the dominating Scots pine and Norway spruce, other tree species are present at the study site e.g. *Betula pendula* and *Betula pubescens* (silver and downy birch), *Populus tremula* (trembling aspen), *Sorbus aucuparia* (rowan) and *Salix caprea* (goat willow). The forest was planted 1962, since then the trees have grown to 18 m height

and the stand density was approximately 1300 ha^{-1}. Depending on the season, ~~and~~the leaf area index varies between 2 and 2.5 (Rautiainen et al., 2012). More information about the surroundings of the station can be found ~~have been described by~~in Hari and Kulmala (2005) and Ilvesniemi et al. (2010). The ~~climatological~~ mean annual temperature ~~i~~was 3.5°C and the mean annual precipitation ~~i~~was 711 mm during the climatological normal period 1981- 2010 (Pirinen et al., 2012). The measurements were conducted on a scaffold tower (61.847407°N, 24.295150°E) and the inlet height was 23 m. The temperature varied between -2°C and 27°C during the measurement periods and the main wind direction was south-southwest.

2.2 Flux measurement setup

The measurements were conducted with a PTR-TOF 8000 (Ionicon Analytic GmbH; Jordan et al., 2009; Graus et al., 2010). It was operated with a drift tube voltage of 600V and a drift tube pressure of 2.3 mbar. Together with the drift tube temperature of 60°C, the E_{PTR}/N_{PTR} (E_{PTR} being the electrical field strength and N_{PTR} the gas number density) was calculated to be 130 Td. The instrument was placed in an air-conditioned cottage next to the measurement tower. Sample air was pumped through a 30 m long (8 mm inner diameter, i.d.) PTFE inlet, with a flow of 20 L min^{-1}. To prevent condensation on the inlet walls, the tube was heated with an 8 W/m passive heating wire. A subsample of 0.5 L min^{-1} was collected via a 10 cm PTFE tubing (1.6 mm i.d.), which le~~ad~~d over a three-way valve (type 6606 with ETFE, Bürkert GmbH & Co.KG) and 20 cm of PEEK tubing (1 mm i.d.) to the PTR-TOF. The PTR-TOF data w~~as~~ere analyzed with the tofTools, which are described in more detail in Junninen et al.~~,~~ (2010~~)~~. A 3-d ultrasonic anemometer (HS-1199, Gill instruments) was placed 10 cm above the inlet. Both VOC and wind measurements were recorded at 10 Hz resolution. In addition, eddy covariance fluxes of carbon dioxide (CO_2) are routinely measured at the site using a closed-path infrared gas analyzer (Licor 6262, USA; Mammarella et al., 2009). CO_2 fluxes were calculated by using EddyUH software (Mammarella et al. 2016).

The instrumental background of the PTR-TOF was measured by guiding ambient air through a catalytic converter, which remove~~s~~d the VOCs. This VOC free air was measured three times a day, starting at 00:02, 08:02 and 17:02 and each measurement session lasted for 25 min. This led to a reduced amount of flux data during these hours. Switching between ambient air and the VOC-free air was done with a 3-way valve (type: 6606 with ETFE, Bürkert GmbH & Co. KG) controlled by the PTR-Manager (Ionicon Analytic GmbH~~, Austria~~).

For calibration this VOC free air was mixed with a calibration gas (Apel Riemer Environmental Inc.~~, USA~~) containing 16 different compounds. For uncalibrated compounds the sensitivities were categorized into three groups C_xH_y (calculated from isoprene, benzene, toluene, o-xylene, trimethylbenzene, naphthalene, α-pinene combined with C_6H_9 fragment), $C_xH_yO_z$ (based on acetaldehyde, acrolein, acetone, 2-butanone) and $C_xH_yN_z$ (set to acetonitrile) similar to the setup Schallhart et al. (2016). The average sensitivities for the different compound groups were: 11.4 ± 2.5 ncps/ppb for C_xH_y, 18.6 ± 3.1 ncps/ppb for $C_xH_yO_z$ and 17.7 ± 2.0 ncps/ppb for $C_xH_yN_z$. Overall the sensitivities are comparable with Schallhart et al. (2016), only the standard deviation increased, due to the longer time period of the measurements. The setup for background and calibration measurements is described in more detail in Schallhart et al. (2016).

~~The PTR-TOF is unable to identify the structure of measured compounds, therefore the identification of specific compounds is not possible. In the remaining manuscript, mass 69.0699 amu with the elemental composition $C_5H_9^+$ is called isoprene, even though 2-methyl-3-buten-2-ol (MBO) fragments to the same mass and has a substantial influence on the signal (e.g. Kaser et al., 2013b). Similarly, the mass 93.0699 amu with the elemental composition $C_7H_9^+$ is called toluene, even though p-cymene fragments may affect the signal (Tani et al., 2003). Formaldehyde has only a slightly~~

2.3 Flux and lag time calculations

VOC fluxes were derived using the eddy covariance (EC) method (e.g. Aubinet et al., 2012). The EC flux is calculated using the covariance:

$$\overline{w'c'}(\lambda) = \frac{1}{n}\sum_{i=1}^{n} w'(i - \lambda / \Delta t)c'(i), \tag{1}$$

where w' and c' are high frequency fluctuations of vertical wind and concentration, respectively, i the number of the measurement, n the sum of all measurements during the flux averaging time (30 min in this study; $n = 18\,000$), Δt the sampling interval (0.1 s) and λ the lag time caused by the sampling system. The cross covariance functions (CCF) were calculated by varying λ from -200 s to 200 s. In this study, vertical wind and VOC concentrations were both recorded at 10 Hz frequency. The flux calculation procedure is called the automated method and is similar to that in Park et al. (2013) and Schallhart et al. (2016), only the lag time was determined differently.

The VOC and the wind data were recorded on two different computers and their clocks shifted considerably (continuous shift of 2 to 5 s day^{-1}; Fig. 1a). Finding the correct lag time is especially challenging when the flux is close to the detection limit. To estimate the proper lag times, three corrections were made:

I. First, the artificial clock shifting was removed using linear regressions. Therefore, the regressions from the monoterpene CCFs were used to correct the CCFs from all compounds (Fig. 1b).

II. In the second step, an average, absolute CCF was calculated (Fig. 2) for each compound. For this the absolute value of each 30 min CCF between 10:00 and 16:00 was taken and then all the absolute CCFs for the time period of interest were averaged. To reduce the influence of noise, especially when small fluxes are measured, a running mean (±24 step averaging) was used. Then the position of the maximum was searched for a ±10 s time window and used as the lag time. This step corrects possible differences in the average lag time between the compound of interest and the monoterpenes. was This lag time was calculated for each month and each compound separately.

III. The third and last step was used to correct for smaller shifts, in case the first correction, with the linear regression, was not precise enough. Therefore, each individual 30 min CCF was smoothed by a running mean (±24 step averaging) and the location of the maximum in a ±10 s time-window around the previously calculated lag time was recorded (Taipale et al., 2010) as shown for the monoterpenes in Fig. 1c.

To classify how many of the hundreds of measured compounds show an exchange, a method described in Park et al., (2013) and Schallhart et al., (2016) was used. This method compares the maximum of the averaged, absolute CCF with a certain noise threshold. To reduce the impact of noise, the average, absolute CCF was smoothed (±12 step averaging) and the location of the maximum in a ±10 s time window detected. This position was used in the average, absolute CCF (not smoothed) and compared with the σ_{noise} (standard deviation of the noise). The σ_{noise} was calculated for 60 s at the borders

of the average absolute CCF. If the ratio between the calculated maximum and the σ_{noise} was higher than three, the compound was classified to have detectable flux (Fig. 2). This method was applied to flux determinations for each month separately.

The flux underestimation caused by high frequency attenuation was estimated using a parametrization described by Horst (1997). The method uses a system response time and information about stability and horizontal wind speed for estimating the attenuation. The system response time was determined to be around 1.2 s for monoterpenes and the same response time was also used for all the other compounds. ~~However, the response time of e.g. water soluble compounds might be larger due to desorption and absorption processes on the tube walls, as a function of relative humidity and sampling line aging (Mammarella et al, 2009; Nordbo et al., 2013 and 2014). This potentially causes errors of a few percentage on the flux values. However, we expect the effect to be reduced, because a heated sampling tube was used. The low-frequency corrections that are based on theoretical transfer function shapes (e.g. Rannik and Vesala, 1999), were not applied in this study.~~

One should note that the determined response time describes the flux attenuation of the whole measurement setup, including the tubing, a horizontal separation between the inlet and the anemometer and the instrument itself. ~~Thus, the response time of this study cannot be used in the case of other PTR-TOF measurements at other locations.~~ In this case, the average attenuation factor was 18%. On average, the correction factor was smaller during the day (16%; 09:00 to 17:00) and larger at night (23%; 20:00 to 04:00).

No additional corrections were applied to the measured fluxes (e.g. storage correction).

2.4 Flux quality criteria

The measured fluxes were filtered by three quality criteria, to reduce the systematic uncertainty and ensure their representativeness:

First, the data were flagged if the tilt angle, resulting from the coordinate rotation of sonic anemometer wind velocity components (Kaimal and Finnigan, 1994), was more than 5°, which was the case for 11.9% of the data. Second, all 30 min records with a friction velocity less than 0.2 m s^{-1} were flagged. Following this, 11.2% of the data ~~was~~ were flagged. Finally, the flux steady-state test was applied according to Foken and Wichura (1996). All flagged flux values were removed from further analysis. The rejection rate between April and June was 34.1%, 35.1% and 30.5% for acetone, butene & butanol and the monoterpenes, respectively. For the monoterpenes, the rejection rates for the measurement periods in April, May and June were 19.1%, 17.6% and 30% (daytime) and 25.6%, 24.0% and 43.7% (nighttime).

2.5 Flux selection

The temporal behavior of the VOC exchange was investigated by measuring periods in April, May and June 2013. These periods give insight to the VOC exchange during snowmelt, start of the growing season and summer. ~~VOC emissions from April, May and June 2013 were selected for a monthly comparison.~~ Because of technical problems with the anemometer~~,~~, which stopped recording data on several occasions during the start of the growing season, only 423 × 30 min files (~9 days of data) of VOC fluxes could be calculated in the period from 04 May 2013 to 24 May 2013~~in May, only a nine-day period, from 04 May 2013 to 24 May 2013, could be used~~. The standard deviation of noise in the averaged, absolute CCFs (σ_{noise}) determines the exchange threshold and is directly dependent on the amount of data. Therefore, the same amount of data (423 × 30 min files) was selected to represent each ~~month~~ period from snowmelt to summer and make ~~the~~a comparison between those periods ~~with the other months~~ possible. For all three ~~months~~periods, the absolute

mean of the CCFs between 10:00 and 16:00 (UTC+2) was used to find compounds with statistically significant flux (Park et al., 2013; Schallhart et al., 2016). For ~~April~~the snowmelt, the measurements were from 14 April 2013 to 24 April 2013 and for ~~June~~ summer the hottest period was selected, from 01 June 2013 to 12 June 2013.

3. Results and Discussion

The PTR-TOF measures the mass of the VOCs in the ambient sample, which can be used to calculate the elemental composition. Therefore, no structural information of the measured molecules is known and the identification of compounds relies on literature and gas chromatograph measurements. Major masses affected by fragmentation and compounds with high uncertainties are discussed in the following.

The mass 69.0699 Da with the elemental composition $C_5H_9^+$ was called isoprene & MBO, as 2-methyl-3-buten-2-ol (MBO) fragmented to this mass and had a substantial influence on the signal (e.g. Kaser et al., 2013b). Similarly, the mass 93.0699 Da with the elemental composition $C_7H_9^+$ was called toluene & p-cymene, as p-cymene fragments were suspected to affect the signal (Tani et al., 2003). Formaldehyde has only a slightly higher proton affinity compared with the primary ion and therefore back reactions, which are humidity dependent, from protonated formaldehyde to water occur (de Gouw and Warneke, 2006; Inomata et al., 2008; Vlasenko et al., 2010). This may have led to an artificial flux, which was caused by water vapor fluctuations. Therefore, the formaldehyde fluxes are very uncertain. The signal at mass 57.0699 with a protonated composition of $C_4H_9^+$ was called butene & butanol, as butanol was suspected to have substantial influence on the signal (see Sect. 3.4). Furthermore, as the butene & butanol fluxes were expected to be caused by the aerosol instrumentation, they were disregarded in all reported net fluxes and total emissions. The monoterpenes ($C_{10}H_{17}^+$) were measured at mass 137.1325 Da only. The monoterpene fragment at mass 81.0699 Da ($C_6H_9^+$) was identified by its Pearson correlation of 0.99 (30 min integrated data) with the signal at 137.1325 Da and was disregarded from further analysis.

3.1 VOC flux variation during the campaign

During the three 9 day measurement periods in April, May and June ~~Overall~~ 22 compounds with a flux were found, of which 16 were identified by their elemental compositions (Table 1). Five compounds, $C_4H_3O_4^+$ (formaldehyde), $C_4H_4O_4N_4^+$ (formamide), $C_4H_7O_4^+$ (crotonaldehyde) and two unidentified peaks with the masses of 84.95~~00 amu~~00 Da and 118.9456 ~~amu~~Da, had a negative net flux, each contributed around 1% or less to the total net flux (Fig. 3). As expected the average net flux increased from ~~April~~ snowmelt (0.~~66~~24 nmol m^{-2} s^{-1}) to ~~May~~the start of the growing season (1.~~2~~07 nmol m^{-2} s^{-1}) and ~~June~~ summer (~~3~~2.~~0~~75 nmol m^{-2} s^{-1}). The compounds with detectable flux~~es~~ increased from three ~~in~~ during the snowmelt ~~April~~ to 12 ~~in May~~at the start of the growing season and 19 in ~~June~~summer. Over ~~80~~75% of the net flux comprised of methanol, acetone and~~,~~ monoterpenes ~~and butene~~. Of those ~~three~~four main compounds, acetone and monoterpenes had similar emission patterns (based on the total net flux) over the measurement period, while methanol had no detectable flux in April. The development of the diurnal cycle can also be seen in Fig. 4, as the measurements in April had a minor flux variation between day and night, whereas the periods in May and June showed a clear dependence on the temperature. The maximum emission was detected between 14:00 and 16:00 (Fig. 4); this is in agreement with the fact that VOC synthesis is driven by temperature and light (Ghirardo et al., 2010; Taipale et al., 2011), while potential evaporation from storage pools is primarily driven by temperature alone (Guenther et al., 1993). The maximum temperatures were typically measured ~~in~~during mid-afternoon, when the light availability has still not yet decreased to a

great extent when compared to the light conditions around noon. Figure 5 shows that the highest emissions of monoterpenes and isoprene coincided with the highest temperatures. ~~This can be seen in Fig. 5 where the highest emissions of the globally most emitted VOCs (excluding methane), the group of monoterpenes and isoprene, are during the hottest period of the campaign.~~ Furthermore, the high monoterpene emissions during low PAR (<200 µmol m^{-2} s^{-1}; grey data points in Fig. 5) conditions can be explained by pool emissions, whereas the de novo isoprene emissions during this time were low. Unlike the maximum emission time, ~~that~~ which was similar for all month~~s~~, the minimum net flux was between 20:00 and 21:00 ~~in~~ during the snowmelt~~April~~, 03:00 and 04:00 ~~in~~at the start of the growing season ~~May~~ and 01:00 and 02:00 in ~~June~~summer. Table 1 shows all the compounds with detectable flux for the three months and their 24 h average emission and deposition.

3.1.1 Low emissions during snow melt

As expected the total emission (0.~~68~~25 nmol m^{-2} s^{-1}) was smallest during the measurement period in April ~~in April~~ (compared to ~~May~~ the start of the growing season and summer~~and June~~). The snow melted during this period and the average temperature and photosynthetically active radiation (PAR) were at their lowest, 4.4°C and 268 µmol m^{-2} s^{-1}, respectively. The total deposition (-0.01 nmol m^{-2} s^{-1}) was also weakest. ~~Butene (C$_4$H$_9$$^+$) dominated the emissions, comprising over 60% of the net flux. C$_4$H$_9$$^+$ had the highest emissions between 14:00 and 15:00 with 0.82 nmol m^{-2} s^{-1} and the lowest between 21:00 and 22:00 with 0.08 nmol m^{-2} s^{-1}.~~ Acetone contributed with ~~almost~~ over 2~~5~~0% to the emissions and was the only compound ~~in~~ during the snowmelt~~April~~ for which a diurnal deposition was detected. Between 22:00 and 23:00 the measured flux reached a minimum of -0.12 nmol m^{-2} s^{-1}, whereas between 13:00 and 14:00 the emission peaked with 0.40 nmol m^{-2} s^{-1}. The heaviest measured compounds with detectable flux ~~was~~were the group of monoterpenes, which contributed ~~17~~48% to the total emission and had the highest emissions between 14:00 and 15:00 with 0.24 nmol m^{-2} s^{-1}. The lowest emissions of 0.06 nmol m^{-2} s^{-1} were measured during morning between 06:00 and 07:00. The anthropogenic emissions of butene & butanol dominated by a factor of 1.7 over the biogenic emissions. C$_4$H$_9$$^+$ had the highest emissions between 14:00 and 15:00 with 0.82 nmol m^{-2} s^{-1} and the lowest between 21:00 and 22:00 with 0.08 nmol m^{-2} s^{-1}.

3.1.2 Increase of emissions at start of growing season

The total emission during the start of the growing season in May was 1.24 nmol m^{-2} s^{-1} and the total deposition was more than 10% of the emission, -0.17 nmol m^{-2} s^{-1}. The night temperatures during this period were above zero and the sun warmed late afternoons to around 20°C. This led to a mean temperature of 11.4°C and the mean PAR was 301 µmol m^{-2} s^{-1}. Methanol dominated the emissions with 40% contribution to the total emission. The diurnal maximum of methanol was in the late afternoon with 2.11 nmol m^{-2} s^{-1}. These results agree with other studies, which showed that methanol is released in plant growth (e.g. Galbally and Kirstine, 2002). On the other hand, methanol showed also the highest deposition, comprising almost 50% of the total deposition. The midday deposition of -0.47 nmol m^{-2} s^{-1} between 11:00 and 12:00 can be explained by rain during or right before this time window, which happened twice during the measurements in the May period. The water-soluble methanol was suspected to be dry deposited on the wet surfaces in the forest, (Laffineur et al., 2012; Wohlfahrt et al., 2015; Schallhart et al., 2016).

The monoterpenes were the second most emitted compound group and contributed 26% to the total emission. Their maximum emission was 0.76 nmol m^{-2} s^{-1} between 15:00 and 16:00 and the minimum emission was 0.13 nmol m^{-2} s^{-1} between 3:00 and 4:00. Recently, Aalto et al. (2014, 2015) have shown that Scots pine needles are a pronounced source

of monoterpenes in spring already before growth onset, and especially after bud break, when the formation of new biomass releases large amounts of terpenoids and other VOCs. The results of this study are in general consistent with those findings in terms of detected mean fluxes and diurnal patterns. Acetone contributed with 19% to the total emission and was the third most emitted compound. It had the maximum emission of 0.61 nmol m^{-2} s^{-1} between 10:00 and 11:00 and the minimum between 03:00 and 04:00 with 0.04 nmol m^{-2} s^{-1}. Formamide passed the 3 σ_{noise} criteria only in the May period, where it explained 2% of the total emission and 24% of the total deposition. The emissions were highest between 19:00 and 20:00 with 0.13 nmol m^{-2} s^{-1} and the deposition peaked between 12:00 and 13:00 with -0.20 nmol m^{-2} s^{-1}.

The emissions of butene & butanol, which is discussed in Sect. 3.4, were not related to the start of the growing season. The flux of $C_4H_9^+$ decreased by almost two-thirds compared to the snowmelt period and would increase the total emission by 11%. The maximum flux of 0.29 nmol m^{-2} s^{-1} was between 15:00 and 16:00 and the minimum of 0.02 nmol m^{-2} s^{-1} between 22:00 and 23:00. However, during the start of the growing season, most of the emissions were biogenic.

Methanol is released in plant growth (e.g. Galbally and Kirstine, 2002), its emissions increased from being not detectable in April to a late afternoon maximum of 2.11 nmol m^{-2} s^{-1} in May. Compared to April's emissions the order of the major emitters reverses in addition to the increase of compounds with observable exchange. In May night temperatures were above zero, while the sun warmed late afternoons to around 20°C. The mean temperature was 11.4°C and the mean PAR was 301 μmol m^{-2} s^{-1}, during the measurements in May. The total deposition was higher than in the other months and reached -0.13 nmol m^{-2} s^{-1}, which is less than 10% of the total emission (1.37 nmol m^{-2} s^{-1}). Methanol was the most emitted (35%) and deposited compound (49%) in May, with the highest deposition of -0.47 nmol m^{-2} s^{-1} between 11:00 and 12:00. This deposition can be explained by the occurrence of rain during or right before this time window, which happened twice during the 9 day measurement period. The water soluble methanol is suspected to be dry deposited on the wet surfaces in the forest, (Laffineur et al., 2012; Wohlfahrt et al., 2015; Schallhart et al., 2016). The monoterpenes were the second most emitted compound group and contributed 23% to the total emission. Their maximum emission was 0.76 nmol m^{-2} s^{-1} between 15:00 and 16:00 and the minimum emission was 0.13 nmol m^{-2} s^{-1} between 3:00 and 4:00. Recently, Aalto et al. (2014, 2015) have shown that Scots pine needles are a pronounced source of monoterpenes in spring already before growth onset, and especially after bud break, when the formation of new biomass releases large amounts of terpenoids and other VOCs. The results of this study are in general consistent with those findings in terms of detected mean fluxes and diurnal patterns. During the start of the growing season, acetone was the third most emitted compound. In May it had the maximum emission of 0.61 nmol m^{-2} s^{-1} between 10:00 and 11:00 and the minimum between 03:00 and 04:00 with 0.04 nmol m^{-2} s^{-1}. The flux of $C_4H_9^+$ decreased by almost two-thirds compared to April comprising 11% of the total emission. The maximum flux of 0.29 nmol m^{-2} s^{-1} was between 15:00 and 16:00 and the minimum of 0.02 nmol m^{-2} s^{-1} between 22:00 and 23:00. Formamide passed the 3 σ_{noise} criteria only in May, where it explained 2% of the total emission and 24% of the total deposition. The emissions were highest between 19:00 and 20:00 with 0.13 nmol m^{-2} s^{-1} and the deposition peaked between 12:00 and 13:00 with -0.20 nmol m^{-2} s^{-1}. However, most of the emissions, were biogenic.

Some of the emissions, e.g. butene which is discussed in Sect. 3.4, were not related to the start of the growing season. However, most of the emissions, were biogenic.

3.1.3 Maximum emissions during summer

During the first weeks of June the highest average temperature and PAR were measured, with 17.2°C and 466 μmol m^{-2} s^{-1}, respectively. As temperature and light are the drivers of biogenic emissions (Guenther et al., 2012), the highest 24 h

total emission of the campaign, 2.87 nmol m^{-2} s^{-1}, was recorded during this time (Table 1). In Fig. 4 the maximum diurnal 1 h net flux is shown at 14:30 with 9.10 nmol m^{-2} s^{-1}. Similar as in the period in May, methanol, the group of monoterpenes and acetone were the most emitted compounds and the emissions of the ten most emitted compounds in summer all increased, if compared to the measurement period in May (Table 1).

In the summer period methanol was the most emitted compound, comprising 42% of the total emission and 17% of the deposition. The methanol flux was highest between 15:00 and 16:00 with 4.56 nmol m^{-2} s^{-1}, while between 03:00 and 04:00 it was deposited (-0.26 nmol m^{-2} s^{-1}). Growing leaf biomass is expected to release methanol due to cell wall demethylation (Galbally and Kirstine, 2002, Hüve et al., 2007, Aalto et al., 2014). The increase of the 24 h methanol emissions from undetectable during the snowmelt to about 0.5 nmol m^{-2} s^{-1} during the start of the growing season and finally well above 1 nmol m^{-2} s^{-1} in summer coincides with the typical coniferous needle biomass growth onset at the beginning of May and maximum needle elongation rate around mid-summer (Aalto et al., 2014).

Other biogenic emissions include the group of monoterpenes contributing 21% and acetone contributing 14% to the total emission. Similar to methanol, the highest monoterpenes and acetone emissions were observed in the late afternoon, with 1.46 nmol m^{-2} s^{-1} and 1.08 nmol m^{-2} s^{-1}, respectively. Formaldehyde contributed over 40% to the total deposition in June, resulting in a flux minima of -0.23 nmol m^{-2} s^{-1}. However, formaldehyde flux measurements are uncertain as discussed in Sect. 3. The anthropogenic flux of butene & butanol had a flux between 0.70 nmol m^{-2} s^{-1} and 0.02 nmol m^{-2} s^{-1}.

When we compared the selected 9 days to the 21 days in June (Fig. 6 and Table 2), we found that five compounds no longer fulfilled the 3 σ_{noise} criteria. Using the longer period lead to the rejection of formaldehyde, phenol, p-cymene and two unidentified masses 84.9500 Da and 99.0201 Da (Table 1 and Table 2). The rejection of formaldehyde was the major reason for the change of deposition from -0.12 nmol m^{-2} s^{-1} to -0.09 nmol m^{-2} s^{-1}. Three new masses had a detectable flux, acetonitrile (42.0338 Da) and two unidentified masses 89.0386 Da and 99.0769 Da. The total emission decreased from 2.87 nmol m^{-2} s^{-1} to 2.16 nmol m^{-2} s^{-1}. This difference can be explained by the lower average temperature of 15°C and the lower PAR of 406 µmol m^{-2} s^{-1} during the longer period.

~~During the growing season in the first weeks of June, the highest total emission, of the campaign, 3.12 nmol m^{-2} s^{-1}, was recorded. The average temperature and PAR were highest in this period being 17.2°C and 466 µmol m^{-2} s^{-1}, respectively. Temperature and light are the drivers of biogenic emissions (Guenther et al., 2012), so as expected the diurnal maximum of the net flux, 9.69 nmol m^{-2} s^{-1}, was observed on the afternoon in June. The four most emitted compounds had the same order as in May and all the emissions of June's ten most emitted compounds increased when compared to May, even if their relative (to the net flux) emissions (Table 1) decreased. In the growing season, methanol was the most emitted compound, comprising 39% of the total emission and 17% of the deposition. The methanol flux was highest between 15:00 and 16:00 with 4.56 nmol m^{-2} s^{-1}, while between 03:00 and 04:00 it was deposited (-0.26 nmol m^{-2} s^{-1}). Growing leaf biomass is expected to release methanol due to cell wall demethylation (Galbally and Kirstine, 2002, Hüve et al., 2007, Aalto et al., 2014). The increase of methanol fluxes from undetectable in April to about 0.5 nmol m^{-2} s^{-1} in May and finally well above 1 nmol m^{-2} s^{-1} in June coincides with the typical coniferous needle biomass growth onset at the beginning of May and maximum needle elongation rate around mid-summer (Aalto et al., 2014).~~

~~Other biogenic emissions include the group of monoterpenes contributing 20% and acetone contributing 13% to the total emission. Similar to methanol, the highest monoterpenes and acetone emissions were observed in the late afternoon, with 1.46 nmol m^{-2} s^{-1} and 1.08 nmol m^{-2} s^{-1}, respectively. C$_4$H$_9$$^+$ was the fourth most emitted compound with 8.2% of the total emission and a flux between 0.70 nmol m^{-2} s^{-1} and 0.02 nmol m^{-2} s^{-1}. Formaldehyde contributed over 40% to the total deposition in June, resulting in a flux minima of -0.23 nmol m^{-2} s^{-1}. However, formaldehyde flux measurements are~~

~~uncertain as discussed in Sect. 2.2.~~~~C₄H₉⁺ was the fourth most emitted compound with 8.2% of the total emission and a flux between 0.70 nmol m⁻² s⁻¹ and 0.02 nmol m⁻² s⁻¹.~~

~~When we compared the selected 9 days to all measurements in June (21 days; Fig. 6), we found that five compounds no longer fulfilled the 3 σ_noise criteria. Using the longer period lead to the rejection of formaldehyde, phenol, p-cymene and two unidentified masses 84.9500 amu and 99.0201 amu (Table 1 and Table 2). The rejection of formaldehyde was the major reason for the change of deposition from -0.13 nmol m⁻² s⁻¹ to -0.09 nmol m⁻² s⁻¹. Three new masses had a detectable flux, these were acetonitrile (42.0338 amu) and two unidentified masses 89.0386 amu and 99.0769 amu. The total emission decreased from 3.12 nmol m⁻² s⁻¹ to 2.36 nmol m⁻² s⁻¹. This difference can be explained by the lower average temperature of 15°C and the lower PAR of 406 µmol m⁻² s⁻¹ during the longer period.~~

3.2 Eddy covariance VOC fluxes above different ecosystems

Ecosystems and their phenomenology define which volatile organic compounds are released. In this study 25 compounds were exchanged, with 17 of them emitted during the 21 days in June. The measured emissions and the observed amount depend on many environmental aspects as well as meteorology, experimental setup (e.g. inlet length) and length and time of the measurements. The 24 h net emission during 21 days in June were 2.~~20~~7 nmol m⁻² s⁻¹, which is on the low side compared to other PTR-TOF fluxes from other ecosystems (Table 2). In the *Pinus sylvestris* (Scots pine) forest in Hyytiälä, the major emissions in June were from methanol, monoterpenes and~~,~~ acetone ~~and butene~~. Measurement gaps were excluded, when calculating the length of the data sets. Most of the studies used a data set between 20 and 35 days, Brilli et al. (2015) being an exception with 129 days. All measurements were carried out around summer, when the plant activities were high. This study was using data from June, Park et al. (2013) and Schallhart et al. (2016) used data from June and July, Kaser et al. (2013a) data from August and September and Brilli et al. (2015) used data from June until the end of October. Out of these studies, the lowest 24 h net flux was measured at a 2-year-old *Populus* (poplar) plantation (Brilli et al., 2015) in Belgium, with 1.99 nmol m⁻² s⁻¹. Isoprene was emitted most, followed by methanol, acetone and the group of green leaf volatiles (measured via a fragment). The low emission can be partly explained by the long measurement period that extended over the summer. Park et al. (2013) reported a net flux of 4.43 nmol m⁻² s⁻¹ above an orange grove. The most emitted compounds were methanol, acetic acid, monoterpenes and acetone. The study was exceptional, as it measured significant fluxes for several hundreds of VOCs. Despite that, the highest net flux was measured by Schallhart et al. (2016) above a mixed *Quercus* (oak) *Carpinus betulus* (hornbeam) forest with 9.78 nmol m⁻² s⁻¹. In their study the most emitted compounds were isoprene, methanol, acetone and methyl vinyl ketone+methacrolein. The high emissions can be explained by the ecosystem, as oaks are known to be strong isoprene emitters (e.g. Potosnak et al., 2014). Kaser et al. (2013a) reported 8 h daytime fluxes only, so a direct comparison with the 24 h net flux ~~is not possible~~from the other studies is not possible. However, the *Pinus ponderosa* (Ponderosa pine) flux was dominated by MBO+isoprene fluxes, followed by methanol and acetic acid. The net flux is almost a factor of 4 higher than in boreal forest in Hyytiälä. However, it should be noted that the day length in summer is much longer in Hyytiälä (62° N) when compared to the Ponderosa pine forest in Colorado (39° N) and, therefore, elevated emissions last longer than 8 h.

The net carbon flux of the VOCs during the campaign in Hyytiälä was ~~8~~7.~~0~~25 nmol C m⁻² s⁻¹ (Fig. 7). The group of monoterpenes was the highest emitter of carbon with ~~54~~59% of the net carbon exchange, followed by methanol (1~~2~~3%), acetone (1~~1~~2%)~~., butene (10%) and~~ isoprene (5%) and acetaldehyde (3%). ~~Acetaldehyde, t~~The C₃H₅⁺ fragment and toluene & p-cymene contributed 2% respectively, while acetic acid and the sum of the remaining compounds both

contributed 1%. Compared to the CO_2 net ecosystem exchange (NEE) of -4266 nmol C m^{-2} s^{-1}, the carbon released as VOC represents less than 0.2% of the NEE of the corresponding period. In Brilli et al. (2015) the VOCs, with 6.36 nmol C m^{-2} s^{-1}, represent 0.8% of the carbon exchange and in Schallhart et al. (2016) VOCs had a carbon flux of 41.8 nmol C m^{-2} s^{-1}, which corresponded to 1.7% of the NEE. Juráň et al. (2017), measured EC exchange of VOCs in a *Picea abies* (Norway spruce) forest in the Czech Republic. In their study the ratio between the carbon released from VOCs and the NEE was 0.3% during the five days of data in July. Other ratios from vDEC studies using PTR-Quad are 0.7% above an oil palm plantation (*E. guineensis* × *E. oleifera* hybrid) in Malaysia (Misztal et al., 2011), 0.16% and 0.24% above two *P. halepensis* (Aleppo pine) forests in Israel (Seko et al., 2017).

There was an order of magnitude difference between the proportion of net assimilated carbon released as VOCs between a Mediterranean oak-hornbeam forest (Schallhart et al., 2016) and a boreal evergreen forest. Also, a middle European poplar plantation (Brilli et al., 2015) clearly released a higher proportion of the assimilated carbon as VOCs than a boreal site in this study. The spruce forest in central Europe came closest to the results in Hyytiälä. These findings strongly imply that there are significant differences between the ecosystems in how they allocate carbon to VOCs, however the reasons for that are rather related to light and thermal conditions, species selection and age structure and soil properties than to the efficiency of an ecosystem to produce VOCs as an indefinable concept. In boreal ecosystems with relatively northern locations, the majority of carbon assimilation is concentrated within a couple of months around mid-summer with very short nights. The structure of forest and the tree species are effective in utilizing the high light availability during the summer months, whereas in more southern locations the light availability and thermal conditions allow more even carbon assimilation throughout a considerably longer period. This partly explains the lower proportion of C released as VOCs determined in this study, when compared to those measured in more southern locations. Additionally, the constitutive emission capacities of boreal evergreen species are known to be low when compared to deciduous species more common in central and southern Europe (Rinne et al., 2009; Ghirardo et al., 2010).

3.3 Comparison between PTR-TOF and PTR-Quad measurements

Generally, the EC method detected more masses than the SLP measurements, which can be explained by the preselection of the masses to be measured by the PTR-Quad and its low duty cycle. The comparison between PTR-TOF using the EC method and the PTR-Quad using the surface layer profile method (SLP, see Rantala et al., 2015) between April and June revealed 12 more compounds with exchange using the EC method (see Table 1, 2 and 3). The PTR-TOF measures all VOCs in a certain mass range, while the PTR-Quad needs a preselection of masses, limiting the number of recorded compounds. However, the classification if a compound has a measurable flux is different between the two methods (Sect. 2.3 and Rantala et al., 2015). Even though the EC method found almost twice the number of compounds with exchange, the total exchange was in on the same order of magnitude for both methods. The discrepancy of between the results of the two measurements are is mainly due to instrument and method differences. The horizontal distance between the inlets of these two instruments was just 25 m and the PTR-Quad was measuring from 13 m higher (calculated height 36 m) than the PTR-TOF, leading to a larger footprint area for the SLP method. This can be seen in Fig. 8, where the daytime (07:00 to 19:00) footprint calculated according to Kormann and Meixner, (2002) for the SLP and EC method are presented. Even though the nominal measurement height of the SLP was 36 m, the shown footprint is calculated for 33 m, as this was the closest height with horizontal wind measurements.

The main compounds (methanol, acetone and monoterpenes) were detected with by both methods. $C_4H_9^+$ (57.0699 Damu) could not be measured by the PTR-Quad, as the unit mass resolution of the instrument is unable to separate the signal

from the water cluster isotope $H_7O_2{}^{18}O_1{}^+$ (57.0432 D~~amu~~). On the other hand, the SLP measurements observed a flux of ethanol+formic acid which was not detected by the PTR-TOF. Interestingly, formic acid fluxes have also been observed at SMEAR II using the EC method with an Iodide-Adduct High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer in 2014 (Schobesberger et al., 2016). Other VOC fluxes, which were not detected by the PTR-TOF were methyl ethyl ketone (73 D~~amu~~), a fragment of the green leave volatiles (83 D~~amu~~) and MBO (87 D~~amu~~). The formaldehyde fluxes were not included in the comparison, as the PTR-TOF detected them just during the first 8 days in June, during which the PTR-Quad had technical problems resulting in less than ten overlapping data points from the two instruments.

Overall, the flux values used for the comparison were small, as the compared data included values from April and May, and unfortunately the SLP measurements were not working during the warm, i.e. high flux, period in the beginning of June. Thus, the comparison was done using flux values that were mostly close to the detection limits of the EC and the SLP setups. The uncertainties of the turbulence measurements and noise of the VOC measurements, together with the different measurement setups, methods and footprints was seen in the scatter of the compared data, which affected correlation, fitting parameters and their uncertainties (Table 3).

~~The~~However, the magnitude of the studied fluxes as well as their diurnal patterns were comparable for methanol, acetone, isoprene and monoterpenes (Table 3 and Fig. 9~~8~~). The monoterpene and ~~and~~ methanol fluxes measured by the two methods ~~had~~ showed ~~also a~~the highest ~~good~~ correlation, which was barely above 0.6 ~~with each other~~ (Fig. 10~~9~~). The fitted slopes of the scatter plots for acetone, isoprene and the monoterpenes were far from unity, as best R^2 values were calculated when using high intercepts.~~the SLP measurements were not working during a warm, i.e. high flux, period in the beginning of June.Thus, the comparison was done using flux values that were mostly close to the detection limits of the EC and the SLP setups.~~

The fluxes of acetonitrile, acetaldehyde, acetic acid and toluene & p-cymene did not agree similarly well. ~~Unfortunately, the SLP measurements were not working during a warm, i.e. high flux, period in the beginning of June. Thus, the comparison was done using flux values that were mostly close to the detection limits of the EC and the SLP setups.~~ Therefore, the correlations between the methods were poor for rest of the compounds. The toluene & p-cymene flux discrepancy was likely caused by a different detection of the toluene & p-cymene signal in the two instrument and not due to the different flux methods. The toluene & p-cymene measurements at mass 93 with PTR-Quad and 93.0454 with PTR-TOF resulted in different concentration values and should be handled with care. Different fragmentation from ~~higher masses (most probably~~ p-cymene~~)~~, influence from two other mass peaks seen at nominal mass 93 (92.5 D~~amu~~ to 93.5 D~~amu~~) and/or unsuccessful calibrations may probably explain the observed differences. Kajos et al. (2015) reported similar discrepancies in toluene & p-cymene concentration measurements with the PTR-Quad at the site. Also acetic acid is fragmenting when measured with the PTR method (Baasandorj et al., 2015). Higher fragmentation in the PTR-TOF (61.0284 D~~amu~~), when compared to the PTR-Quad (60.5 D~~amu~~ to 61.5 D~~amu~~), could account for a part of the lower acetic acid fluxes with the EC method. However, even if the acetic acid main fragment $C_2H_3O_1{}^+$ (Baasandorj et al., 2015) is taken into account, in addition to the signal from the parent mass, the EC fluxes are still lower than the SLP results. Another uncertainty comes from the lack of acetic acid in the calibration standard. For the uncalibrated compounds the sensitivity can be calculated (Sect 2.2; Rantala et al., 2015), they, however, are more uncertain and can lead to systematic discrepancies. A recent study compared PTR-TOF measurements with gas chromatography mass spectrometer measurements and also in this study the PTR-TOF underestimated the acetic acid concentration (Helén et al., 2016). The authors suggest~~ed~~ that a possible memory effect in the inlet or instrument could lead to this underestimation, which was

also reported by de Gouw et al. (2003). This effect could lead to an additional attenuation of the acetic acid signal, and thus decrease the measured flux.

In addition to the differences between the PTR-Quad used in SLP and the PTR-TOF used in EC, the flux calculation methods could also lead to discrepancies: i) the SLP fluxes have larger footprints, which was seen as different flux values, ii) either the SLP or the EC method work improperly for these compounds. One should also note that the comparison was based on a small data set only (Table 3) and, thus, random variations also affect the results. The net flux for all compounds in Table 3 was 1.120 nmol m^{-2} s^{-1} for the PTR-TOF and 1.471 nmol m^{-2} s^{-1} for the PTR-Quad. If the net flux is calculated for all the compounds, which were measured by the individual instrument, it is 1.425~~276~~ nmol m^{-2} s^{-1} for the PTR-TOF, not including butene & butanol, and 1.802 nmol m^{-2} s^{-1} for the PTR-Quad.

3.4 Anthropogenic flux of C$_4$H$_9^+$

The identification of the compound with the elemental composition of C$_4$H$_9^+$ is problematic as it could be protonated butene, which can be emitted by forests (Goldstein et al., 1996; Hakola et al., 1998) and from anthropogenic sources (Harley et al., 1992; Na et al., 2004). Another possible contribution to the C$_4$H$_9^+$ signal comes from the fragmentation of butanol, which as many other alcohols, can lose an OH during ionization (Spanel and Smith, 1997). Denzer et al. (2014) reported that the most abundant signal of butanol, when measured with PTR-Quad, is for the C$_4$H$_9^+$ mass. Fragmentation tests using the PTR-TOF confirmed this. In Fig. ~~10~~11 the average C$_4$H$_9^+$ flux from different wind sectors and the windrose for the individual 30 min C$_4$H$_9^+$ fluxes are shown. The sources of the C$_4$H$_9^+$ clearly lay in the western part of the forest as there are just low emissions and depositions in the east side. The highest average flux of C$_4$H$_9^+$ came from south-southwest (195°) with ~~an average flux of~~ 0.57 nmol m^{-2} s^{-1} while another maximum lay in north-northwest (345°) with 0.42 nmol m^{-2} s^{-1}. The cottages where the butanol using aerosol measurements, condensation particle counters (CPCs), of the station are located (Fig. 1~~0~~1, orange circles), lie approximately in these directions. An additional CPC was mounted on a mast located west of the VOC flux measurements. Therefore we conclude that the C$_4$H$_9^+$ signal is mainly from butanol used by the aerosol instruments and thus the flux is anthropogenic. During 2013, approximately 100 L of butanol were evaporated in the CPCs at the station. During our measurements the contribution of the butanol fragment to the total emission was 63% ~~in~~ during the measurement period in April, 11% in the May period and 8% during the measurements~~in~~ in June.

4. Conclusion

Overall, the exchange of 25 compounds was observed over a boreal Scots pine forest. During the transition from early spring to mid-summer the net flux increased by a factor of five and the number of compounds changed from three to 19. The highest emissions occurred in late afternoon, while deposition was observed mainly at night. The majority of the net VOC flux was comprised of methanol, monoterpenes, acetone and butene & butanol. The measured butene & butanol flux was most likely a fragment of butanol and created by evaporation in the particle counters used at the SMEAR II station. Twelve compounds were measured either only in May or June, which implies a strong seasonal cycle and a high diversity of VOC emissions from the boreal forest in Hyytiälä.

Compared to EC fluxes from other ecosystems measured with the PTR-TOF, the VOC emission in the boreal forest was small, 2.1~~3~~6 nmol m^{-2} s^{-1}, even though the measurements in June had the longest day length, up to 19.5 h. In relation to the CO$_2$ exchange, the VOCs are only less than 0.2% compared to the net ecosystem carbon exchange.

The EC fluxes measured with PTR-TOF and the SLP fluxes measured with PTR-Quad had similar results for the main flux compounds: methanol, monoterpenes and acetone, thus, confirming the feasibility of the indirect SLP method at the site. For small fluxes, like acetonitrile, isoprene and acetaldehyde the results weare affected by noise. Toluene & p-cymene and acetic acid show significant differences, which could hint at differences in the fragmentation patterns of the instruments. Further research is still needed to close the gap between the fluxes measured by the two instruments.

Therefore, longtime measurements with the PTR-Quad or other instruments, which create less data and do not need such work intensive data post processing as the PTR-TOF, are essential. If a research network of sites with VOC flux measurements is established in the future, cheaper and easier to use instruments are needed (Rinne et al., 2016). Still, intensive campaigns with more selective instruments are an important asset to understand biosphere-atmosphere exchanges and air chemistriesy in different ecosystems.

Table 1: The exchange of the different compounds in during the measurements in April, May and June. All the presented emission (E) and deposition (D) values are in percentages in relation to the total emission or deposition of the month (stated in the last line). Emissions of butene & butanol are in red as they are anthropogenic (Sect. 3.4) and, therefore, not included in the total exchange.

mass [~~amu~~Da]	elemental composition	possible compound	~~April~~snowmelt		~~May~~start of growing season		~~June~~summer	
			E	D	E	D	E	D
33.0335	$C_{\cancel{1}}H_5O_{\cancel{1}}^+$	methanol			~~35.3~~39.6	49.1*	~~38.7~~42.1	16.5*
137.1325	$C_{10}H_{17}^+$	monoterpenes	~~47.7~~17.6	0	~~23.~~6.02	0	~~19~~21.20	0
59.0491	$C_3H_7O_{\cancel{1}}^+$	acetone	~~52.3~~19.3	100*	~~16.8~~8.9	0	~~13~~14.13	<1*
57.0699	$C_4H_9^+$	butene & butanol	170.5~~63.0~~	0	~~10.8~~2.1	0	8.~~2~~9	0
45.0335	$C_2H_5O_{\cancel{1}}^+$	acetaldehyde					5.~~1~~5	4.0*
69.0699	$C_5H_9^+$	isoprene			2.~~2~~4	<1*	4.~~2~~6	1.2*
61.0284	$C_2H_5O_2^+$	acetic acid					2.~~4~~6	4.1*
43.0178	$C_2H_3O_{\cancel{1}}^+$	fragment					2.~~2~~4	7.7*
41.0386	$C_3H_5^+$	fragment			2.~~6~~9	3.7*	2.~~3~~5	<1*
31.0178	$C_{\cancel{1}}H_3O_{\cancel{1}}^+$	formaldehyde					<1	41.4
60.0471	60.0471	unknown			3.~~4~~8	6.8*	1.~~2~~3	9.0*
93.0699	$C_7H_9^+$	toluene & p-cymene			2.~~4~~6	<1*	<1	1.8
69.0352	69.0352	unknown					<1	<1*
67.0542	$C_5H_7^+$	cyclopentadiene					<1	<1*
70.0696	70.0696	unknown			<1	2.6	<1	1.7*
99.0201	99.0201	unknown					<1	3.6*
84.9500	84.9500	unknown					<1*	4.8
95.0491	$C_6H_7O_{\cancel{1}}^+$	phenol					<1	1.1*
135.1168	$C_{10}H_{15}^+$	p-cymene					<1*	<1*
46.0287	$C_{\cancel{1}}H_4O_{\cancel{1}}N_{\cancel{1}}^+$	formamide			~~1~~2.91	23.9		
118.9456	118.9456	unknown			~~≤1~~<1*	9.0		
71.0491	$C_4H_7O_{\cancel{1}}^+$	MVK & MACR			~~≤1~~<1	7.9		
total emission and deposition [nmol m^{-2} s^{-1}]			0.~~68~~25	-0.01	1.~~39~~24	-0.17	~~32.1~~28.7	-0.12

(*) Values under the limit of detection (2 σ_{ind}). σ_{ind} was calculated using the propagation of error formula and the standard deviation at the borders of the individual 30 min CCFs.

Table 2: Comparison between different studies using a PTR-TOF with the EC method. The listed compounds are limited to the ones measured in Hyytiälä. Numbers in parentheses describe deposition and emission, respectively. All values are 24 h averages, except ~~in Kaser et al., (2013a), where 8h average daytime values are presented~~ values marked with [b]. **Emissions of butene & butanol are in red as they are anthropogenic (Sect. 3.4) and, therefore, not included in the total exchange.**

|		net flux [nmol m^{-2} s^{-1}]					
mass [Da]	elem. comp.	this study (21 days June)	Schallhart et al. (2016)	Park et al. (2013)[a]	Brilli et al. (2015)	this study (21 days June)[b]	Kaser et al. (2013a)[b]
33.0335	CH_5O^+	0.965* (-0.044/1.010)	1.168 (-0.365/1.533)	1.655 (-0.102/1.757)	0.884	2.09[b]	3.53[b]
41.0386	$C_3H_5^{\pm}$	0.050* (-0.001/0.051)		0.085 (-0.005/0.089)		0.10[b]	
42.0338	$C_2H_4N^+$	0.003 (-0.008/0.011)	0.046 (-0.005/0.051)			<0.01[b]	
43.0178	$C_2H_3O^+$	0.027* (-0.011/0.038)		0.075 (-0.001/0.076)		0.07[b]	
45.0335	$C_2H_5O^+$	0.099* (-0.004/0.103)	0.228 (-0.001/0.229)	0.133 (-0.016/0.148)	0.004	0.17[b]	1.05[b]
57.0699	$C_4H_9^{\pm}$	0.199 (0/0.199)		0.016 (-0.011/0.027)		0.30[b]	
59.0491	$C_3H_7O^+$	0.297* (-0.001/0.297)	0.335 (-0.01/0.345)	0.281 (-0.004/0.286)	0.035	0.48[b]	0.13[b]
60.0471	unknown	0.022* (-0.005/0.026)				0.03[b]	
61.0284	$C_2H_5O_2^{\pm}$	0.044* (-0.003/0.048)	0.214 (-0.096/0.311)	0.413 (-0.005/0.418)		0.09[b]	1.64[b]
67.0542	$C_5H_7^{\pm}$	0.006* (-0.001/0.007)		0.012 (-0.004/0.017)		0.01[b]	
69.0352	unknown	0.013* (-0.001/0.013)				0.03[b]	
69.0699	$C_5H_9^{\pm}$	0.083* (-0.003/0.086)	6.466 (0/6.466)	0.025 (-0.001/0.025)	1.009	0.17[b]	5.87[b]
70.0696	unknown	0.007* (-0.001/0.008)				0.01[b]	
89.0386	$C_7H_5^{\pm}$	0.001 (-0.004/0.005)				>-0.01[b]	
93.0699	$C_7H_9^{\pm}$	0.020* (-0.001/0.021)		0.058 (0/0.058)		0.04[b]	
99.0769	unknown	0.001 (-0.004/0.004)				0.01[b]	
137.1325	$C_{10}H_{17}^{\pm}$	0.430 (0/0.430)	0.219 (-0.001/0.219)	0.290 (0/0.290)[2]	0.005	0.63[b]	0.71[b]
Net flux in study		2.07	9.78	4.43	1.99	3.93[b]	15.07[b]
Length of data set [days]		21	21	33	129	21	31
Highest emitted compound		methanol	isoprene	methanol	isoprene	methanol	MBO & isoprene
# of compounds with flux		17	29	494	13	17	15[c]

(*) Values for downward flux are under the respective limit of detection (2 σ_{ind}). σ_{ind} was calculated using the propagation of error formula and the standard deviation at the borders of the individual 30 min CCFs. ([a]) Park et al. (2013) published the 24 h values of the identified masses, therefore no comparison of the unidentified compounds was possible. ([b]) 8 h average daytime values (10:00 - 16:00). ([c]) 8 of the 15 compounds were only recorded after a hail storm event.

~~(*) Values for downward flux are under the respective limit of detection (2 σ_{ind}). σ_{ind} was calculated using the propagation of error formula and the standard deviation at the borders of the individual 30 min CCFs. ([a]) Park et al. (2013) published the 24h values of the identified masses, therefore no comparison of the unidentified compounds was possible. ([b]) Kaser et al. (2013a) published average daytime fluxes (10:00 - 18:00) and therefore their results cannot be directly compared with the 24h average values. ([c]) 8 of the 15 compounds were only recorded after a hail storm event.~~

Table 3: Statistics of the major compounds of SLP and the EC flux measurements. ~~The compound names are educated guesses (see Sect. 2.2 for possible interferences).~~ The EC fluxes are in bold whereas the SLP fluxes are written in normal text. The fitting parameters describe the slope (upper value) and the intercept (lower value) of the linear model between the EC and the SLP fluxes. N is the number of the data points for each compound. The numbers in parenthesis are lower and upper quartiles. The unit for the mean, median, intercept and quantile values is nmol m^{-2} s^{-1}.

nominal mass	R^2	mean	median	5% and 95% quant.	fitting	N
33 (methanol)*	0.374	0.447	0.204 (-0.177, 1.161)	-1.602, 2.920	0.810 ± 0.220	92
		0.553	**0.730 (-0.931, 1.910)**	**-2.107, 3.296**	0.171 ± 0.306	
42 (acetonitrile)	0.003	-0.009	-0.003 (-0.026, 0.005)	-0.052, 0.026	0.296 ± 1.545	55
		-0.017	**-0.050 (-0.103, 0.072)**	**-0.209, 0.228**	-0.015 ± 0.040	
45 (acetaldehyde)	0.033	0.019	0.024 (-0.106, 0.131)	-0.382, 0.481	-0.195 ± 0.310	49
		0.063	**0.114 (-0.116, 0.245)**	**-0.406, 0.507**	0.067 ± 0.082	
59 (acetone)	0.051	0.176	0.090 (0.004, 0.262)	-0.156, 0.696	0.242 ± 0.191	119
		0.173	**0.210 (-0.046, 0.373)**	**-0.469, 0.677**	0.131 ± 0.074	
61 (acetic acid)*,a	0.064	0.336	0.244 (0.059, 0.504)	0.003, 1.052	0.116 ± 0.130	49
		0.025	**0.058 (-0.029, 0.093)**	**-0.115, 0.195**	-0.014 ± 0.061	
69 ~~—~~ (isoprene & MBO)	0.127	0.082	0.033 (0.005, 0.091)	-0.009, 0.383	0.274 ± 0.160	82
		0.035	**0.035 (-0.013, 0.052)**	**-0.054, 0.104**	0.013 ± 0.025	
93 (tol.~~uene~~ & p-cym.)	0.089	0.138	0.081 (0.024, 0.209)	-0.063, 0.519	0.088 ± 0.061	88
		0.027	**0.037 (-0.013, 0.052)**	**-0.054, 0.104**	0.015 ± 0.014	
137 (monoterpenes)	0.364	0.282	0.208 (0.084, 0.365)	0.023, 0.754	0.503 ± 0.123	116
		0.261	**0.225 (0.135, 0.349)**	**0.019, 0.583**	0.118 ± 0.051	

(*) sensitivity was derived from the instrumental transmission curve for the PTR-Quad. (a) the acetic acid sensitivity was estimated
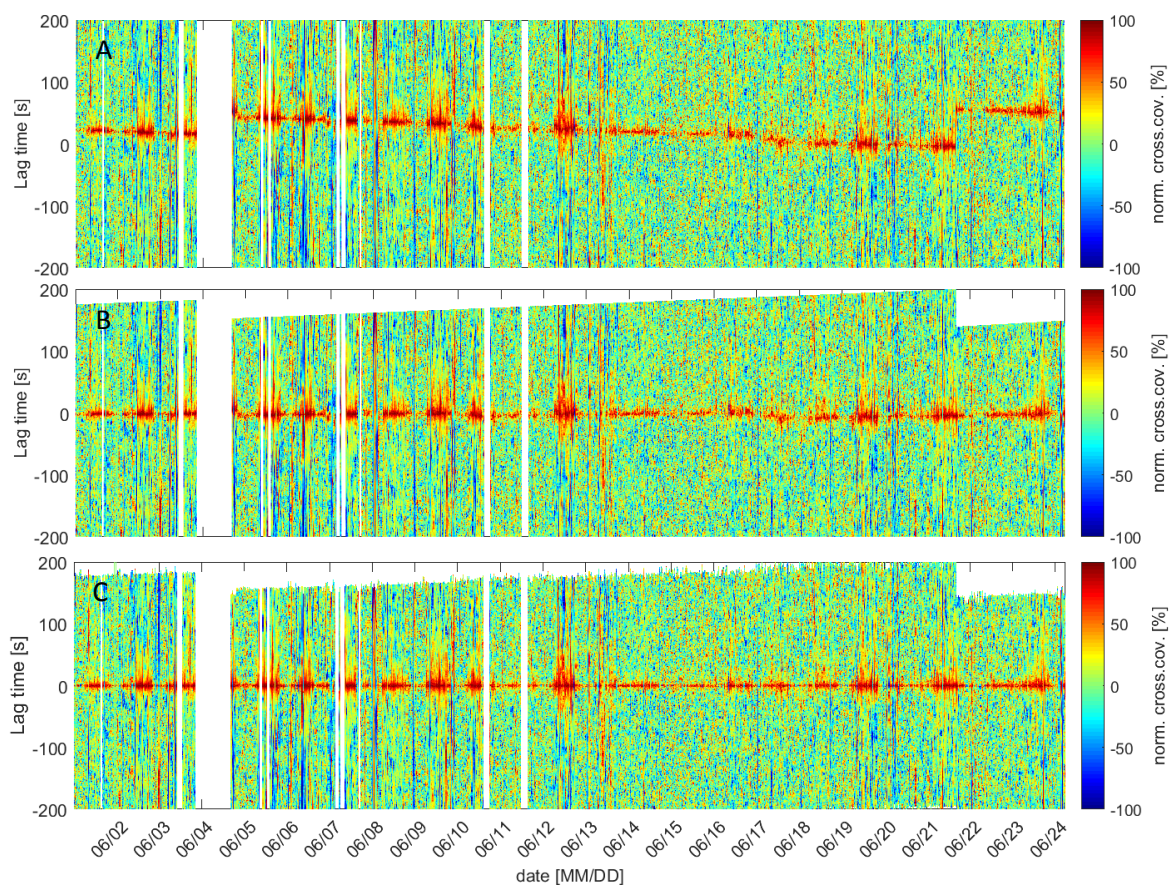
Figure 1: A) Normalized CCFs for monoterpene measurements in June, without time shift correction. The shift between the two computer clocks is clearly visible. B) CCFs after correcting for lag time shifts. C) The CCFs of monoterpenes after the final lag time correction. In the final (third) step, the smoothed maximum of the CCF function (see Fig. 2) was sought for each compound and 30 min data individually, in a ± 10 s window of the previous lag time (step 1 & 2).
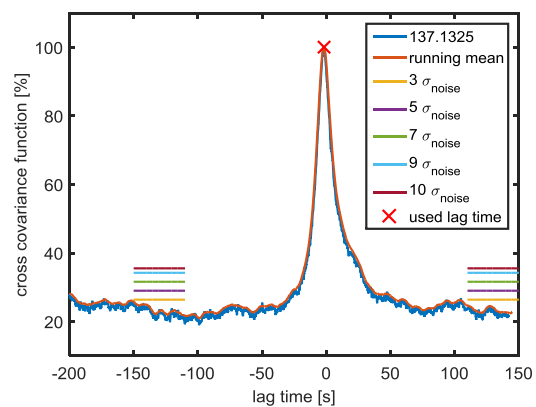
Figure 2: For each compound which had a maximum above 3 σ_{noise}, the deviation of the CCF maxima from zero was used as the lag time correction.
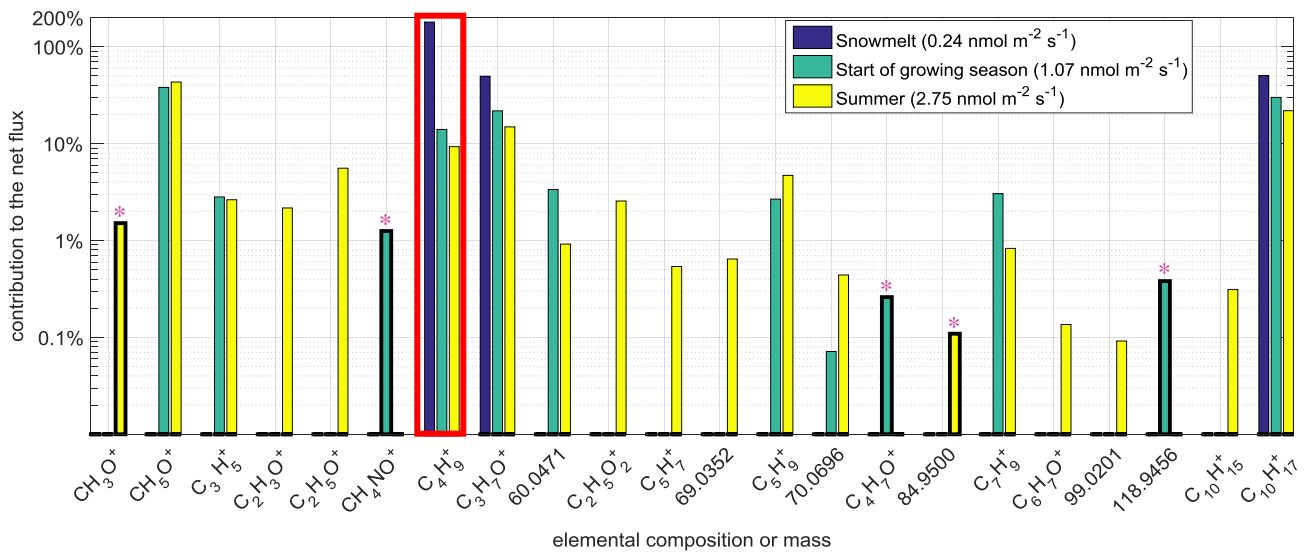
Figure 3: Contribution of each compound to the 24 h average net flux of the respective month. Bars with thick outlines and * above them correspond to negative fluxes, where the absolute value was taken before plotting them in the logarithmic scale. See Table 1 for corresponding compound names. Emissions of $C_4H_9^+$ are highlighted in a red as they are anthropogenic (Sect. 3.4) and, therefore, are not included in the net flux.
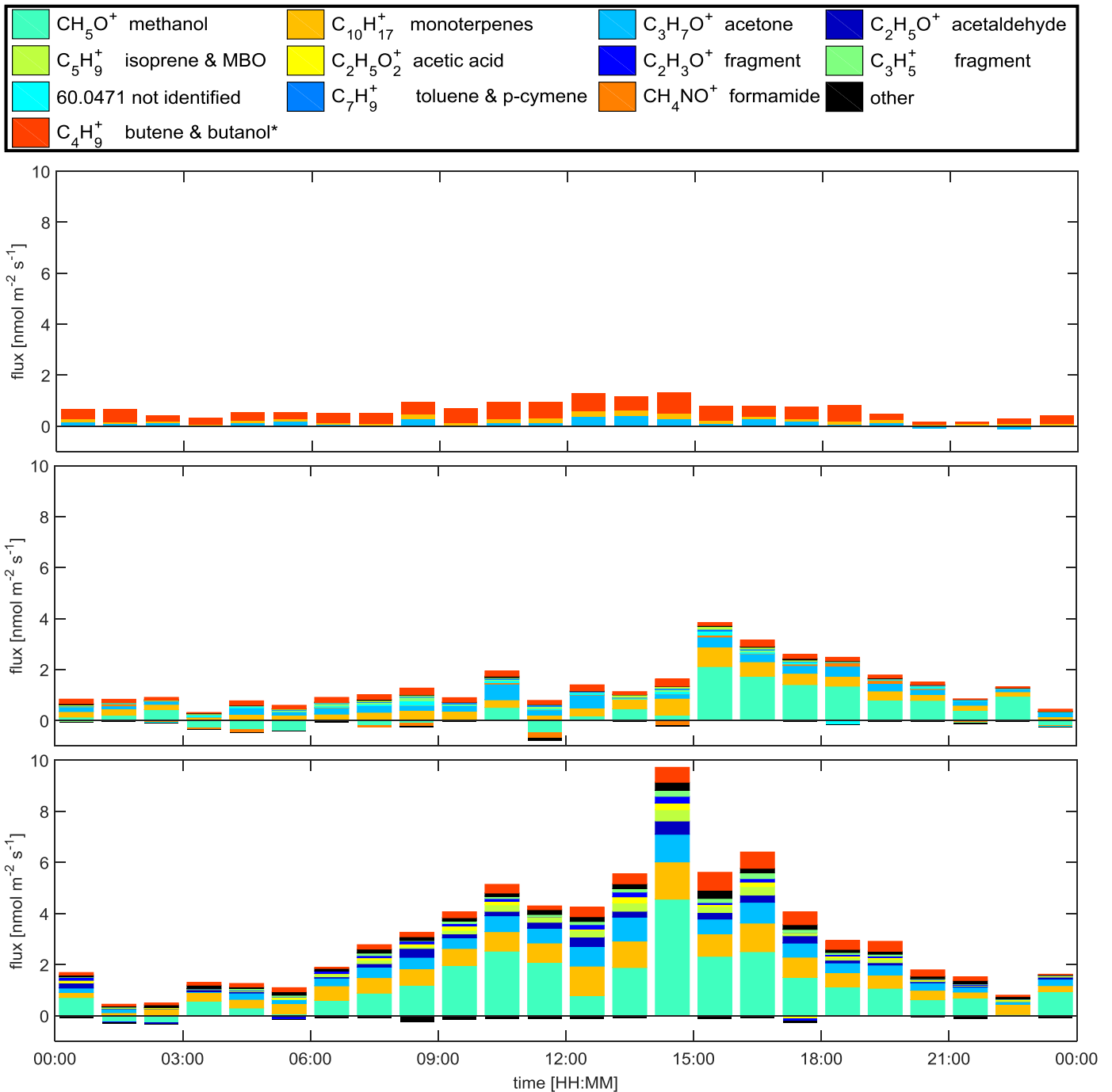
Figure 4: Diurnal pattern of the 9 compounds with the highest fluxes, the remaining compounds being summed up as 'other'. The panels show the fluxes for ~~April~~ snowmelt (top), ~~May~~start of growing season (mid) and ~~June~~summer (bottom). The number of data points per hour is dependent on the quality criteria filtering and whether it is in an hour when the automatic background was measured. (*) The butene & butanol exchange is anthropogenic and thereby not emitted by the forest (Sect. 3.4).
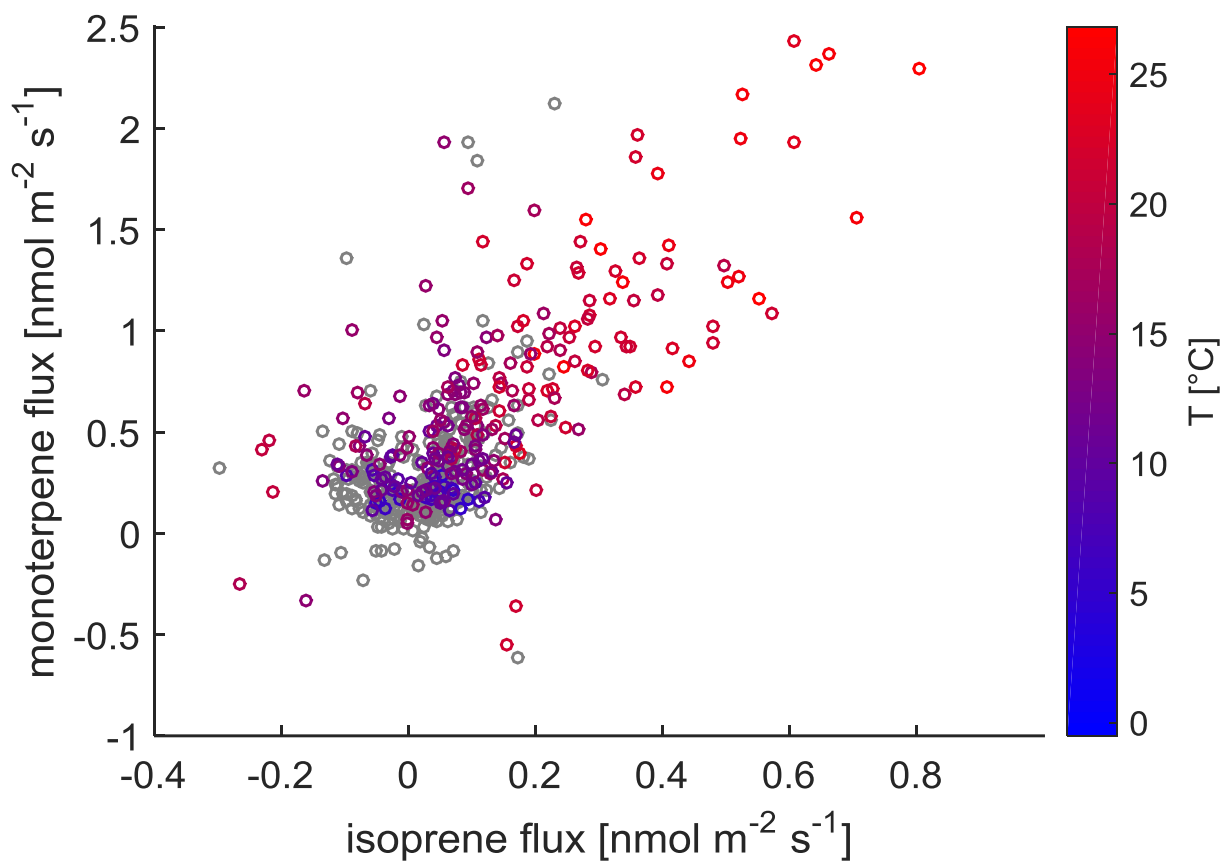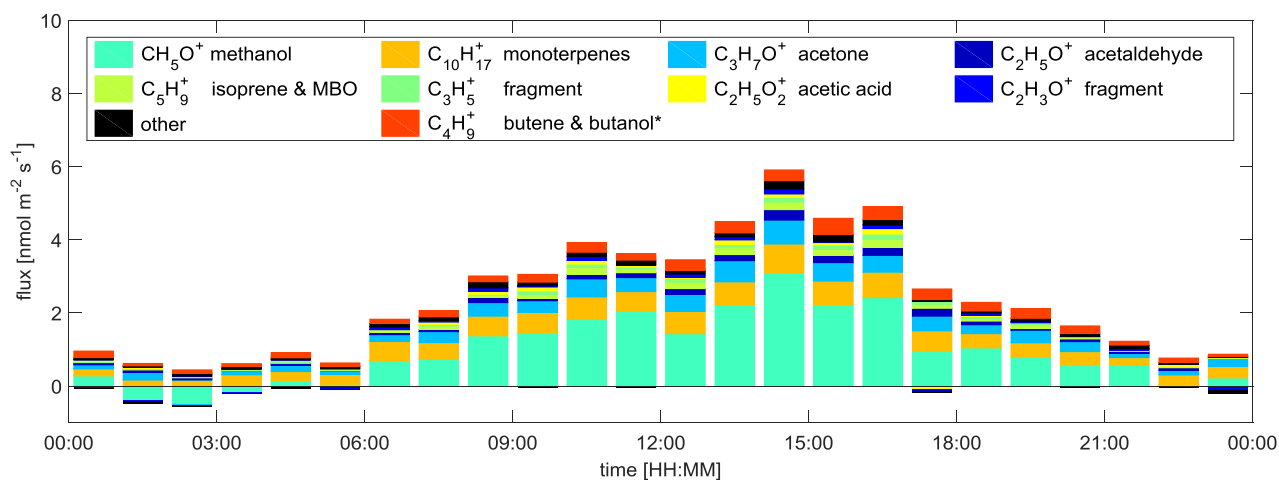
Figure 5: Scatterplot of 30 min isoprene and monoterpene flux. The gray data points are values where the PAR was smaller than 200 μmol m^-2 s^-1. Isoprene fluxes are very low and especially during low PAR conditions they are heavily affected by noise and a mirroring effect (Langford et al., 2015).

Figure 6: Diurnal variation of the nine most emitted compounds during the 21 days of measurement in June. The remaining compounds are summed up as 'other'. The high variation in the flux seen in Fig. 4 (diurnal plot of 9 days of measurements in June) is reduced, as meteorological events (e.g. rain) have less impact on the result. (*) The butene & butanol exchange is anthropogenic and thereby not emitted by the forest (Sect. 3.4).
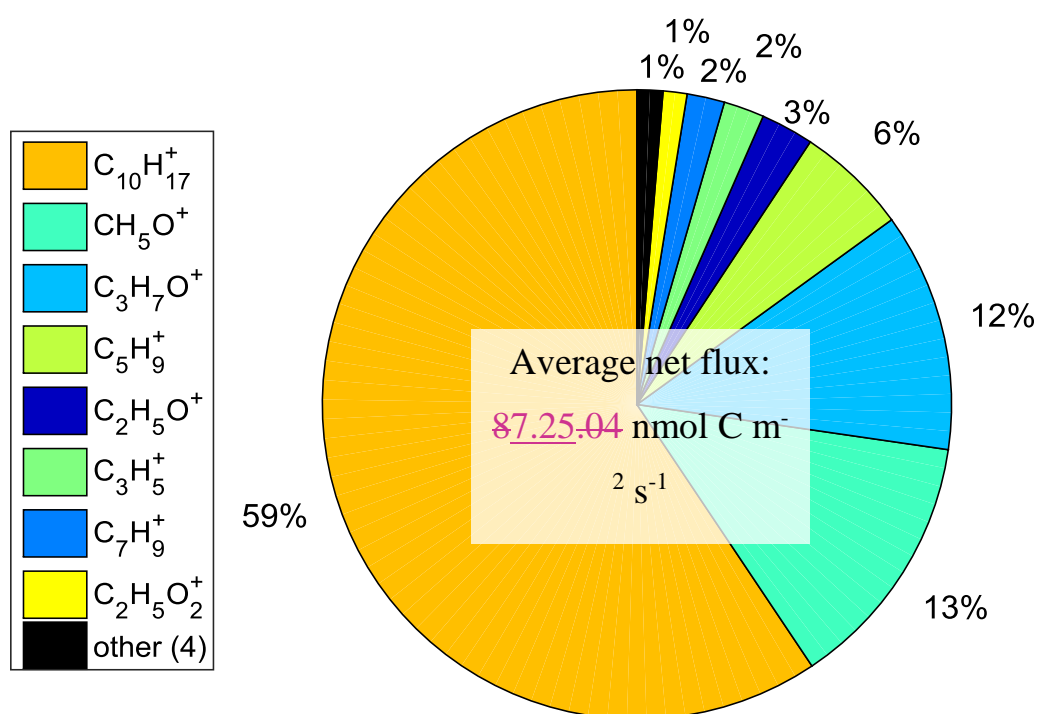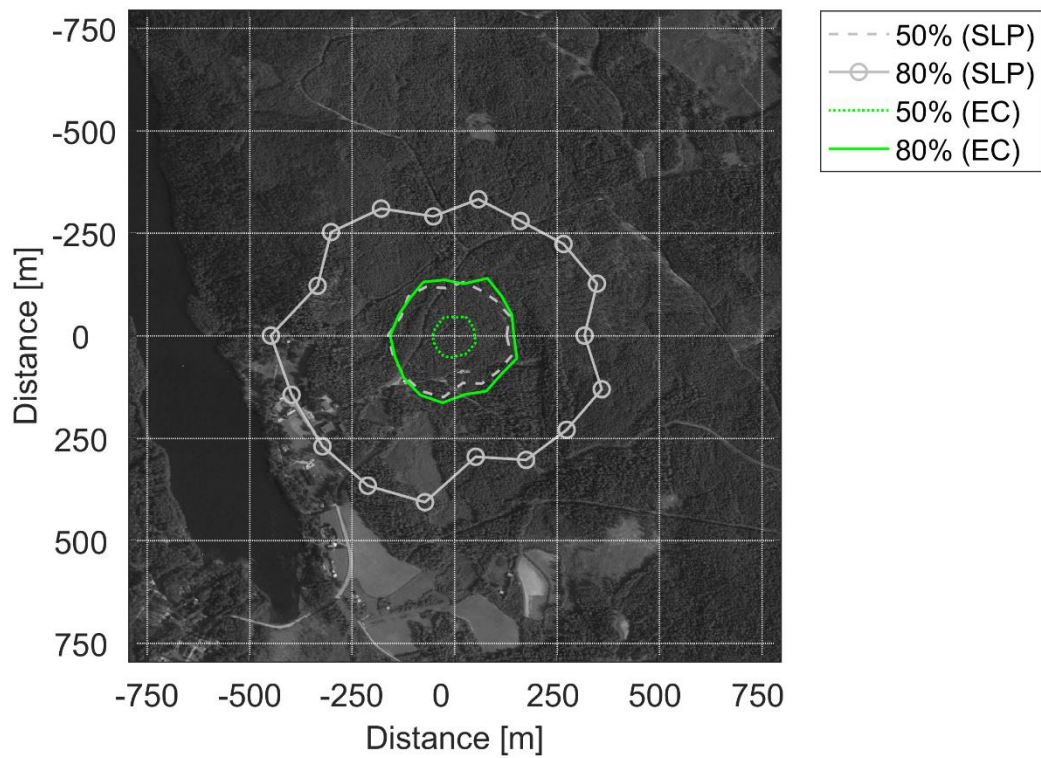
Figure 7: Average net flux of the major carbon emitters. Compounds whose elemental composition could not be identified were disregarded. See Table 1 for the corresponding compound names. The butene & butanol emissions were disregarded in this figure.

Figure 8: Footprint of the SLP and EC method. The higher nominal measurement height of the SLP fluxes increases the footprint drastically, when compared to the EC measurements. This could be a possible cause for the discrepancies in the results.
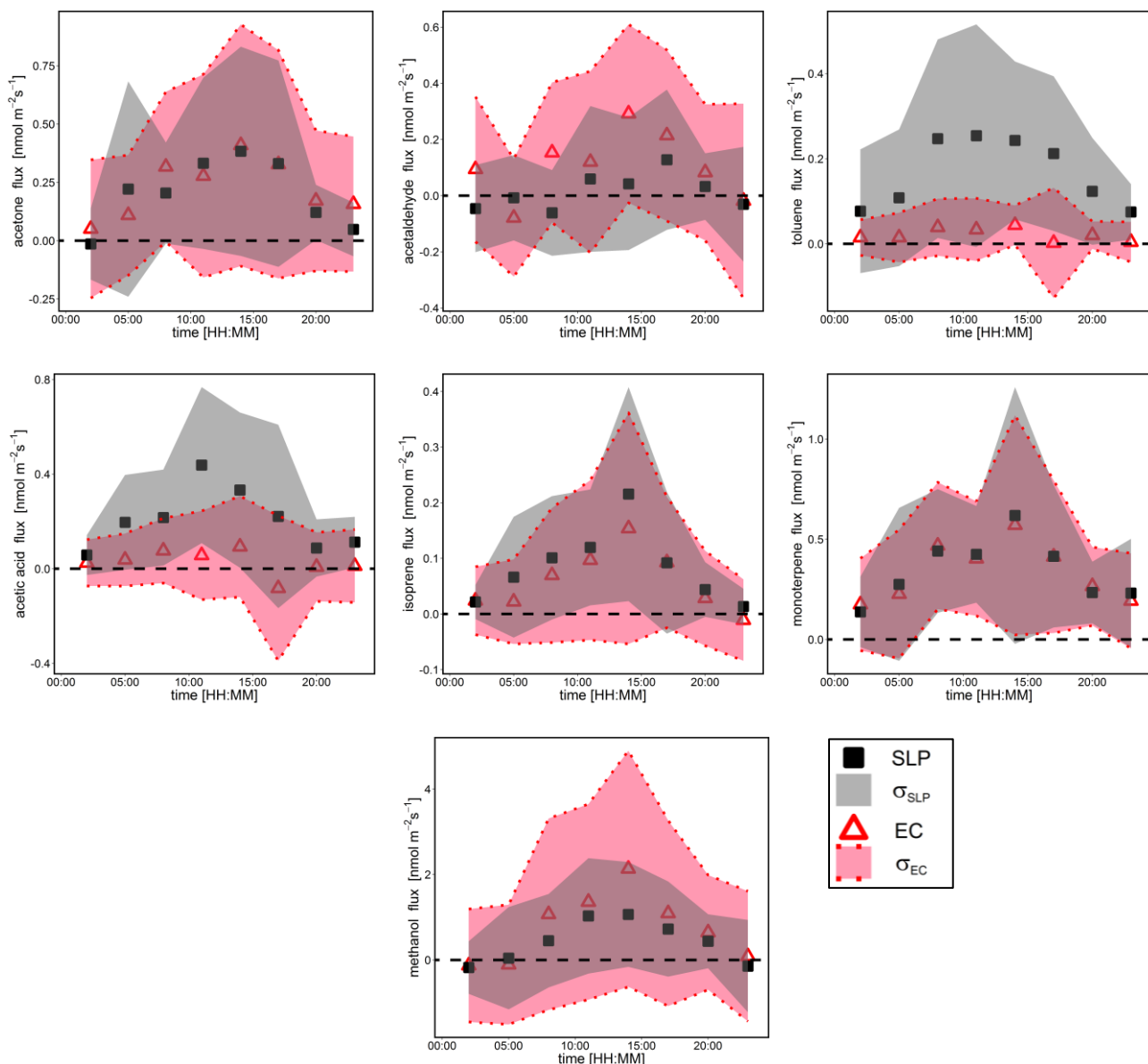
Figure 89: Diurnal mean and standard deviation of the eddy covariance (red triangles) and the surface layer profile (black squares) flux of the major compounds measured by EC and SLP. The data is from April to the end of June 2013.
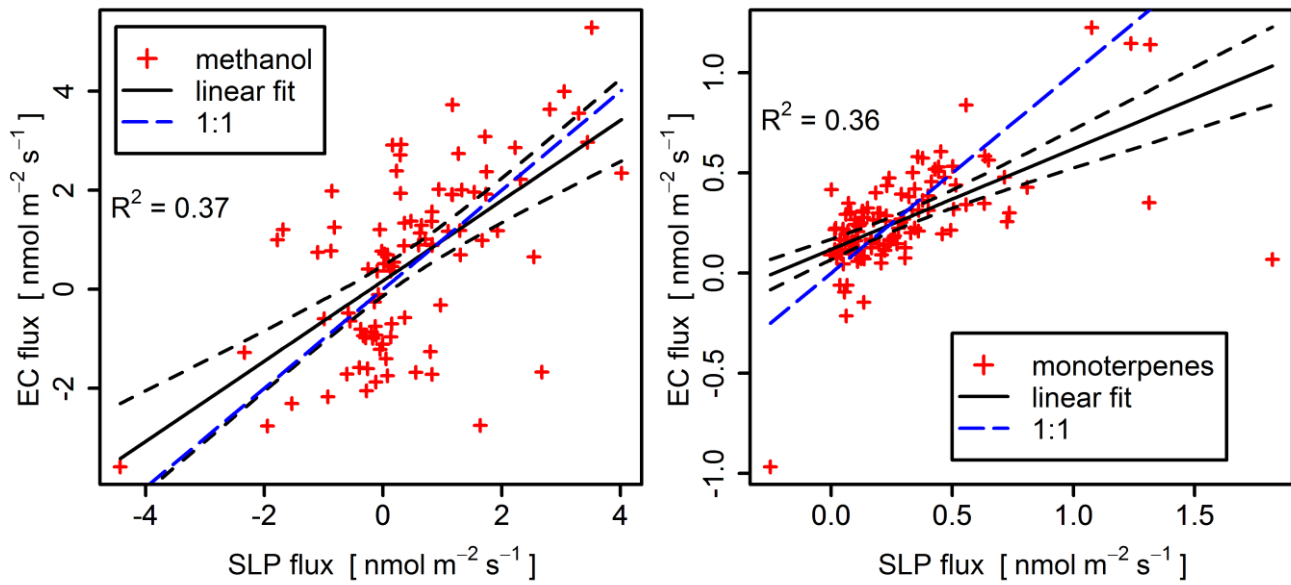
Figure 910: The eddy covariance fluxes against the surface layer gradient fluxes (methanol and monoterpenes, April-May 2013). In addition to the actual scatter plots, the figures include linear fits (black solid lines) with confidence intervals (black dashed lines) and R^2 parameters.
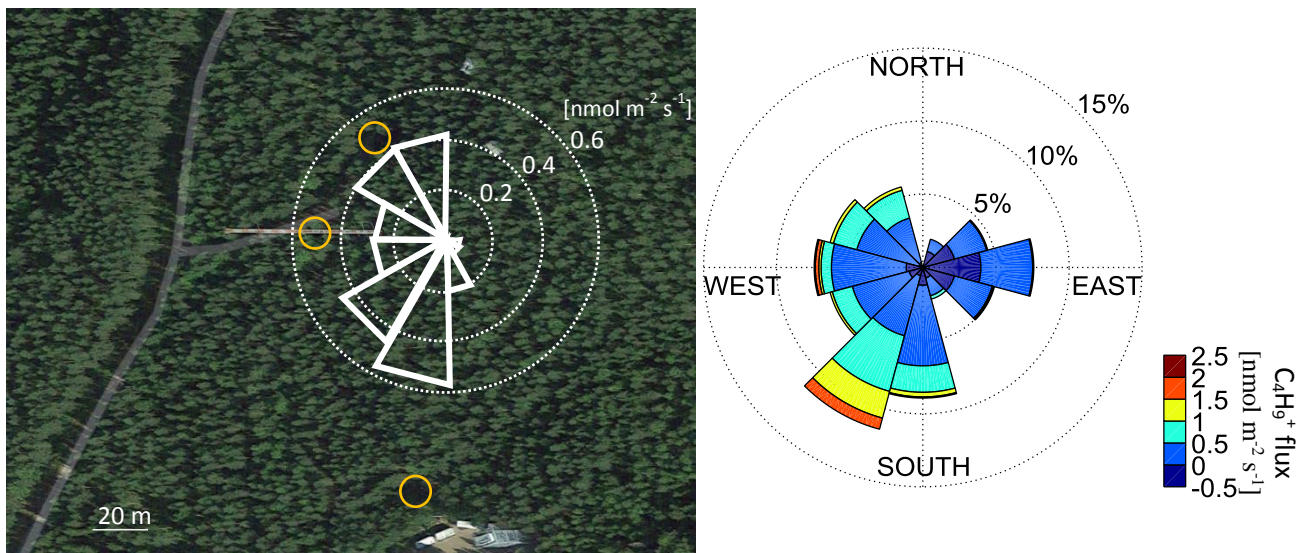
Figure ~~10~~11: On the left side the average $C_4H_9^+$ flux is shown (data of the whole campaign) in white. The orange circles illustrate the locations of the ~~butanol using~~ aerosol instruments, which use butanol. The average fluxes from north to south-southeast are under 0.05 nmol m^{-2} s^{-1}. The map was taken from Google Maps (Imagenary©2016 Google, Map data©2016 Google). The windrose of the $C_4H_9^+$ fluxes is shown on the right.

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