We would like to thank the reviewers for their detailed and helpful comments and suggestions, which improved the manuscript.
The comments of the reviewers are in black, while our replies are marked in red. Attached figures are marked as Fig. Z1, Fig. Z2 and Fig. Z3.
The revised manuscript is attached after comments and answers to all reviewers.

Anonymous Referee #1

Summary

This study presents a set of tower-based VOC flux observations acquired with PTR-TOF-MS in a mixed deciduous forest over a period of ~22 days. TOF-MS instruments measure a lot of ions, and special attention is given to method development and proper use of such a dataset. Several unique aspects of the dataset are explored in further detail, including flux divergence from in-canopy MVK/MACR production and methanol deposition to wet surfaces.
The data presented are new. The analysis generally follows previously-published procedures but does make an effort to compare several methods, which will be useful to the community. The English is OK but could be improved beyond the technical comments listed below. The paper is appropriate for publication in ACP after consideration of the following minor revisions.

General Comments

None.

Specific Comments

P27635, L15: "For compounds included in the standard, the calibration implicitly accounts for the fragmentation pattern." Based on the later discussion, this statement seems incorrect. If the fragments were "accounted for" in the calibration, then one would not have to filter them from the automated flux list.

We agree with the referee and changed the sentence to: "Fragments from compounds included in the calibration gas were not taken into account when calculating the sensitivities."

P27637: Was any filtering done for wind sector to exclude time when the wind is coming through the tower? Vertical wind measurements are likely unreliable at these times.

The 3d-anemometer and inlet were fastened on a pole 1.7 m away from the tower. The impact of the tower on fluxes was assessed using the turbulent statistics and rotation angle used to realign measurements of u and w (ψ). This assessment showed that the tower had little or no impact on fluxes (this topic is discussed in the Supplementary information in the revised manuscript in Acton et al. (2015). We did not exclude data based on the wind direction.

P27639, L3: This equation does not appear to be correct. Assuming spectral similarity between c' and theta', the transfer function should be the ratio of the normalized cospectra, not the product. Thus, in the case where the spectra are identical Hwc(f) = 1 at all frequencies. This is also consistent with Eq. (10) in the limiting case tau = 0. Presumably the values in Fig. 3 were calculated with the correct equation since they range from 1 to 0.

We thank the referee and corrected the equation, as suspected the calculations for Figure 3 were done the right way.

P27639: A 26% upward correction seems substantial. Why is the instrument time constant so large? Does it really take so long to flush out the internal volume?

The corrections were smaller during daytime (on average 9%) and larger during nights due to more stable situations. Thus, the correction for the average isoprene flux was only around 10% because isoprene is not emitted during nighttime.
We agree that the instrument time constant is pretty large but the value is still well in line with some previous results. Karl et al. (2001) reported the maximum response time of a PTR-Quad (Drifttube volume and inlet flow should be similar to the PTR-ToFs) to be 0.8 s. However, the confidence intervals of the response time of this study are quite large, indicating a possible systematic error source in the order of a few percent. The response time can also vary between water-soluble and non-soluble compounds as the attenuation of water vapor depends heavily on the relative humidity (e.g. Mammarella et al., 2009). We added more information about the response times and flux losses to the manuscript.

P27640: Please provide some metric of calculated OH values (midday mean, range, whatever works).

The calculated midday mean ($1*10^6$ cm^{-3}) was added to this section.

P27641, L16: The left-hand size should be called F_Q or something similar, as it is a flux and not a rate (and Q is used for the rates in Eq. 14-15). Also, might be worth mentioning/justifying that MVK+MACR chemical loss in the canopy does not affect flux, since it is not explicitly accounted for.

The left hand side of the equation was changed as suggested. The MVK/MACR chemical loss in the canopy from the flux created by isoprene is included in the 35% isoprene to MVK/MACR yield.
The chemical destruction (F/E and F_Q) of MVK/MACR was not calculated, as the reaction rates with the oxidants and the concentration are smaller than those of isoprene.

P27644, L1: " . . . as it is not possible to differentiate between deposition and other sinks terms . . . ". To the reviewer, this rationale supports *not* calling these fluxes deposition and emission, since the latter two terms refer to specific processes. Why not just call these downward and upward fluxes? This avoids confusing observation of a flux and attribution of its drivers.

We changed most of the depositions / emissions to upward flux and downward flux (except the times when we talked about the specific processes).

P27643, L7: Most of the methods section discusses the distinction between two methods; however, here and in Table 2 there are three methods presented. If possible, Sect. 2.3.3 should be modified to more clearly set up what is presented here. Alternatively, it could still be presented as two methods, and the discussion of the results with the "compound filter" could come a little later.

We changed Table 2 so it just compares the classical and the automated method and restructured Sect.2.3.3.

P27644, L3: This is the first time the phrase "compound filter" appears (other than abstract), and it is presented without a proper definition. If possible, this could be defined in Sect. 2.3.3. Also, this may not be the best label, since "compound" simply means a combination of several things. Other terms might be considered, e.g. "redundant ion filter" "double-counting filter," etc.

In the revised manuscript we do not use the term 'compound filter' any longer (please see our response to question 6 raised by Referee 3).

P27644, L21: This paragraph is confusing. In section 2.3.3, no mention was made of calculating noise with absolute values. This would not be a correct procedure (since, as noted in the text, it alter the statistics) and thus does not warrant discussion. Perhaps these methods are still in development, but it seems that one could also the RMS error (P27638, L8), rather than the standard deviation, to define a cutoff value for the automated case. This would also account for any non-zero offsets in the CCF. All we are really talking about here is defining a flux detection limit and the signal/noise ratio where we say observed fluxes are "real."

We agree with the reviewer, that the use of the standard deviation is not perfect and the use of RMS may capture additional uncertainties such as low frequency drifts (even though it presents less well defined criteria).However, the RMS is more justifiable when examing CCFs for individual 30 min flux averaging periods. It is less clear what the intercept represents once CCFs are averaged. We realized that this effect is corrected by the subtraction of the average noise. We added a discussion to the manuscript (Sect. 3.1; Fig. A4 & A5).

P27647: It is not clear that Figure 7a is necessary. Suggest deleting it.

Deleted

P27647, L28: Several other papers have also dealt with this topic, with varying results (Fares et al., 2015; Karl et al., 2009; Karl et al., 2010).

The paragraph has been extended and the citations added.

P27648, L4: "ISPOOH reacts readily with NO . . . ". This is not true. What is true is that ISOPOOH is made through ISOPO2 + HO2, which is a low-NOx channel, so that its production is dependent on the fate of ISOPO2 radicals (which do react with NO). Please revise. Also, from a flux perspective, any such interference would likely give a downward flux contribution due to deposition of peroxides (Nguyen et al., 2015).

We thank the reviewer and changed the paragraph according to the comment.

P27650, L1: not sure this logic makes sense. Why would low wind speeds imply a source outside the forest? Is it also possible that it is a ground source (e.g. rotting leaves), and fluxes are only observed when turbulence is sufficient to mix out the lowermost canopy?

We agree with the reviewer, there could be a ground source of methanol. But it cannot be the source of the observed increase of concentration, as we see a downward flux of methanol at the same time. This means that the source of our measured methanol cannot be in our flux footprint. Therefore we must have a source outside our flux footprint but close by, as the wind speeds were very low. We clarified the section.

P27650: How does the deposition lifetime compare with oxidation for methanol?

As suggested we added a part to the VOC deposition chapter where we compare the deposition lifetime to the chemical lifetime. With our measurements just an upper limit for the lifetime can be given, because the downward flux is the sum of deposition and emission and cannot be separated with our setup. The chemical lifetime we compare to was used from Heikes et al (2002) as the vertical profile of the $[OH]_{proxy}$ is unknown.

Table 3: Deposition velocities would also be helpful.

The deposition velocities have been added to the Table 3.

Technical Comments

P27627, L9: 65% by mixing ratio or by mass?

P27628, L22: delete hyphen.
P27629, L16: “measurements have inherently”
P27630, L19: “study of dew potentially causing methanol deposition in the morning.”
P27634, L1: “PTFE” (I assume)
P27636, L13: “eddy covariance (EC) method. In EC,…”
P27638, L18: “method will bias”
P27636, L15: If the vertical wind measurement is instantaneous, and the time lag is caused by gas sampling and can vary from ion to ion, it makes more sense (to the reviewer) to present this equation with the lag time applied to c’ rather than w’. Done
P27642, L24: delete “chapter”
P27645, L28: replace “influence” with “contribution”
P27646, L23: replace “rates” with “fluxes”
P27647, L6: replace “rates” with “fluxes”
P27647, L19: “25th and 75th percentiles”
P27649, L22: “night”
Table 3: In footnote “a”, replace “do” with “to”.
Figure 3 caption, second line: “measurements”
Figure 4 caption, third line: “abundant”
Figure 5: need better y-axis label: flux of what?
Figure 6: please describe what the % circles mean in the top panel.

All technical comments were changed as suggested.

References

Fares, S., Paoletti, E., Loreto, F., and Brilli, F.: Bidirectional Flux of Methyl Vinyl Ketone and Methacrolein in Trees with Different Isoprenoid Emission under Realistic Ambient Concentrations, Environ Sci Technol, 49, 7735-7742, doi: 10.1021/acs.est.5b00673, 2015.

Karl, T., Guenther, A., Turnipseed, A., Tyndall, G., Artaxo, P., and Martin, S.: Rapid formation of isoprene photo-oxidation products observed in Amazonia, Atmos. Chem. Phys., 9, 7753-7767, 2009.

Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A., and Jardine, K.: Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation, Science, 330, 816 - 819, doi: 10.1126/science.1192534, 2010. 4

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Nat. Acad. Sci. USA, 112, E392-E401, doi: 10.1073/pnas.1418702112, 2015.

Wohlfahrt, G., Amelynck, C., Ammann, C., Arneth, A., Bamberger, I., Goldstein, A. H., Gu, L., Guenther, A., Hansel, A., Heinesch, B., Holst, T., Hörtnagl, L., Karl, T., Laffineur, Q., Neftel, A., McKinney, K., Munger, J. W., Pallardy, S. G., Schade, G. W., Seco, R., and Schoon, N.: An ecosystem-scale perspective of the net land methanol flux: synthesis of micrometeorological flux measurements, Atmos. Chem. Phys. Discuss., 15, 2577-2613, doi:10.5194/acpd-15-2577-2015, 2015.

Karl, T., Guenther, A. B., Jordan, A., Fall, R. and Lindinger, W.: Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting, Atmospheric Environment, 35, 491–495, doi:10.1016/S1352-2310(00)00405-2, Volume 35, Issue 3, 2001.

Mammarella, I., Launiainen, S., Gronholm, T., Keronen, P., Pumpanen, J., Rannik, Ü., and Vesala, T.: Relative humidity effect on the high-frequency attenuation of water vapor flux measured by a closed-path eddy covariance system, Journal of Atmospheric and Oceanic Technology, 26, 9, 1856-1866, 2009.

Heikes, B.G., Chang, W.N , Pilson, M.E.Q., Swift, E., Singh, H.B., Guenther, A., Jacob, D.J.,. Field, B.D, Fall, R., Riemer, D. and Brand, L.: Atmospheric methanol budget and ocean implication, Global Biogeochemical Cycles, 16, 1133, 2002.

Anonymous Referee #2

Received and published: 5 November 2015

Schallhart and co-authors report on a 3-week BVOC flux campaign above a Mediterranean oak-dominated forest in Northern Italy. This is a solid piece of work, well-written and nicely presented. In terms of contents, the paper can be divided into two parts:

First, a comparison of two approaches for determining significant fluxes of the various compounds measured with the PTR-TOF and second a presentation/discussion of the significant fluxes. I see the first part having the largest innovative character, while the second part is fairly routine its value lying mostly in that the obtained data are a useful addition to the existing literature on BVOC emission from terrestrial ecosystems.

The first part, however, could be expanded in my view in order to make it more accessible to non-specialists on this topic and thus to increase the overall significance of the paper. What I would like to see is that the authors present more details on the two approaches which allow non-specialists to better appreciate the differences and also better illustrate the different approaches using illustrative examples. At present the reader has to check back with the paper of Park et al. (2013) or actually with their supplement in order to fully understand their method. I would like to see the authors present this method in a stand-alone fashion and also illustrate the difference to the manual method in a more easily understandable fashion. This will make the paper a more significant original contribution and more accessible to non-specialist readers. Except for this issue, I only have a few more minor comments listed below.

We reformulated the description in the methods part, extended the Table 1 which describes the differences of the methods. Furthermore, we added several figures to the appendix which show the different CCFs, how the two methods differ in lag time detection and compound with flux classification and what side effects different steps could have.

Details:

p. 2763, l. 12: figures should be referenced in chronological order; what are the footprint extents in the major wind directions?

The Figures are referred now in the correct order. The footprint extents which describe 80% of the measured fluxes have now been added to Fig. 1.

p. 27632, l. 6-10: The term "leaf surface temperature“ is not correct, at least with the usal use of this term as the temperature inferred on the basis of the emitted longwave radiation; what the authors are doing is inverting the equation of the sensible heat flux for the so-called “aerodynamic temperature”; did the measurements include a four-component net radiometer or an infrared temperature sensor? If so these data could be used to estimate surface temperature

Unfortunately, the measurement setup did not include a four component net radiometer. We agree with the reviewer and changed leaf surface temperature to aerodynamic temperature.

p. 27633, l. 23: use SI units throughout

As requested we changed to SI units.

p. 27637, l. 4-5: the term “block averaging” means arithmetic averaging, without any filtering, e.g. linear detrending, applied – the sentence as it stands is thus contradictory

We rephrased the sentence to make it clearer. Block averaging was just used for the vertical wind measurements, whereas the concentrations were linearly detrended.

p. 27638, l. 25: and blockaveraging and linear detrending

Added to the sentence

p. 27647, l. 18: photosynthetically active radiation

Changed

Fig. 9: is hard to read – what about creating an average diurnal course of the methanol flux, Tdew and Taero – is it possible to better get the message from this presentation?

We followed the suggestion and changed the figure.

Anonymous Referee #3

Received and published: 10 November 2015

This manuscript reports “total ecosystem scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest”, measured by PTR-TOF-MS for a period of 22 days. A main focus of the manuscript is on methodology used for flux calculations and the determination of what constitutes a detectable flux.
The main strengths of the manuscript include a thorough description of methods used for flux calculation (both manual and automated data processing approaches), the observation of deposition of methanol due to dew (very interesting, although not a novel result), confirming evidence for the bidirectional exchange of MVK+MAC, and providing new information on fluxes observable by PTR-TOF-MS in an oak dominated system which serves as an important source of BVOCs in Mediterranean regions.

My main concern with the manuscript is that the authors report detectable fluxes for 12 compounds in the abstract, ignoring the extreme data filtering that lead to this small number, leaving the reader with an incorrect impression of how many compounds are really exchanging between the ecosystem and the atmosphere. A careful reading of the manuscript reveals that this is based on a 10_noise threshold, which is an extreme signal to noise filter for defining detectable fluxes. For most scientific measurements a threshold of 3_noise would be considered typical and appropriate. In the manuscript they report 42 masses contributed to the total VOC flux at a 3_noise threshold. If the manuscript is going to focus on reporting how many masses (or compounds) had detectable fluxes, a more complete description is needed of how many masses were observed to have detectable mixing ratios, and then how many masses were excluded by each of the criteria used to filter the data.

We added a list containing all found peaks, which were classified as background, which sigma threshold they fulfilled and if they were classified as fragment/cluster. During this progress we found that we had a small error in the threshold classification which changed the maximum found masses to 57 (before 62) after background masses were filtered we had 36 masses. Additionally, we filtered the fragments (former AM with CF; see question 6) which left 29 masses. In the abstract we report now up to 29 masses.

Specifically: a) How many masses had mixing ratios that were determined to be above the “limit of detection (LOD = 2_zero, where _zero is the standard deviation of the zero-air signal)”? What amount of time averaging was used to determine the LOD (should be very different for 0.1 sec, 1 sec, 60 sec, etc)? Reporting information on detection limits and absolute sensitivities, or at least primary ion count rates would be useful. For example, it is possible that detection limits were low due to low primary ion counts.

The LOD was calculated from the sigma of 10 Hz data points during the 30 minute background measurements, we also clarified this in the manuscript. A sentence was added to Sect. 2.3.2 which states the average primary ion counts. The ion count was approx. 1500 cps at m/z 21.0221 (which is on the lower side) which accounts after all corrections to around $1e^7$ H_3O^+ ions. The signal was not increased as otherwise the resolution (4000 at mass 21) would have suffered. Detection limits for 30 min concentrations were around 1 to 20 ppt (see Table A1), one exception being methanol which had a LOD of 31 ppt. Absolute sensitivities were not added, as the TOF analyzer results are by default primary ion and duty cycle corrected (Müller et al., 2013).

It would also be useful for the reader to see averaged CCFs and absolute value CCFs for a couple of ions that cover the range 0-10 sigma. Adding a supplement with the sigma of ALL detected ions would be appropriate. Averaged background and ambient air signals could also be included to help the reader assess the LOD determination. b) How many of these detected masses were excluded from the flux calculations based on each criteria used to filter the data?

Several different (original, smoothed, absolute) CCFs were added to the appendix. Also a peak list with all detected ions and their classification (sigma criteria, background, fragment, LOD for calibrated compounds) was added. Masses were excluded due to the σ threshold, being under the LOD or being sorted out because they are fragments.

- "stationarity criteria introduced by Foken and Wichura, (1996): every 30 min period was divided into six 5 min sub-periods and VOC fluxes were calculated from both 5 and 30 min intervals. If the values differed more than 30 %, the period was disregarded from further analysis." - "For the calculation of the diurnal 30 min flux data, a trimmed mean function was used, which disregarded the lowest and highest 5 % of the data and then averages the remaining 90 % of the data." This exclusion criteria is particularly concerning because it might discard many species for which an otherwise detectable flux was present (e.g. a flux which only showed up in 5% of the data but was otherwise significant), and also might cause distortion of the data including the mean. Furthermore, 'outliers' should not be discarded unless there is a very clear technical reason. In the latter case there must be a smarter way to get rid of the unwanted data. More discussion on the nature of the outliers is needed.

No species were disregarded because of these criteria. Just single 30 min flux data points of compounds were sorted out, after the 'compound with exchange' detection (was clarified in the text). In the current state of the manuscript no trimmeans were used and the quoted parts were adjusted. The difference between the mean (new version) and trimmean (ACPD version) was very small, thus, there were no significant outliers.

-Any other criteria used. c) What fraction of the masses determined to be above the LOD also had detectable fluxes (at the 3_noise threshold)?

57 masses fulfilled the 3 σ criteria, 21 were under the limit of detection and filtered out, leaving 36 above the limit of detection. Out of those, seven were classified as fragments, leaving 29 masses with exchange (for details please see Table A1).

Additional suggestions and concerns: 1) It would be interesting to specifically compare the number of "masses that are found to contribute to the total VOC flux: 42 (3_noise), 35 (4_noise), 28 (5_noise), 24 (6_noise), 23 (7_noise), 22 (8_noise), 20 (9_noise), 19 (10_noise)" to the results from Park et al. 2013 shown in their Figure 1. Park et al only found 4 ions with fluxes above 10_noise and these only accounted for 46% of the total net flux, 18 ions with fluxes above 7_noise accounting for 66% of total net flux, and 494 above 3_noise accounting for 97% of total net flux. Several major differences exist between the locations of these studies including: a) The current paper reports measurements for a location that is dominated by isoprene emissions with a total midday flux (10_noise, including 19 masses) that is approximately 1 full order of magnitude larger than the orange orchard studied by Park et al (10_noise, including 4 masses). Almost all of this difference in total flux magnitude between the sites is due to isoprene. b) The current paper reports "Figure 5 shows the diurnal variation of the net flux for the different approaches. The difference in the net flux between a 3 _noise threshold and a 10_noise threshold is less than 1.6 nmol m−2 s−1". The Park et al paper shows a Net Flux difference of approximately 2 nmol m−2 s−1 between a 3_noise threshold and a 10_noise threshold.

A new section was added which compares the results from Park et al. (2013) with the findings of this manuscript. Furthermore a table was added to the supplement, where all compounds which contribute to the VOC flux from Bosco Fontana are compared with the same compounds which were found from the Park et al. (2013) supplement. The problem with a similar picture as Fig. 1 in Park et al. (2013) is that the masses between 3 and 10 σ_{noise} contribute to the net flux by less than 0.5 nmol m^{-2} s^{-1} (approx. 5%).
We clarified the statement: "The maximum difference in the hourly net flux between a 3 σ_{noise} threshold and a 10 σ_{noise} threshold was less than 1.3 nmol m^{-2} s^{-1} and the daily average differed less than 0.5 nmol m^{-2} s^{-1}."

Thus, there seems to be strong agreement between these studies in the quantitative difference of total ecosystem scale BVOC exchange using 3 vs 10_noise thresholds. The main difference in these studies is in the number of masses for which fluxes were "detected", and the dominance of isoprene emission in the total bVOC exchange of the oak forest versus the orange orchard. These similarities are not obvious from the text of the current manuscript which seems to suggest that Park et al overstates the number of masses for which flux is observable and the amount of total flux that is contributed by masses between the 3 vs 10_noise thresholds.

In Section 3.2 we added a discussion about the differences and similarities of the results between Bosco Fontana and the orange grove.

2) It would be good to see more in-depth discussion of the actual results and science. In the current manuscript the focus is mainly on flux calculation and data processing details which are interesting but might be more relevant for the AMT audience.

We added the comparison to the Park et al. (2013) results, expanded the methanol deposition part and presented all compounds which contributed more than 1% of total emission/deposition.

3) Similarly, the conclusions are very narrow, focused on the methods and not so much on the total ecosystem scale exchange that is expected based on the title.

The conclusions were rewritten. We concentrate now more on the ecosystem scale exchange in Bosco Fontana and less on the methods.

4)PTR-TOF-MS (without SRI or variable E/N) cannot distinguish between methyl acetate (MA) and hydroxyacetone (HA) each at the same m/z 75.0441 ($C_3H_6O_2H^+$). It is likely that MA is incorrectly attributed because isoprene-dominated atmospheres should have high concentrations of HA. Therefore deposition of MA is less likely than HA deposition (Nguyen et al. 2015 showed clear deposition of HA).

We thank the referee and changed the possible compound for 75.0441 to hydroxylacetone.

5) Calculation of concentration of uncalibrated compounds was done using average sensitivities for families of compounds (CxHy, etc.) instead of using the transmission approach. This may be inaccurate if the detected families contain fragments (e.g. in CxHy propyl/isopropyl, in CxHyO1 dehydrated acid fragments, etc.). Therefore the total budget may be biased. Transmission is very important to consider because the authors used low mass compounds for an average family sensitivity and the transmission greatly increases with the mass scale (which they do not discuss).

For correcting the transmission, all signals (sensitivities, measurements) were duty cycle corrected (Herbig et al., 2009; see manuscript p27635, l14), which corrects the higher duty cycle (= higher transmission) of heavier masses. We reformulated the sentence to: "Normalized counts per second (ncps) have been corrected for transmission (pusher duty cycle losses) and primary ion fluctuations (Herbig et al., 2009)."

6) The authors' double-counting argument does not make sense. If they use calibrated sensitivities for some of the compounds, they should remove the fragments and isotopes related to the parent mass. Alternatively, they should use proton reaction rate constants derived from the calibrations. Their text misleads the reader that the auto- mated approach is worse because it might lead to double counting while the selective approach is better because it relies on more accurate sensitivities. The selective approach inhibits scientific progress because it focuses on those compounds which are routinely in the standards while ignoring newly observed and low concentration compounds.

As suggested, the updated manuscript now filters fragments and waterclusters which could be identified from the calibration (which are marked as such in Table A1).

7) Typo on p27637, line 9: Park 2013 not 2014

We thank the reviewer and corrected the typo.

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Nat. Acad. Sci. USA, 112, E392-E401, doi: 10.1073/pnas.1418702112, 2015.

Herbig, J., Müller, M., Schallhart, S., Titzmann, T., Graus, M., and Hansel, A.: On-line breath analysis with PTR-TOF, Journal of Breath Research, 3, 027004, doi:10.1088/1752- 7155/3/2/027004, 2009.
Müller, M., Mikoviny, T., Jud, W., D'Anna, B. and Wisthaler, A.: A new software tool for the analysis of high resolution PTR-TOF mass spectra, Chemometrics and Intelligent Laboratory Systems, 127, 158-165, 2013.

Anonymous Referee #4

Received and published: 23 November 2015

Schallhart et al. present interesting measurements of VOC concentrations and fluxes from a mixed forest dominated by oak and hornbeam trees in the Po Valley. The number of direct measurements of VOCs above biogenic sources using PTR-ToF is very small so the results of BVOC emission and in particular less known BVOC/VOC deposition could be extremely valuable. Another interesting aspect of the study is that it is located in a region strongly emitting biogenic VOC close to anthropogenic influences (often high NOx) so should enable investigations of the atmospheric chemical interactions between BVOCs during polluted vs unpolluted/less polluted times. The context of pollution is brought up only to say that the conversion of MVK+MAC is unexpected. It would be very interesting to see also the anthropogenic ions such as aromatics which hopefully were not excluded from the analysis. The paper makes a good impression initially, before it becomes clear that it is overly focused on specific nuances in flux filtering methodology which can be interesting but only for a relatively small subset of ACP readers. Specifically, large part of the paper is spent on arguing about which technicalities of flux quantitation in PTR-ToF systems are better, "objective" or "labour intensive", yet basic information about flux criteria and quality are missing. I found this very distracting from the otherwise potentially interesting science which unfortunately seems to be only ancillary. The title is so inconsistent with the content. The content is more technical than scientific, thus it would be strongly suggested that the paper is sent for discussion in AMTD or if it is intended for ACP it should be refocused on the science and implications from observed BVOC fluxes, which in the current version seem largely fragmentary and adjunct. Even though the PTR-ToF is used, only a few selected species are reported and even basic details such as mass range, the list of detected ions, etc. are not reported or clear. I have numerous concerns mostly about the presentation of the flux analysis which is either not explained at all or presented in a particularly confusing way. I have strong reservations about misinterpretation of the published literature and confusing method comparison. Hopefully, the authors can significantly improve the paper in terms of clarity and consistency of the methods and in particular they should focus on a coherent and structured science story to make this manuscript relevant for the majority of the ACP audience.

General

1) After reading Park et al., 2013a whose approaches are used and compared in this paper, I agree more with Park et al. that their comprehensive flux approach makes more sense in that it treats the mass spectra fully with clearly defined criteria. In Schallhart et al. it is completely unclear how fluxes were processed, how quality of the flux was assessed, what corrections were applied and if they were derived for each ion consistently (e.g. lag time, stationarity, u* criteria). Park et al. approach is a significant advancement for PTR-ToF flux processing because it does not disregard ions other than the internal ions. The selective approach is defended in this manuscript but it seems like a return to the old school of quadrupole systems when one was forced to preselect the ions to keep the flux quality high. Because ToF systems measure the whole mass range instantaneously, selecting the ions no longer makes sense. I think this is clearly a step backward relative to what in principle should be possible from these comprehensive PTR-ToF datastets which allow for non-disjunct flux of the entire mass spectrum, so one would expect to see clear fluxes for many more masses than presented in this paper even at standard sensitivities.

The authors reformulated Sect 2.3.3, where the lag time calculation, the compounds with flux classification, as well the filtering criteria are described. The exclusion of fragments and water clusters identified from calibrations as well as the exclusion of background peaks is described in Sect. 2.3.2. Furthermore, a table with all measured masses (compounds), including additional information was added to the appendix. Compared with the Park et al. (2013) results (494 ions showing flux), we agree that 29 ions showing flux is a lower number than expected. However, this is the measured result from Bosco Fontana.

2) The drastic exclusion of ions without any reason is surprising also because one would expect many interesting ions above the standard flux detection limit (e.g. Spirig et al., 2005). It is unclear why 10-sigma

threshold is used instead of the 3-sigma threshold. It makes the impression that this was done to justify not reporting the full results. The companion paper (Acton et al.) shows that similar results are possible with just the quadrupole PTR-MS, so why invest in much more expensive PTR-ToF only to ignore its broader capabilities?

The intention was to compare the major 10 compounds in a table. This was then extended to the 10 σ compounds in the progress of the paper. Another argument was that the difference between the classical and automated method should be lowest in the 10 σ case (= clearest compounds to manually detect). We refer now to the added Table A1 and A2, where all compounds with flux are presented. In the manuscript all compounds with flux above 1% contribution of the total upward or downward flux are mentioned. Whereas for the instrument comparison: The quadrupole PTR-MS can determine disjunct eddy covariance fluxes for a set of some 10-20 compounds, while the PTR-ToF method can measure the full set of masses with 10 Hz resolution enabling eddy covariance fluxes without preselection of observed masses.

3) I fully agree with the clear evaluation by Reviewer 3 who has already explained the issues with misinterpretation of selective vs full approach. While I do not want to repeat the similar comments, I would also like to see more clarification and transparency of the flux methodology presented in such a way that the comparison between the selective and full flux approaches is fully transparent and based on solid criteria, as well as accounting for differences between the studies (ecosystem, season, temperature, climate).

We clarified the text in the manuscript. For more details please see answer to your question 1.

Specific:
4) Flux methodology is completely missing which is unacceptable in a flux-reporting paper. What is discussed in Sect. 3.1 is only a rough comparison of procedures to identify “detectable” fluxes which is confusing. Table 1 showing the differences between the full approach (which is referred to as “automatic”) and the selective approach (which is referred to as “manual”) lacks the specificity expected in scientific papers.

The flux methodology is described in chapter 2.3.3 ‘Flux calculations’ and it describes the differences of the methods. In chapter 3.1 only the differences in the results are described and discussed. The Sec. 2.3.3 is now clarified, and describes the flux methodology better. The table comparing the ‘classical’ and ‘automated’ method was expanded to give a better (and more scientific) comparison of the methods. However, all the details are still in Sect. 2.3.3.

For example, a) first row: standard flux corrections:
Classical (yes) Automated (yes). This is surprising. I can see that both approaches are based on classical foundations. It is unclear why suddenly the selective approach is more classical?

The names for the methods relate only on deciding which mass shows a significant flux, and not to the way the fluxes themselves are processed. We chose the name ‘classical’ approach as it was used for finding compounds with flux in the previous PTR-TOF flux publications (Ruuskanen et al., 2011; Kaser et al., 2013) and it was also used with PTR Quadrupole measurements. The automated method is a novel method (for finding ions with flux), as no citations to a previous publication using the same method is cited in Park et al. (2013), therefore we classified it not to be classical.

b) Third row: Manual evaluation of CCFs (several 100s): Classical (yes) Automated (no). This seems incorrect. See Figure 3 in Park et al. (2013b).

We agree with the reviewer that this statement is not precise. We wanted to show the differences in the compound with flux detection. We reformulated the statement: “amount of CCFs checked per compound” under the topic “‘compound with exchange’ detection”

c) Fourth row: Average absolute CCFs: Classical (no) Automated (yes). This is misleading because as I understand the comprehensive approach uses average CCFs as additional information and not instead of the standard CCF.

As in the case before, this was thought to describe the compound with flux detection. We clarified the statement.

d) Filter results (fragments, isotopes, clusters): Classical (yes) Automated (no). This is again a major misinterpretation. See Park et al. (2013) SI "Sect. 2 Determination of m/z ratios exchanging with the ecosystem ."

We deleted this statement

e) Work intensive: Classical (yes) Automated (no). This is a very subjective comparison. Each method is work intensive, in particular in the comprehensive methods there are more ions to go through the extensive quality control. Analysis of millions(?) of CCFs manually not only does not make sense and is a waste of time but is inappropriate due to potential pseudo peaks which need intelligent lag-time verification approaches, not just an arbitrary visual assessment.

We agree with the referee. This statement was meant to describe the very tiring process of checking several thousand of CCFs for the classical method. We would also like to add that this comparison was not indented to discredit the automated method. Thus, the statement was deleted.

f) Maximum of found masses in literature: Classical (10-20) Automated (ca. 500). This is misleading, because there were only few reports of fluxes in the literature and the number might be dependent on other factors such as detection limits, m/z range, and the number of ions passed for the flux evaluation and then the ecosystem type or the amount of air pollution (other VOC sources) in the region.
Overall, Table 1 is extremely confusing and should either be deleted or expanded to contain the full account of like for like comparison.

We think that in a comparison of two methods, the difference of found masses is very important especially when it differs so much (in the publications so far). However, we agree that the publications were from different ecosystems with different meteorological characteristics. We added a footnote to the Table 1 and state it again in the text when comparing the results from Bosco Fontana with Park et al. (2013).

5) The scientific conclusions can be different depending on which filtering approach is used (i.e. selective vs comprehensive). The reader is lost with the most important take home messages. This kind of debate on which method approach is better should be more appropriate for methodological journals (e.g. AMTD). Despite much effort spent on explaining the methods, the essential information related to flux quality criteria and justification of the controversial filtering (10 sigma, 10% cutoff) is missing. This justification is particularly important as the authors speculate on which approach (selective or full) is better or worse, and the reader is confused about what the real picture of the total ecosystem exchange in the Po Valley is. This is unfortunate, because the authors would be in a good position to give a more in-depth insight into the science.

We shortened and clarified the methods part. The trimmean was replaced by mean values. Furthermore, we just compare the classical and automated method and removed the automated method with compound filter from the manuscript.

6) Part of the community might have no idea what the automated, classical, manual, comprehensive method is and might be deterred from using novel approaches which seem to be misrepresented here. I think the authors might not realize that the automatic method should be fully consistent with conventional

flux methods (all criteria including lag time and covariance assessment+verification should also be thoroughly included) and that it enables comprehensive treatment of entire TOF spectra. There are subtle differences which need to be compared more clearly.

We anticipated this argument and are using just one name for each method ('classical' and 'automated') in the manuscript, to not confuse the reader (the referee will not find the names: comprehensive method, manual method, full method, selective method in the manuscript). Both methods are described using the stated names. The lag time differences have been described in section 2.3.3:" Next, we calculated cross covariances between the vertical wind and the volume mixing ratios for every 30 minute measurement period and determined a lag time by maximizing the smoothed cross covariance function from a lag time window of 0–5 s (classical approach, Taipale et al., 2010). For the automated approach, like in Park et al. (2013), a constant lag time was used for all compounds.[…]" . The lag time was calculated from the averaged cross covariance function of isoprene and was 2.6 s". We agree that Sect. 2.3.3 unclear, therefore we clarified the differences of the two methods.

7) The companion paper (Acton et al.) cites Park et al. 2013a approach for their reported PTRTOF fluxes so the recommendation from Schallhart et al paper for automated method with a mass filter is inconsistent and surprising.

In (Acton et al.) the PTR-ToF fluxes were calculated according to Park et al. 2013a, which represented (in the ACPD version of this manuscript) the automated method and automated method with compound filter. The fluxes (from the PTR-ToF) used in Acton et al. were monoterpenes and isoprene, which are exactly the same if calculated with the automated method or the automated method with compound filter (which we recommended). Please be aware of (stated in Sect. 3.1): "It is important to keep in mind that the absolute flux-values of each compound for the automated method and the automated method with compound filter are the same."

Table 2 with the flux mass ions looks like a selection of abundant and unabundant ions out of many more expected and misinforms the reader.

We refer to the answer of question 2.

Automated method with the compound filter is not a new method. Whether you include the fragments or not depends on whether you use transmission method or calibration method.

We also agree that the automated method with compound filter is not a new method. We want to clarify that the manuscript did not state that it is a new method.

If you use calibration method it would be better to sum up fragments and use the sum of the sensitivities of the fragments and the parent ion. What it seems is that the authors have calibrated a single ion for monoterpenes (m/z 137.123) assuming that the proportion of fragments is constant. This is actually not the case for different monoterpenes as well as in particular when instrumental conditions change. The standard contained a-pinene only, so the sum of fragments must be used in order to prevent an error in case monoterpenes other than a-pinene were present. In the PTR with quadrupole detector not summing up the fragments could be justified by potential interference at m/z 81 from hexenal, but here the authors should be able to include and sum up all the relevant exact-mass ions (at least 81.07, 95.09 and 137.123 for total monoterpenes) and use the sum of their calibrated sensitivities. Using the compound filter does not make sense.

We refrained from summing up the 10Hz concentration data of the fragments (and calculate the flux from the summed up signal). This cancels the possible influence of noise that one fragment could have to the others. Calculating individual fluxes for all fragments is more reliable.

The main reason why we did not sum up the individual fluxes of the fragments is, that e.g. for the monoterpenes the fluxes of the 3 masses (M137.1325; M81.0699; M95.0855;) is needed. However, due to the stationarity criteria, the data coverage where all of the 3 masses passed the quality criteria is 50% less than if we just use the up scaled M137.1325 (used in the manuscript). This is mainly caused by M95.0855 (amount of 30 min flux values that passed the criteria: M137.1325: 507; M81.0699: 505; M95.0855: 401, please keep in mind that they past the criteria not always at the same time). Next, we disregarded M95.0855 and calculated the flux using the fragments of M81.0699 and M137.1325. This time the average flux was 14% lower in comparison with up scaled M137.1325. Furthermore, we compared the up scaled fluxes of M81.0699 and M137.1325 (Fig. Z1). The correlation coefficient is 0.94 and the average flux differed by 2.5%. Therefore we are using the up scaled M137.1325 for the monoterpene signals.

8) 27% of upward flux of MVK and MACR from photo-oxidation seems interesting but it assumes constant yield (which I understand was taken from MCM based on chamber studies). Do authors suggest that NO/HO2 does not vary diurnally at the Po Valley? There is nothing like “high NOx” and “low NOx” environment, and you need to be aware of the pathways changing diurnally. The value of 27% also does not seem reasonable if it was based on the analysis in Figure 7 which suggests that relatively small flux footprints are compared with much larger concentration footprints. Do the authors suggest that majority of MVK+MAC is directly emitted from plants and ignore the longlived MVK+MAC from aged air mass which would be expected from isoprene oxidation? How did Isoprene/(MVK+MAC) ratio vary at the Po Valley site?

We agree with the reviewer. Those are valid points. The NO/HO_2 is varying diurnally and the pathways may change during the day. We intended to calculate diurnal values, but due to the lack of measurements of several parameters (see Sect. 2.4) and the uncertainties related to that, we refrained from doing so. Instead of that, we wanted to give an estimation of the maximum contribution from oxidized isoprene. The highest conversion rate of isoprene to MVK/MACR is during midday and chemical conversion is of lesser interest during night when the isoprene flux is small anyway. Therefore, we chose to calculate the box model for this time which results up to around 30% contribution. During midday, Bosco Fontana had relatively high NOx concentrations. In the case when the NO/HO2 ratio changes, reviewer 1 (in the comment related to P27648, L4) wrote: “Also, from a flux perspective, any such interference would likely give a downward flux contribution due to deposition of peroxides (Nguyen et al., 2015).” Therefore the contribution of isoprene to the upward flux of MVK/MACR would be still less.
The 27% is the result (Fig. 7) of a simple model, which compares the oxidation effect (amount of MVK/MACR flux created by the oxidation of isoprene) in the column under the measurement height with the measured MVK/MACR flux. Please keep in mind that the 27% is the influence on the MVK/MACR flux not concentration. The long-lived MVK/MACR concentration from aged air masses should not affect the emissions at all. We agree that the concentration footprint is much bigger as the flux footprint. Therefore, it is still valid to calculate how much influence this ‘background effect’ (from a bigger area) has on the ‘local’ flux (which has a much smaller footprint). The small difference in the results of the F_Q estimation and the F/E ratio, was surprising to the authors.
The remaining (at least) 70% we cannot account for. The authors wanted to discuss other possibilities but do not want to suggest that all of the remaining MVK/MACR was directly emitted, as with the measurement setup used in Bosco Fontana, it is not possible to determine the remaining sources.
A histogram with the isoprene flux/(MVK+MACR)ratio is shown in Fig. Z2.

9) Table 2. CT ions are dependent on the optimization of NO+ and O2+, so the authors should report the percentage of NO+ and O2+ relative to H3O+. On what basis is it concluded that 67.05 must be isoprene fragment and not for example cyclopentadiene or other isomer? Did you compare the signals? I suggest to include the full mass list (concentrations and fluxes) of identified ions. How many ions did the ToF-Analyzer software detect? How many ions were selected for concentrations (manual selection)? How many ions were included in the flux evaluations? And finally how many ions passed any given filtering criteria or in other words which ions were filtered by which criteria?

We added the requested percentages of impurities.
The assumption was made, because during calibrations (contains no cyclopentadiene or isomer) M67.0542 correlated with isoprene (R= 0.985). The correlation between the fluxes of the M67. 0542 and isoprene during the whole campaign was calculated to be 0.94.
The full mass list is attached in the appendix with additional information. Overall, 163 compounds were detected with the TofTools-Software. Concentrations and fluxes for each mass were calculated. After that sorting was done due to BG/LOD, fragments/water clusters/isotopes and flux classification (all information is included in the appendix).

10) Section 2.3.2 shows average sensitivities for the entire compound families. This seems inappropriate as has been pointed out in other reviews. It would make more sense to use compound-specific sensitivities or to convert sensitivities to proton transfer reaction rate coefficients for compound families and use the transmission equation which accounts for mass discrimination of each ion mass within the compound family.

All used signals were corrected for transmission. Please see the answer to question 5 of Reviewer 3.

11) Table 3. Deposition for m/z 61.028 (attributed to acetic acid) is shown. Was acetic acid calibrated on a standard or did you use the sensitivity for CxHxOz family (19.1 ncps/ppb, P.27635, L10)? Most acids including acetic acid dehydrate in PTR, so the sensitivity on the parent mass can be relatively small and is humidity dependent (e.g. Baasandorj et al., 2015). The sensitivity of 19.1 ncps/ppb seems by a factor of _2 higher than previously reported in the literature (Table 1 in Baasandorj et al., 2015). Nowhere in the text it is shown whether the fragment on m/z 43.018 was accounted for.

We thank the reviewer for this comment. Acetic acid was not calibrated (as indicated by the missing “c” in Table 2) and the sensitivity of $C_xH_yO_z$ family has been used. In the same table you can find mass 43.0178 which is accounted as a CHO- fragment. We addressed this problem in the revised Sect. 2.3.2 and corrected for the missing signal.

12) Figure 1. Can you show overlaid flux footprint on the map?

The footprint was added to Figure 1.

13) Figure 2. Could be moved to SI. Would it be possible to show the flow rates, temperatures of the lines if they were heated, and internal diameters of the lines.

The figure did not contain units, but in Sect.2.3.1 the units were converted. We restrain from adding all additional information to the figure, as it would be very confusing for a reader. The heated lines were drawn red. We added missing information for the ambient air measurements (Sect. 2.3.1). The tubing used for zero air (common line to catalytic converter: PTFE: 4 mm i.d. afterwards (till the 3 way valve): PTFE: 1.6 mm i.d.) is not mentioned in the manuscript, as the dimensions should not influence the background measurements.

14) Figure 3. Why are the response times different for the first and second water cluster? 26% of high frequency correction (P.27640 L5) seems like there were substantial losses in the system. It would be interesting to see how these losses vary with the flow rates, heating, dimensions of the tubing, data acquisition rate, and other factors.

We agree that the response times should be similar. However, although there was a 0.1 s difference in the response times, they were still inside the uncertainty estimates. Attenuation of water vapour (and probably water soluable compounds as well) do depend on tube length, heating, filters and the age of the used inlet.

However, flow rates and other tube dimensions do have only a negligible effect as long as the flow in the tube is turbulent (See Nordbo et al., 2013, 2014).

15) Figure 6. It is unclear what this figure is supposed to teach the reader or at least it is not discussed sufficiently. The wind roses look quite random in pattern. It is unclear where the pollution sources are. It would be interesting to add an aromatics tracer such as benzene and/or C8, C9 aromatics, as well as NO.

The wind roses were added to estimate the horizontal homogeneity of the main flux compounds. Especially as the flux footprint can exceed the forest, we wanted to show that no strong sources were outside the forest that affected our measurements. We did not add benzene and NO wind roses to the manuscript (Fig. Z3), as the pollution did not come from a specific direction.

16) Figure 7. Why to show isoprene concentration vs MVK+MACR flux, instead of flux vs flux and concentration vs concentraiton? The MVK+MACox.isop figure assumes constant yields from isoprene but the yields change during the day as the ratio of HO2/NO changes. The authors seem to treat the chemistry as black or white without the shades of grey. It would be more instructive to show the diurnal trends of isoprene/(MVK+MAC) concentration (and/or flux) ratio vs concentration (and/or flux).

The indention of Figure 7 was to show the gain in correlation by calculating the oxidized isoprene (Figure 7a was deleted). The yields were indeed constant as we used the maximum yield of the day, to give a maximum estimation. We refer to the answer of question 8 for the reasoning of a constant yield.

17) Figure 8. Was isoprene filtered out from the 10 most abundant compounds? I do not see the C5H8+ ion in the figure.

We thank the reviewer for spotting this out, Fig. 8 had the wrong legend. After replotting the figure, isoprene (in our case $C_5H_9^+$, as we report protonated masses) is on the fifth position.

18) Figure 9. The interruptions are not described in the figure. Was the night turbulence well developed to observe the night time fluxes (mostly deposition). Again, what were the filtering criteria (u*, stationarity performed for each ion?)?

The long interruption (06.06 -08.06) was due to an air condition failure, where the turbo pumps of the PTR-TOF shut down to prevent overheating (mentioned in the last sentence of Sect. 2.3.1). Remaining gaps are caused by background or calibration measurements, or by the filtering criteria (described in Sect. 2.3.3: 5 degree tilt angle correction and 70% stationarity). No friction velocity filtering was applied in the manuscript.

19) P27644 L17-24 “Compared to the classical method, the automated method gives a fast and objective result, but the _noise threshold can vary, as the standard deviation of the noise can be reduced by taking its absolute value. The reduction of the standard deviation takes place if the signal, which is used for the error calculation, is around zero and, therefore, varies between negative and positive values. If there is some offset, so that the signal is just positive or just negative inside the error areas, using absolute values does not influence the value of _noise.” I do not understand this paragraph. Is it correct? Do you suggest that the standard deviation will be affected by where the mean value is? The standard deviation will depend on the CCF averaging (e.g. Taipale et al., 2010) if this has been done.

The standard deviation describes the variation of a signal ($\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2}$). Let’s assume now the worst case (which is not realistic): The background signal is just jumping between -1 and 1. The standard deviation would be $\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(\pm 1 - 0)^2}$ =1 (as the mean value would be 0). If the absolute of this arbitrary signal is taken, the mean value becomes 1 and thereby the standard deviation 0.

We clarified the text and added CCF figures (Fig. A4 & A5) to the appendix, which show an example of an underestimation of the standard deviation.

If the standard deviation was calculated from the smoothed (running mean) CCF, it would lead to an enormous underestimation. In Taipale et al. (2010), the smoothed CCF is just used to find the lag time; the error and the flux are taken from the original CCF (unsmoothed).

Technical:

20) P27633 L23 needs to provide SI units here and later in the text. Also provide inner diameters of the tubing not just ODs.

We changed to SI units and replaced the outer diameters with the inner ones.

21) P27634 L1 PDFE acronym is undefined.

Typo: PTFE

22) P27634 L6 what valve was used? Needs to provide material and brand.

We added the information.

23) P27634 L8 30 mL/min is taken by the drift-tube in most PTR instruments. What was the flow in the subsampling inlet line and what was the temperature?

We refer to the previous sentence ("…from where a subsample of 0.5 Lmin-1 were pumped") the temperature was between 40°C and 60°C (added to text).

References:

Baasandorj, M., Millet, D. B., Hu, L., Mitroo, D., and Williams, B. J.: Measuring acetic and formic acid by proton-transfer-reaction mass spectrometry: sensitivity, humidity dependence, and quantifying interferences, Atmos. Meas. Tech., 8, 1303-1321, doi:10.5194/amt-8-1303-2015, 2015.

Park., J-H., A.H. Goldstein, J. Timkovsky, S. Fares, R. Weber, J. Karlik, R. Holzinger, Active Atmosphere-Ecosystem Exchange of the Vast Majority of Detected Volatile Organic Compounds, Science, Vol. 341 no. 6146 pp. 643-647, doi: 10.1126/science. 1235053, 2013a.

Park, J.-H., A. H. Goldstein, J. Timkovsky, S. Fares, R. Weber, J. Karlik, and R. Holzinger, Eddy covariance emission and deposition flux measurements using proton transfer reaction – time of flight – mass spectrometry (PTR-TOF-MS): comparison with PTR-MS measured vertical gradients and fluxes, Atmos. Chem. Phys., 13, 1439-1456, doi:10.5194/acp-13-1439-2013, 2013b.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 5, 465-481, doi:10.5194/acp-5-465-2005, 2005.

Taipale, R., Ruuskanen, T. M., and Rinne, J.: Lag time determination in DEC measurements with PTR-MS, Atmos. Meas. Tech., 3, 853-862, doi:10.5194/amt-3-853-2010, 2010.

Kaser, L., Karl, T., Guenther, A. B., Graus, M., Schnitzhofer, R., Turnipseed, A., Fischer, L., Harley, P., Madronich, M., Gochis, D., Keutsch, F. N., and Hansel, A.: Undisturbed and disturbed above canopy ponderosa pine emissions: PTR-TOF-MS measurements and MEGAN 2.1 model results, Atmos. Chem. Phys., 13, 11935-11947, doi:10.5194/acp-13-11935-2013, 2013.

Nordbo, A., Kekäläinen, P., Siivola, E., Lehto, R., Vesala, T., and Timonen, J.: Tube transport of water vapor with condensation and desorption, Applied Physics Letters, 102, 2013.

Nordbo, A., Kekäläinen, P., Siivola, E., Mammarella, I., Timonen, J., and Vesala, T.: Sorption-Caused Attenuation and Delay of Water Vapor Signals in Eddy-Covariance Sampling Tubes and Filters, Journal of Atmospheric and Oceanic Technology, 31, 2629–2649, 2014

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Nat. Acad. Sci. USA, 112, E392-E401, doi: 10.1073/pnas.1418702112, 2015.

Ruuskanen, T. M., Müller, M., Schnitzhofer, R., Karl, T., Graus, M., Bamberger, I., Hörtnagl, L., Brilli, F., Wohlfahrt, G., and Hansel, A.: Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, Atmos. Chem. Phys., 11, 611-625, doi:10.5194/acp-11-611-2011, 2011.

Attachment:

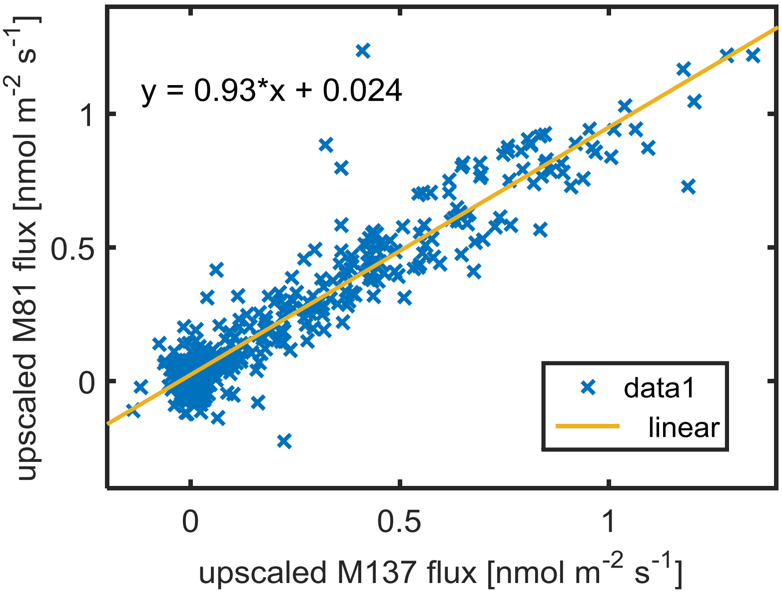

Figure Z1: Scatter plot of upscaled M81 and M137

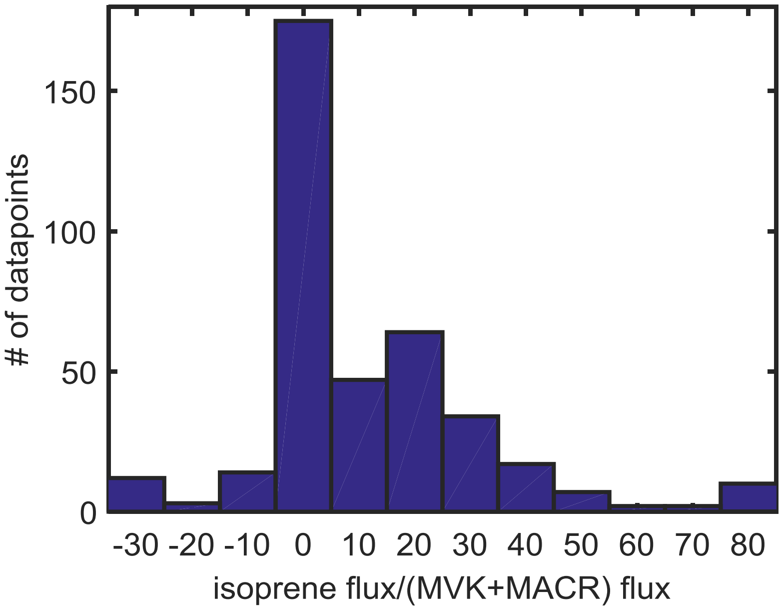

Figure Z2: Histogram of the ratio between the isoprene and MVK/MACR flux the -30 bin includes all data with a ratio lower than -25 and the +80 bin all data with a ratio above 75.

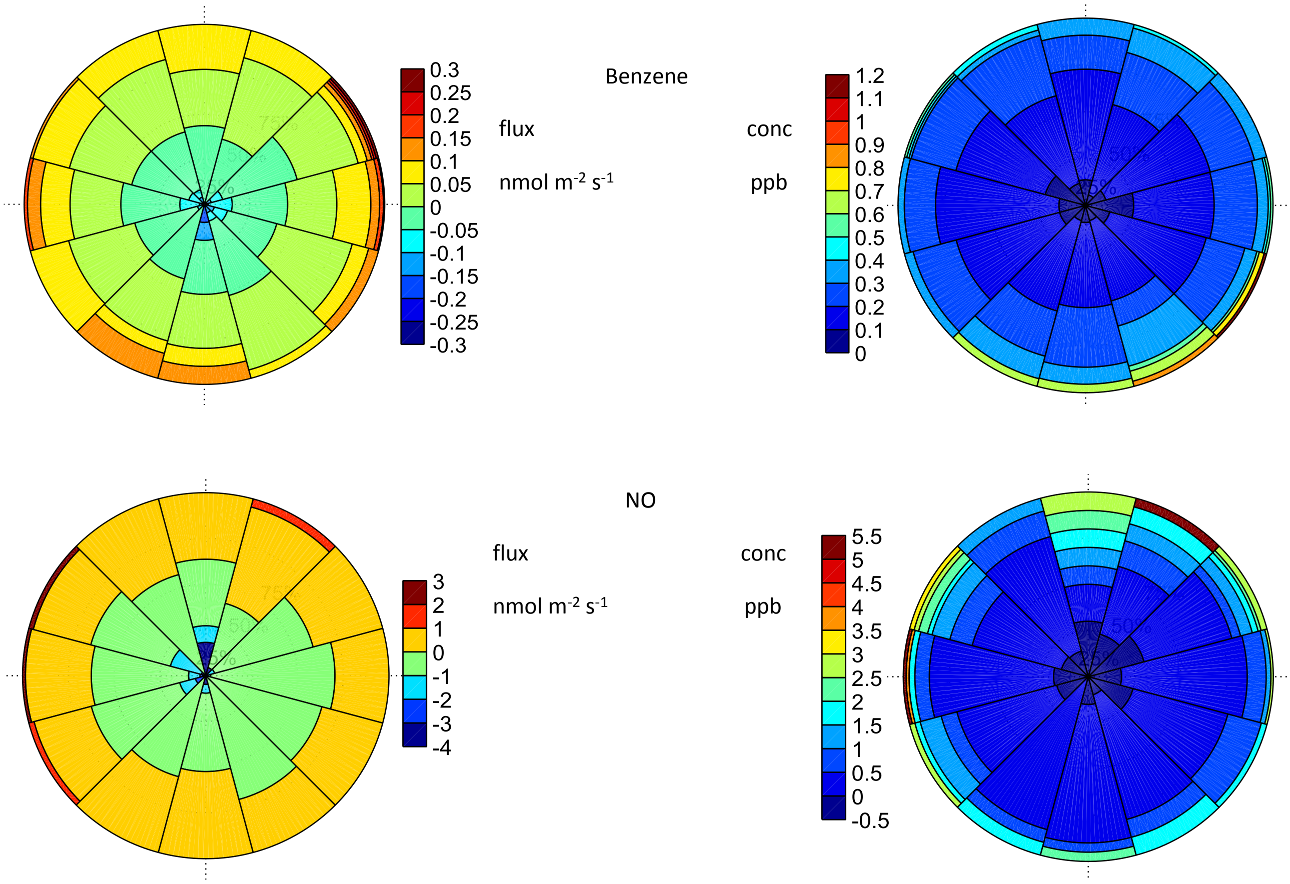

Figure Z3: Wind roses of benzene (top) and NO (bottom). Fluxes are given on the left hand side and concentrations on the right hand side.

Characterization of total ecosystem scale biogenic VOC exchange at a Mediterranean oak-hornbeam forest

S. Schallhart[1], P. Rantala[1], E. Nemitz[2], D. ~~Mogensen[1]~~Taipale[1,3,4], R. ~~Tillmann[3]~~Tillmann[5], T. F. ~~Mentel[4]~~Mentel[5], B. ~~Loubet[5]~~Loubet[6], G. ~~Gerosa[6]~~Gerosa[7], A. ~~Finco[6]~~Finco[7], J. Rinne[1,~~-7,~~8,9,10], and T. M. Ruuskanen[1]

[1]{Department of Physics, University of Helsinki, Helsinki, Finland}

[2]{Centre for Ecology & Hydrology (CEH), Penicuik, United Kingdom}

[3]{Department of Plant Physiology, Estonian University of Life Sciences, Tartu, Estonia}

[4]{University of Helsinki, Department of Forest Sciences, University of Helsinki, Helsinki, Finland}

[5]{Forschungszentrum Juelich GmbH, Juelich, Germany}

[6]{National Institute of Agronomic Research UMR ECOSYS INRA, AgroParisTech, Université Paris Saclay, France}

[7]{Department of Mathematics and Physics, Catholic University of Brescia, Brescia, Italy}

[~~4~~8]{Department of Geosciences and Geography, University of Helsinki, Helsinki, Finland}

[~~5~~9]~~-~~{Finnish Meteorological Institute, Helsinki, Finland}

[10]{Department of Physical Geography and Ecosystem Science, Lund University, Lund, Sweden}

Correspondence to: S. Schallhart (simon.schallhart@helsinki.fi)

Abstract

Recently, the number and amount of biogenically emitted volatile organic compounds (VOCs) has been discussed vigorously. Depending on the ecosystem the published number varies between a dozen and several hundred compounds. We present ecosystem exchange fluxes from a mixed oak-hornbeam forest in the Po Valley, Italy. The fluxes were measured by a proton transfer reaction-time-of-flight (PTR-ToF) mass spectrometer and calculated by the eddy covariance (EC) method. Detectable fluxes were observed for ~~twelve~~ up to 29 compounds, dominated by isoprene, which comprised over ~~65~~60% of the total upward flux (in molar basis)~~ emission~~. The daily average of the total VOC ~~emission~~upward flux was ~~9~~10.~~5~~4 nmol m^{-2} s^{-1}. Methanol had the highest concentration and accounted for the largest ~~deposition~~downward flux. Methanol seemed to be deposited to dew, as the

~~deposition~~downward flux happened in the early morning, right after the calculated surface temperature came closest to the calculated dew point temperature.

We estimated that up to ~~27~~30% of the upward flux of methyl vinyl ketone (MVK) and methacrolein (MACR) originated from atmospheric oxidation of isoprene. A comparison between two methods for the flux detection~~ methods~~ (classical~~/visual~~ and automated) was made. Their respective advantages and disadvantages were discussed and the differences in their results shown. Both provide comparable results~~; however we recommend the automated method with a compound filter, which combines the fast analysis and better flux detection, without the overestimation due to double counting~~.

1. Introduction

Volatile organic compound- fluxes between vegetation and atmosphere affect atmospheric chemistry by controlling the oxidation capacity of the atmosphere (Fehsenfeld et al., 1992, Fuentes et al., 2000). The non-methane biogenic VOC emissions are dominated by terpenoids, e.g. isoprene and monoterpenes, followed by oxygenated VOCs such as methanol and acetone (Kesselmeier et al., 1999, Guenther et al., 2012). The emitted VOCs are physically removed by dry or wet deposition or are oxidized by e.g. OH, O_3 and NO_3 (Mogensen et al., 2015). Their oxidation contributes to the tropospheric ozone formation and destruction processes (e.g. Derwent et al., 2003, Bloss et al., 2005), aerosol formation and aerosol growth and, thereby, influences air quality and climate (Kulmala et al. 1998, Tunved et al., 2006, Monks et al., 2009, Riipinen et al., 2012, Paasonen et al., 2013). To assess these effects caused by the biogenic VOCs, reliable flux budgets are necessary.

Most ecosystem scale VOC ~~emission~~flux measurements have been conducted with disjunct eddy covariance method by mass scanning using proton-transfer-reaction quadrupole-mass-spectrometer (PTR-QMS), ~~or ~~relaxed eddy accumulation or surface layer gradient techniques with gas chromatography - mass spectrometry applying selected ion mode (e.g. Lamb et al., 1985; Businger and Oncley, 1990; Fuentes et al., 1996; Guenther et al., 1996; Rinne et al., 2001; Karl et al., 2002; Rinne and Ammann, 2012). These methods require pre-selection of target compounds and in case of the PTR-QMS suffer from the limitation of unit mass resolution, making it impossible to separate isobaric compounds, i.e. compounds with identical integer mass, but different chemical composition. Thus, measurements have inherently focused on compounds already known to be emitted by vegetation and thereby hinder the discovery of fluxes of compounds not previously known to be emitted by vegetation. Furthermore, extreme weather conditions ~~like ~~such as hail can change the VOC flux pattern (Kaser et al., 2013), which is difficult to measure with such methods.

Lately, new insights were provided by the more universal and sensitive PTR-ToF. Park et al. (2013) analysed flux data obtained by the PTR-ToF and revealed many previously unobserved compounds to be emitted, but this approach has so far only been applied to very few vegetation types (e.g. Ruuskanen et al., 2011, Park et al., 2013, Kaser et al., 2013).

In this study we have conducted VOC flux measurements at a remnant natural oak-hornbeam dominated forest (Bosco Fontana) in northern Italy as part of an intensive field campaign organized by the European FP7 project 'ÉCLAIRE' (Effects of climate change on air pollution impacts and response strategies for European ecosystems). The objectives of the ÉCLAIRE Bosco Fontana experiment were (a) to quantify the exchange of a range of pollutants with this ecosystem in one of the most polluted regions of Europe, (b) to assess the importance of in-canopy chemical interactions on the biosphere / atmosphere exchange of reactive gases and aerosols and (c) to provide a supersite in the framework of a spatial Po Valley study that combined resources from two EU projects (ÉCLAIRE, PEGASOS: Pan-European gas aerosol climate interaction study) with a national Italian initiative.

In this paper, we present the results of the application of state-of-the-art PTR-ToF mass spectrometry and eddy covariance technique to derive the total biogenic VOC flux above the Bosco Fontana ecosystem. The aims of this study were: i) the comparison of two data processing approaches to identify compounds for which fluxes were above the detection limit, contrasting the automated method used by Park et al. (2013) with the "classical" method, which is using manual cross covariance peak checking (e.g. Taipale et al., 2010; Ruuskanen et al., 2011; Kaser et al., 2013); ii) the characterization of the total ecosystem scale ~~total~~ VOC ~~emission~~fluxs from a Mediterranean oak forest, with particular emphasis on iii) the quantification of the contribution of non-terpenoid VOCs to the total VOC ~~emission~~flux, iv) the estimation of the possible contribution of secondary compounds to the observed above-canopy fluxes, and v) the study of ~~the~~ dew potentially causing ~~the~~ methanol deposition in the morning~~s~~.

A companion paper (Acton et al., 2015) compares the PTR-ToF-MS measurements with simultaneous measurements by PTR-QMS and a bottom-up estimate of the canopy flux scaled up from leaf level emission measurements, and also derives emission factors for the use in emissions models.

2. Materials and methods

2.1. Bosco Fontana site description

The measurements were performed from June 15th to July 6th 2012 in Bosco Fontana, Lombardy, Italy. Bosco Fontana is a 233 ha forested nature reserve located in the north-east of the Po valley. The main tree species are *Quercus cerris* (turkey oak), *Quercus robur* (pedunculate oak), *Quercus rubra* (northern red oak) and *Carpinus betulus* (Hornbeam) (Dalponte et al., 2008). The typical height of the trees varied between 26 and 28 ~~metres~~m. The surroundings of the Bosco Fontana forest area are agricultural land and some roads. The largest city nearby is Mantua, with 48000 inhabitants, which is located 8 km to the south-east. The measurement site is 25 m above sea the level. The temperatures varied from 18 to 32 °C during the campaign and the main wind directions were east and west~~ (Fig. 6a)~~. The measurement tower was 42 m high and located in the south-western part of the nature reserve (45.20°N, 10.74°E~~; Fig. 1~~). Figure 1 shows a satellite image of the area, with the position of the tower and the mean 80% footprint (Acton et al., 2015). The climatological mean annual temperature is 13.3°C and the mean annual precipitation is 834 mm (Willmott and Matsuura, 2012a and 2012b).

2.2. Meteorological and trace gas data

The measurement tower was equipped with temperature and relative humidity sensors at several heights. The turbulence data were measured with a 3-d anemometer (HS 50, Gill Instruments~~, United Kingdom~~) at 32 m above ground level (later referred as agl) and the instrument was fastened on a pole 1.7 m away from the lattice tower. An additional measurement of wind direction was provided by a 2-d ultrasonic anemometer as part of an integrated weather station (Weather Transmitter WXT610, Vaisala~~, Vantaa, Finland~~; 32 m agl), which also measured air pressure, relative humidity and temperature. The O_3 concentration was determined with a chemiluminescence analyser (Model 202, 2B Technologies) at 40 m agl and NO_2 and NO with a chemiluminescence analyser equipped with a thermal converter (Model 42C, Thermo Scientific) at a height of 32 m agl.

Carbon dioxide flux measurements were performed, using the eddy covariance technique, at the top of the tower where a sonic anemometer (USA 1, Metek) and a fast IRGA analyzer (mod. 7500, LICOR) were mounted on a pole, 1.7 m far from the edge of the tower. The sonic anemometer was working at 20 Hz and the fast IRGA was calibrated before and after the field campaign and no significant drift was observed. Carbon dioxide fluxes were measured from June 18th to July 12th. Several procedures were applied in order to obtain the correct flux calculations: despiking (Vickers and Mahrt, 1997), double rotation of the reference system (Kaimal and Finnigan, 1994), linear detrending (Lee at al., 2004), frequency loss corrections using the ogive methodology (Ammann et al., 2006), WPL corrections for density fluctuations (Webb et al. 1980), stationarity test (Foken and Wichura, 1996); finally a manual selection of the data was performed too and data after rainfalls were discarded.

The dew point temperature, T_d, was calculated according to Lawrence (2005):

$$T_\mathrm{d} = T\left[1 - \frac{T\ln\left(\frac{\mathrm{RH}}{100}\right)}{\frac{L_\mathrm{vap}}{R_\mathrm{w}}}\right]^{-1} \quad (1)$$

where T is the ambient temperature, RH is the relative humidity, L_vap is the enthalpy of vaporization (2.501 x 10^6 J kg^{-1}) and R_w is the gas constant of water vapour (461.5 J K^{-1} kg^{-1}).

The average aerodynamic ~~leaf surface~~ temperature $T(z_0')$ was estimated using a method described by Nemitz et al. (2009) as

$$T(z_0') = T + \overline{\theta' w'}(R_a + R_b), \quad (2)$$

where z_0' is the notional mean height of the canopy exchange, $\overline{\theta' w'}$ and T are the measured heat flux and temperature at the measurement height of z_m, respectively. In this study, the roughness length z_0 was estimated to be ca. 1 m (e.g. Dolman, 1986). For the zero displacement height d we used the common approximation of $d = 2/3 \times z_\mathrm{c}$, where z_c is the canopy height (28 m).

The resistance parameters R_a and R_b were determined as (Owen and Thompson, 1963; Garland, 1977~~, Owen and Thompson 1963~~)

$$R_a = \frac{u}{u_*^2} - \frac{\Psi_h\left(\frac{z_m - d}{L}\right) - \Psi_m\left(\frac{z_m - d}{L}\right)}{k u_*} \quad (3)$$

and

$$R_b = (B u_*)^{-1}, \quad (4)$$

where L is the Obukhov length. The sublayer-Stanton number (B) can be estimated by

$$B^{-1} = 1.45 Re_*^{0.24} Sc^{0.8}, \quad (5)$$

where roughness Reynolds number Re_* is given by

$$\mathrm{Re}_* = \frac{z_0 u_*}{\upsilon} \quad (6)$$

and the Schmidt number Sc by

$$\mathrm{Sc} = \frac{\upsilon}{D} \quad (7)$$

The friction velocity u_* and the horizontal wind u were taken from the measurements at z_m and k is von Karman's constant (0.4). The kinematic viscosity of air, υ, was assumed to be constant ($\approx 1.56 \times 10^{-5}$ m^2 s^{-1}), so was the thermal diffusivity temperature in air, D ($\approx 1.9 \times 10^{-5}$ m^2 s^{-1}). The integral stability correction functions Ψ_h and Ψ_m for heat (h) and momentum (m), respectively, were taken from ~~Businger et al. (1971) and Dyer (1974)~~ Rannik (1998).~~.~~

2.3. VOC measurements

2.3.1 PTR-ToF measurements

The PTR-ToF (Ionicon Analytik GmbH~~, Austria~~; Graus et al., 2010, Jordan et al., 2009) combines the soft ionization of a PTR source with the high mass resolution of a time of flight of mass spectrometer ~4500 m/Δm (determined as the full width at half maximum of the ion peak). The precise mass of a compound can be derived from the time of flight and the elemental composition can be calculated from the observed mass defect. Therefore the instrument can separate isobaric compounds~~; ~~. ~~i~~It cannot, however, distinguish between isomeric compounds, as it gives no information about the compound structure. The real-time measure of full spectra at 10 Hz allows for flux measurements with the eddy covariance technique.

The PTR-ToF was placed inside a container next to the measurement tower. Air from 32 m height was sampled through a 40 m long and ~~0.5 in~~9.5 mm wide (~~outer~~inner diameter; ~~o~~i.d.) PT~~D~~FE tube (hereafter referred to as common sampling line), which was pumped at 63 l min^{-1}. The pressure drop induced by the pumping was sufficient to prevent condensation in the sampling line outside of the container. Inside the air conditioned container, the inlet line was heated (self-regulated heating wire with 11 W/m at 30 °C).~~.~~ The 3-d wind measurements were obtained with a frequency of 10 Hz 10 cm above the inlet.

The PTR-ToF was connected to the inlet line via a 3-way valve (type: 6606 with ETFE, Bürkert GmbH & Co. KG), from where a subsample of 0.5 l min^{-1} were pumped through a ~~1/8~~1.6 mm ~~in~~ (~~o~~i.d.) and ~~1/16~~1 mm ~~in~~ (~~o~~i.d.) PEEK capillary (together around 20 cm long; heated between 40°C and 60°C) to the instrument. The PTR-ToF used a 30 ml min^{-1} flow for analysis, the remaining flow was discarded and served only as a by-pass flow in order to decrease the response time of the PTR-ToF and associated wall losses in the inlet capillaries. The drift tube was operated at 600 V and temperature of 60 °C. Together with a drift tube pressure of 2.3 mbar this resulted in an E_{PTR}/N ratio of 130 Td, where E_{PTR} is the electrical field strength and N is the gas number density. The instrument produced a time series of 22 days, with a 1.5 day break when the air-conditioning in the container failed.

2.3.2 Calibration & concentration calculation

The instrument background was measured one to three times per day. A small pump (N86KNE , KNF Neuberger) established a 1.4 l min^{-1} flow from the common sampling line to a custom made catalytic converter. This converter was heated to 350 °C and created VOC-free (zero-) air at ambient humidity.

The zero air was connected to the second port of the three way valve and passed an overflow in order to achieve a constant zero air flow at a constant pressure (Fig. 2). The background ~~(zero air)~~ measurements were used for the calculations of the concentrations as well as the determination of the limit of detection.

The instrument was calibrated every second week, i.e. a total of three times. A custom build calibration unit, which ~~spiked~~ mixed zero air with the calibration gas, was inserted between the catalytic converter and the overflow (Fig. 2). The calibration gas (Apel Riemer Environmental Inc~~., USA~~.) contained 16 different compounds with the mass range from 33 to 180 amu at known concentrations of around 1 ppm. ~~The~~ As the gas was diluted with zero air (calibration gas: 10 ml min^{-1}; zero air: 1.4 l min^{-1}) the resulting ~~in~~ mixing ratios were around 7 ppb. The sensitivities were calculated from the observed count rates of the zero air and the calibration gas measurements in the ppb range. For the VOCs that were not included in our calibration standard, we used average sensitivities for compound families C_xH_y (based on isoprene, benzene, toluene, o-xylene, trimethylbenzene, naphthalene, α-pinene combined with $C_6H_9^+$ fragment), $C_xH_yO_z$ (considering acetaldehyde, acrolein, acetone, 2-butanone) and $C_xH_yN_z$ (set to that of acetonitrile). The averaged sensitivities were: C_xH_y = 13 (± 1.7) ncps ppb^{-1}, $C_xH_yO_z$ = 19.1 (± 1.3) ncps ppb^{-1} and $C_xH_yN_z$ = 18.1 (± 1.3) ncps ppb^{-1}. The ranges given in the brackets ~~is~~are the standard deviations of the average sensitivities calculated for the compounds in each group from the calibrations. Normalized counts per second (ncps) have been corrected for transmission (pusher duty cycle losses) and primary ion fluctuations (Herbig et al., 2009). The average signal of the primary ion signal (upscaled via the isotope $H_3{}^{18}O_1{}^+$) was around 750000 cps (Transmission corrected: 10^7 cps). The impurities were: O_2^+ 4% and NO^+ 0.3% of the H_3O^+ primary ion. The monoterpene sensitivities were derived from the α-pinene calibrations (in the calibration gas). Fragments from compounds in the calibration standard were not taken into account when calculating the sensitivities.~~.~~ For example, the signal at $C_5H_9^+$ (*m/z* 69.0699) relates to the protonated parent ion of isoprene and is scaled up to the total isoprene, although some isoprene fragments also show up at other masses. As a consequence it is important that fluxes at those fragments are excluded to avoid double-counting. The result of this procedure can be found in Table A1.~~. The importance of this procedure is assessed in Sect. 3.1 below.~~

For compounds/fragments not included in the calibration standard, ~~including those that could not be linked to a parent ion,~~ the average sensitivities for the ~~fragment~~ compound families are applied as previously described. In this case the fragmentation pattern is not accounted for and all fragments have to be added up to arrive at the total flux, excluding those that could be associated with calibrated compounds. Two exceptions were made, as acetic acid was not calibrated, but its major fragment

($C_2H_3O^+$; Baasandorj et al., 2015) was disregarded, the sensitivity for acetic acid was halved (9.55 ncps ppb^{-1}). For ethanol ($C_2H_7O_1{}^+$) the methanol sensitivity was used.

For the data post processing the ToF Analyzer V2.45 software was used, which has been described in Müller et al. (2010 and 2013). A peak list (Table A1) was created with the TofTools software (Junninen et al., 2010), by integrating the 10 Hz raw data for one hour and then fitting and identifying the different peaks. The measured mass peaks were identified by matching them with the calculated masses of different combinations of H, C, O, N and S atoms. The range of atoms allowed to appear in a compound was set from 0 to 50.

After peak fitting was performed on the 10 Hz data the output of the ToF analyzer were aggregated to provide 30 min concentration data in a three-step process: first, the 10 Hz data were averaged over 30 minutes. From these 30 min data the zero air measurements were subtracted, wherein values for the times between the zero air measurements were linearly interpolated. The resulting signals were then compared to the limit of detection LOD = $2\sigma_{\mathrm{zero}}$, where σ_{zero} is the standard deviation of the 10 Hz zero-air signal during a 30 min measurement. To calculate the volume mixing ratios, all compounds above the LOD were divided by the measured or assigned sensitivity. Compounds with signals below the LOD were disregarded from the further analysis (Table A1).

2.3.3 Flux calculations

Fluxes were derived using the eddy covariance (EC) method. In ~~the~~ EC, the flux is calculated using a discretized covariance:

$$\overline{w'c'} = \frac{1}{n}\sum_{i=1}^{n} w'(i \cancel{-\lambda/\Delta t})c'(i+\lambda/\Delta t), \tag{8}$$

where w' and c' are high frequency fluctuations of vertical wind and concentration, respectively, i the number of the measurement, n is the sum of all measurements during the flux averaging time (30 min in this study), Δt is the sampling interval (0.1 s) and λ is the lag time caused by the sampling tubes (e.g. Kaimal and Finnigan, 1994).

In this study, vertical wind and VOC concentrations were both recorded at 10 Hz frequency. The flux calculation procedure was the following:

~~The compounds for which the flux was deemed detectable were identified with two different methods, which are termed the “classical method” (Taipale et al., 2010) and the “automated method” (Park et al., 2013).~~

~~The flux calculation procedure was the following:~~

First, the wind vector was 2-d~~D-~~ rotated using the method described by Kaimal and Finnigan, (1994). If the vertical rotation was more than 5°, the period was flagged and after the ‘compound with exchange’ detection rejected from further analysis. Data which were measured during periods when the wind was coming through the tower was not filtered out (discussed in Acton et al., 2015).

The linear trend was removed from the concentrations while block averaging was used for the vertical wind measurements.~~Block averaging was used for the vertical wind measurements and the linear trend was removed from the concentration measurements.~~

Next, ~~we calculated~~ cross covariance~~s~~ functions (CCFs) were calculated between the vertical wind and each of the volume mixing ratios for every 30 minute measurement period. The lag time and compounds for which the flux was deemed detectable were identified with two different methods (Table 1), which are termed the “classical method” (Taipale et al., 2010) and the “automated method” (Park et al., 2013).

For the classical method the lag time was determined for each 30 min periods and compounds individually by maximizing the smoothed cross covariance function from a lag time window of 0–5 s (Taipale et al., 2010). The smoothing of the CCF decreases possible flux overestimation caused by noise when using the maximum covariance method (Taipale et al., 2010; Langford et al. 2015). In the next step compounds with detectable flux were identified by checking the cross covariance functions manually for each individual compound and for several different 30 min periods. The total number of manually identified CCFs was well over 1000. Compounds for which a clear CCF maximum was found were used for the further flux calculations.

For the automated method, such as in Park et al. (2013), a constant lag time (2.6 s) was used for all compounds and all 30 min measurement points. This avoids overestimation in the flux, which can happen if the maximizing method is used for flux values close to the detection limit (Langfold et al., 2015). This lag time used here was calculated from the averaged absolute cross covariance function of isoprene, which exhibits a clear maximum. The individual 30 min lag times from the selected time window were also calculated to confirm that the lag time did not shift during the campaign. To identify the compounds with detectable flux, an automated flux searching routine was used. First, absolute CCFs for each compound were calculated using daytime values from 10:00 to 16:00 (CET), i.e. when good conditions for turbulence and high flux are present (see Fig A5; Park et al., 2013). Next, the absolute values of the 30 min CCFs in this time window were averaged over the entire measurement period (Fig. A6 to A9). From this averaged CCF, the routine automatically calculated the flux (at 2.6 s lag time), the average noise and the standard deviation of the noise (σ_{noise}). The mean and standard deviation of the noise were determined from areas at the left and right border of the CCF spectra (Fig A6 to A9). Finally, the mean noise was subtracted from the flux and then divided by σ_{noise}. For ratios >3 the respective compound was used for the further flux calculations.

The final flux values were calculated for each method from the original (not smoothed or absolute) 30 min CCFs by using the respective lag time and compound. The fluxes of both methods were then filtered using the stationarity criteria introduced by Foken and Wichura, (1996): every 30 min period was divided into six 5 minute sub-periods and VOC fluxes were calculated for each 5 min period. If the flux values calculated using 5 min averages differed by more than 30%, the period was disregarded from further analysis. The stationarity criteria together with the 5° tilt angle disregarded 43% of the data for each method.

For those compounds for which a flux could be detected, the uncertainty of the flux was calculated from the two 60 s time windows at the border of the CCFs for each 30-minute flux value. The root mean square of each window was calculated and the results averaged. This follows the approach of Langford et al. (2015) and ensures that offsets (from zero) from the noise in the CCF tails are taken into account. For estimation of the uncertainty of the diurnal net flux, it was assumed that the errors of different flux values are independent, and the uncertainty can be calculated with the Gaussian propagation of error. The independence assumption is not fully correct, as fluxes from different compounds are derived using the same vertical wind data.

For the calculation of the diurnal 1 h flux data, all measurements which passed the quality checks were averaged. The daily average was then calculated by averaging the diurnal data. This ensures that periods, which have fewer data points (due to quality criteria filtering, background or calibration measurements) do not get underrepresented in the daily average.

~~and determined a lag time by maximizing the smoothed cross-covariance function from a lag time window of 0–5 s (classical approach, Taipale *et al.*, 2010). For the automated approach, like in Park et al. (2014), a constant lag time was used for all compounds. This minimizes overestimations, which happen if the maximizing method is used for flux values close to the detection limit. The lag time was calculated from the averaged cross covariance function of isoprene and was 2.6 s. The individual 30 min lag times from the selected time window were also calculated to ensure that the lag time did not shift during the campaign.~~

~~Finally, the fluxes were filtered using a stationarity criteria introduced by Foken and Wichura, (1996): every 30 min period was divided into six 5 minute sub-periods and VOC fluxes were calculated from both 5 min and 30 min intervals. If the values differed more than 30%, the period was disregarded from further analysis.~~

~~Next we assessed which compounds flux was above the limit of detection.~~

~~In the classical approach the cross covariance functions (CCFs) are checked manually for several different 30 min periods and it is determined if there is a clear maximum.~~

~~The automated method calculates fluxes as presented by Park et al. (2013). They used an automated flux searching routine, which calculated the average of absolute CCF. Therefore, a time window is chosen when good conditions for turbulence and high emissions are present. As in Park et al. (2013), a daily window from 10:00 to 16:00 (CET wintertime) was used in this study. The absolute values of the 30 min CCFs in this time window were averaged over the entire measurement period. From this averaged CCF a routine automatically finds the maximum value and compares it to a manually chosen noise level (3-10 σ_{noise}, the standard deviation of the noise). The standard deviation is calculated from areas at the left and right border of the CCF spectra. The filtering of the data was done according to Park et al. (2013), where a 5° tilt angle and 70% stationary criteria were used. The quality criteria disregarded 43% of the data for the automated method and 43% for the classical method. A comparison of the two methods is presented in Table 1.~~

~~For those compounds for which a flux could be detected, the uncertainty of the flux was calculated from the two 60 s time windows at the border of the CCFs for each 30-minute flux value. The root mean square of each window was calculated and the results averaged. This follows the approach of Langford et al (2015) and ensures that offsets (from zero) from the noise in the CCF tails are taken into account. For the diurnal net flux error it was assumed that the errors are independent, and the error was calculated with the Gaussian propagation of error. The independence assumption is not fully correct, as fluxes from different compounds are derived using the same vertical wind data.~~

~~For the calculation of the diurnal 30 min flux data, a trimmed mean function was used, which disregarded the lowest and highest 5% of the data and then averages the remaining 90% of the data. The flux data is not normally distributed and thereby this averaging method is will bias the result, but the positive aspects of limiting the influence of outliers were more important. The daily average was then calculated by averaging the diurnal data.~~

2.3.4 Spectral corrections

Due to the high frequency attenuation and low frequency cut~~-~~off, the measured EC flux underestimates the real flux (e.g. Moore, 1986; Horst, 1997~~; Moore, 1986~~). ~~This~~ High frequency attenuation is caused by the tubing, the sensor separation ~~and~~ and the time-response of the instrument itself, whilst low frequency attenuation is caused by linear detrending or block averaging.

The effect of low-pass filtering can be quantified by the use of a transfer function. Formally the transfer function H_{wc} can be written as,

$$H_{wc}(f) = \frac{C_{wc}(f)}{\overline{w'c'}} \cdot \left(\frac{C_{w\theta}(f)}{\overline{w'\theta'}}\right)^{-1}, \tag{9}$$

where C_{wc} and $C_{w\theta}$ are the cospectra of a scalar c and w, and potential temperature θ and w, respectively. $\overline{w'c'}$ and $\overline{w'\theta'}$ are ‘un-attenuated’ turbulent fluxes of a scalar and temperature, respectively, and f is the frequency. A commonly used approximation for the first order transfer function is (Horst, 1997)

$$H_{wc} \approx [1 + (2\pi\tau f)^2]^{-1}, \tag{10}$$

where τ is a system response time.

In this study, we determined the high frequency attenuation using a method described by Horst (1997). In the method the attenuation factor α is calculated by the equation

$$\alpha = \frac{\overline{(w'c')}_a}{\overline{w'c'}} = \frac{1}{1+\left(\frac{2\pi n_m \tau \bar{u}}{z_m - d}\right)^{\beta}}, \tag{11}$$

where z_m is the measurement height (32 m), d the zero displacement height ($d = 2/3 \times z_c$, where z_c is the canopy height, 28 m), $\bar{u}$ the mean horizontal wind speed, $\overline{(w'c')}_a$ is the attenuated flux and $\overline{w'c'}$ is the real flux. For neutral and unstable stratification $(z_m - d)/L \leq 0, \beta = 7/8, n_m = 0.085$ and for stable stratification, $(z_m - d)/L > 0, \beta = 1, n_m = 2.0 - 1.915/[1 + 0.5(z_m - d)/L]$.

We selected daytime (10:00-16:00 CET wintertime), unstable ($\overline{w'T'} > 0$) periods, and calculated cospectra of temperature, isoprene and water clusters for every 30 min interval. Response times of isoprene and water clusters were then derived by using Eq. (10) and the median transfer functions (Eq. 9). After that, the flux losses were derived using the correction factor α^{-1} (Eq. 11) and the response time of the isoprene measurements, ~~(~~τ = 1.1 s~~;~~ (Fig. 3)~~,~~. ~~which~~ This value is similar to that obtained by Rantala et al. (2014), ~~where~~ who utilized disjunct EC ~~was utilized~~ with a PTR-QMS. The correction factor α^{-1} was finally multiplied to each VOC flux value. During daytime, the factor was mostly less than 10%, and during nighttime typically around 20%, resulting in overall correction of the~~. On average this factor was 1.26~~ isoprene flux, dominated by daytime emission, of 11%.

The value τ = 1.1 s represents the response time of the whole system including the instrument and the inlet line. Therefore, the response time should be determined for each measurement setup individually as e.g. the length of the inlet line has ~~for example~~ an effect on the attenuation (Nordbo ~~et al~~et al., 201~~3~~3 and 2014). The response time is also probably compound dependent because the attenuation of water vapo~~u~~r increases as a function of relative humidity (Mammarella et al., 2009). Thus, similar kind of behavior could be expected for water solvable compounds, such as methanol. In that sense, the high frequency corrections should be taken as rough estimates.

2.3.5 Flux loss due to chemical degradation

The chemical degradation of different VOCs is dependent on their concentration, reaction rates and concentrations of oxidants (O_3, NO_3, OH). Therefore the proxy for OH concentration, $[\mathrm{OH}]_{\mathrm{proxy}}$, was calculated according to Peräkylä et al. (2014) and Petäjä et al. (2009):

$$[\mathrm{OH}]_{\mathrm{proxy}} = 5.62 \times 10^5 \times \mathrm{UVB}^{0.62} \tag{12}$$

The calculated average midday concentration of the $[\mathrm{OH}]_{\mathrm{proxy}}$ was $1\cdot10^6$ # cm^{-3}.

As the UVB radiation was not measured directly during the Bosco Fontana study, an upper limit calculation was made by using the tropospheric ultraviolet model 4.1 (TUV; Madronich 1993, Madronich and Flocke, 1999). The model was used via the link http://cprm.acd.ucar.edu/Models/TUV/Interactive_TUV/, using the Pseudo-spherical discrete ordinate 4 streams radiation transfer model and an albedo of 0.1. The NO_3 concentration was calculated as described in Peräkylä et al. (2014) from the measured concentrations of NO_2 and O_3.

The influence of chemical degradation on the measured eddy covariance fluxes depends on the relative magnitude of the chemical lifetime of the measured compound and its transport time. The transport time is the time the compound needs to get from its emission point to the actual measure point, and it can be characterized by turbulent mixing time-scale. The effect is often assessed using the Damköhler number (Damköhler, 1940), which is the ratio of the mixing time-scale to the chemical lifetime. The smaller the Damköhler number is, the less influence the chemical degradation has on the flux. However, since both the transport time and the chemical lifetime are height dependent, a more accurate assessment of the loss is achieved by calculating the ratio of the flux at the measurement height (F) to the true surface ~~emission~~ exchange (E) e.g. using a stochastic Lagrangian transport model (Rinne et al., 2012). In Bosco Fontana, the F/E for isoprene was 0.95-0.97, ~~meaning~~ indicating that the measured fluxes are between 3% and 5% lower than the emission~~of the emissions are lost~~ due to the chemical degradation. For the monoterpenes (we used α-pinene), which have the lowest F/E ratio (shortest lifetime) of the measured ~~flux~~ compounds, the F/E was between 0.8 and 0.95. No corrections for the chemical degradation have been made in this ~~manuscript~~study.

2.4 Modelled MVK/MACR production

After having quantified the average fraction of the isoprene flux lost between point of emission and the measurement height, this section ~~seeks~~ uses an alternative method to quantify the ~~amount of~~fraction of the observed MVK/MACR flux that is expected to be produced by the atmospheric oxidation of isoprene below the measurement height. This is done ~~an alternative approach,~~ by integration of the chemical kinetic equation.

The chemical destruction of isoprene F_Q~~Q~~, in an air column below the measurement level can be calculated as

~~Q~~$F_Q = \int_0^{z_m} \sum_i k_i [R_i]\, [\mathrm{C_5H_8}]\, \mathrm{d}z$, (13)

where k_i is the rate constant, $[R_i]$ the concentration of reactant i, and $[\mathrm{C_5H_8}]$ the concentration of isoprene. The integration is done from surface to the measurement height z_m. Even though $[\mathrm{C_5H_8}]$ and $[R_i]$ are height dependent (Andronache et al., 1994, Hens et al., 2014), we assumed constant reactant and isoprene concentrations for the integration range as no profiles were measured, in order to get an order of magnitude estimate. ~~We estimated t~~The chemical destruction was estimated for two ranges: from the ground level 0 to the measurement height and from the notional height $(d + z_0)$ to the measurement height. The angle brackets $\langle\ \rangle$ indicate that the values are constant:

$$\mathrm{Q} = \mathrm{k_i} \langle [\mathrm{R_i}] \rangle \langle [\mathrm{C_5H_8}] \rangle \mathrm{z_m} \quad (14)$$

$$\mathrm{Q} = \mathrm{k_i} \langle [\mathrm{R_i}] \rangle \langle [\mathrm{C_5H_8}] \rangle (\mathrm{z_m} - d - \mathrm{z_0}) \quad (15)$$

Due to the smaller reaction rates and the lower MVK/MACR concentration, we did not calculate the chemical destruction of MVK/MACR.

In order to estimate the yield of ~~methyl vinyl ketone (~~MVK~~)~~ and ~~methacrolein (~~MACR~~)~~ from isoprene, we selected the isoprene chemistry mechanism from the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997, Saunders et al., 2003), via website http://mcm.leeds.ac.uk/MCM/. The concentrations of MVK and MACR were calculated using the Kinetic PreProcessor (Damian et al., 2002) coupled to the box model MALTE-BOX (Boy et al., 2013). The simulation was executed using an initial concentration of isoprene ($5.33 \cdot 10^{10}$ # $\mathrm{cm^{-3}}$; measured) and constant concentrations of OH ($1 \cdot 10^{6}$ # $\mathrm{cm^{-3}}$; calculated), O_3 ($2 \cdot 10^{12}$ # $\mathrm{cm^{-3}}$; measured), NO ($3.5 \cdot 10^{9}$ # $\mathrm{cm^{-3}}$; measured), NO_2 ($8 \cdot 10^{10}$ # $\mathrm{cm^{-3}}$; measured), SO_2 ($1 \cdot 10^{9}$ # $\mathrm{cm^{-3}}$; estimated) and CO ($3.5 \cdot 10^{12}$ # $\mathrm{cm^{-3}}$; estimated). The temperature was further kept constant to a value of 303 K, while the start of the simulation was assumed to be at noon (local time). By dividing the initial concentration of isoprene by the summed maximum concentration of MVK and MACR, we estimate that the summed yield of MVK and MACR from oxidized isoprene is 0.35. This factor accounts for oxidation losses of MVK and MACR. A sensitivity test showed that the MVK/MACR yield response to a change in temperature and SO_2 concentration is minor. For CO, a concentration change to $5 \cdot 10^{13}$ # $\mathrm{cm^{-3}}$ results in a 5% lower yield. Due to the high NO_x concentration in Bosco Fontana, the reaction way via isoprene hydroxy hydroperoxides (ISOPOOH) does not form MVK/MACR.

3. Results and discussion

3.1. Comparison of procedures to identify detectable fluxes

In the following ~~chapter~~ the data from 22 days of flux measurements are used by different analysis routines, and the results are compared. Negative fluxes are called ~~deposition~~downward fluxes, as it is not possible to differentiate between deposition and other sink terms such as chemical losses below the measurement height~~;~~. ~~t~~The positive fluxes are called ~~emission~~upward fluxes~~s~~. The diurnal cycles of the fluxes derived by the ~~ten most~~classical method and automated method (evaluated using a 10 σ_{noise} threshold) ~~emitted compounds for each calculation method~~ are shown in Fig. 4. The signal~~s~~ of the remaining masses with detectable flux (between 3 and 10 σ_{noise}) quantified by ~~both methods~~ the automated method ~~are~~is summed up and plotted as 'other'. The 24 h average fluxes of the different compounds and different methods ~~i~~are~~s~~ shown in Table 2.

~~The average total deposition of the VOCs detected with the three different methods was -0.4 (±0.1) nmol m^{-2} s^{-1} and the average total emission was 9.5 (± 1.0) nmol m^{-2} s^{-1}.~~ The classical method identified the ~~smallest~~ lower number of compounds (5), accounting for the ~~lowest~~ lower total upward flux ~~emission~~ (8.53~~2~~ nmol m^{-2} s^{-1}) and also the ~~lowest~~ lower total downward flux ~~deposition~~ (-0.28 nmol m^{-2} s^{-1}). The only compound with a flux that was deemed quantifiable by the classical method but not by the ~~the others~~automated method with 10 σ_{noise} was $C_5H_9O_2^+$ (protonated), which contributed by ~~0.5~~1.2% to the total downward flux~~deposition~~ and by 0.~~2~~1% to the total ~~emission~~upward flux.

The automated method with a 10 σ_{noise} threshold found ~~most~~ eleven compounds with detectable flux ~~(19)~~ and ~~had~~ derived a ~~the highest~~ total ~~emission~~upward flux of ~~(10~~9.~~6~~6 nmol m^{-2} s^{-1}~~)~~. The downward flux reached -0.48 nmol m^{-2} s^{-1}. If the 3 σ_{noise} threshold was used, the number of compounds with detectable flux increased to 29 but the total upward flux was nearly the same (10.4 nmol m^{-2} s^{-1}) while the downward flux increased to -0.58 nmol m^{-2} s^{-1}. The main additional masses with detectable flux were acetone, acetaldehyde and acetic acid. ~~However, several of the compounds were recognized as fragments, water-clusters or charge transfer peaks of compounds included in the calibration standard~~As discussed in Sect. 2.3.2 fragments, waterclusters and isotopes identified during calibrations were removed from the data~~, especially $C_3H_5^+$, $C_6H_9^+$, $C_2H_3O^+$ and the $C_1H_7O_2^+$~~. ~~This~~ The disregarded masses are shown in Table A1. ~~can lead to an overestimation of the emission or deposition, due to double-counting (see Sect. 2.3.2). Furthermore, the diurnal pattern of water-cluster ionized compounds will be heavily influenced by the amount of $H_3O^+ \cdot H_2O$, which is dependent on the RH (as well as several instrumental settings, which, however, did not change during the measurements). In this study, this was especially important, as over 60% of the total emission were~~

~~caused by isoprene, therefore even minor fragments of isoprene can have a considerable impact on the net flux. Overall, 7.3% of the total deposition and 9.6% of the total emission were caused by fragments, clusters and charge transfer peaks of calibrated compounds. When the masses with detectable flux were filtered for known fragments, the total emission decreased by 10% and the compounds with flux decreased to 12. It is important to keep in mind that the absolute flux values of each compound for the automated method and the automated method with compound filter are the same. The filtering only changes the relative flux (due to the change of the net flux).~~

Figure 5 shows the diurnal variation of the net flux for the ~~different~~ two approaches. The maximum difference in the hourly net flux between a 3 σ_{noise} threshold and a 10 σ_{noise} threshold ~~is~~ was less than 1.~~6~~3 nmol m^{-2} s^{-1} and the daily average differed less than 0.5 nmol m^{-2} s^{-1}. The major difference lies in the number of masses that are found to contribute to the total VOC flux: ~~42~~ 29 (3 σ_{noise}), ~~35~~22 (4 σ_{noise}), ~~28~~22 (5 σ_{noise}), ~~24~~19 (6 σ_{noise}), ~~23~~15 (7 σ_{noise}), ~~22~~14 (8 σ_{noise}), ~~20~~12 (9 σ_{noise}), ~~19~~11 (10 σ_{noise}).

The classical method is rather labor intensive, because the CCF must be checked for many different mass peaks (>150, depending on the environment where the measurements are recorded), for several different times of the campaign (overall well over 1000 CCFs). Another weakness is that the definition of a ‘clear maxima’ is not objective and depends on the person who is working with the data. A positive aspect is that during the manual evaluation of the data possible problems or analysis faults can be detected more easily.

Compared to the classical method, the automated method gives a fast and objective result and the quality of the fluxes can be selected by the different σ_{noise} criteria. However, using the absolute value of the signal changes the mean value of it and thereby reduces the variation and the standard deviation of the signal (see Fig. A4 and A5). For example, the standard deviation of the averaged absolute CCF was 21% smaller than the standard deviation of the averaged CCF for acetone. This effect can be seen in the difference of the mean noise in Fig. A4 and A5. The higher mean noise corrects for the lower σ_{noise}, but it is constant for different σ_{noise} criteria.

In the remaining paper, all mentioned flux values were calculated using the automated method with 3 σ_{noise} threshold and the time zone used was CET wintertime (UTC +1 h).

~~Compared to the classical method, the automated method gives a fast and objective result, but the σ_{noise} threshold can vary, as the standard deviation of the noise can be reduced by taking its absolute value. The reduction of the standard deviation takes place if the signal, which is used for the error calculation, is around zero and, therefore, varies between negative and positive values. If there is some offset, so that the signal is just positive or just negative inside the error areas, using absolute values does not influence the value of σ_{noise}.~~

~~As shown, when combining calibrated and uncalibrated data, double-counting of fragments can lead to an overestimation of the flux and should therefore be filtered. In the remaining paper, all mentioned flux values will be calculated using the automated method with compound filter and all times will be CET wintertime (UTC +1 h).~~

3.2 Comparison to other studies

Comparing VOC concentration and especially fluxes from different locations (and/or times) is challenging as the results are dependent on ecosystem type, meteorology and the surroundings of the measurement site, as well as the instrumental setup (e.g. inlet length).

The most obvious difference compared to the study by Park et al. (2013) was the number of masses showing fluxes. Park et al. (2013) found 494 (out of 664 masses) showed flux above the orange grove, whereas in this study only 29 (out of 163 masses) were found to have flux. While in both studies the results depended heavily on the σ_{noise} threshold, in this study the differences were much more subtle. In the study by Park et al. (2013), the number of ions with flux differed by two orders of magnitude. In our study compounds which fulfilled the three 3 σ_{noise} criteria, but not the 10 σ_{noise} criteria, contributed 16% to the total downward flux, and 7% to the total upward flux. However, the amount of compounds filtered by the σ_{noise} criteria changed from 29 (3 σ_{noise}) to 11 (10 σ_{noise}).

A comparison between the measured fluxes from this study and their values at the orange grove (Park et al., 2013) can be found in Table A2. The major difference was the large upward flux of isoprene measured in Bosco Fontana, which contributed with 65% to the total net flux of 9.8 nmol m^{-2} s^{-1}. This net flux of all compounds is twice as much as at the orange orchard. All the major compounds (> 8 σ_{noise}) from the orange grove, except para-cymene, were also present in Bosco Fontana. Six of the remaining major compounds (> 8 σ_{noise}) of the orange grove had net fluxes which agree within 50% with the measured net fluxes in this study (isoprene and MVK/MACR being the exception).

The net carbon exchange in Bosco Fontana is shown in Fig. 6. Isoprene is the dominating compound and contributed 77% to the carbon net flux, followed by the monoterpenes (5%), MVK/MACR (3%), methanol (3%), acetone (2%) and acetic acid (2%). Overall, the measured and identified compounds had a net carbon flux of 41.8 nmol C m^{-2} s^{-1}. Two masses were not taken into account, as their elemental composition could not be determined (Table A2).

This net flux of carbon at Bosco Fontana is about four times higher than the values published by Park et al. (2013). If the net carbon emission of the measured compounds is compared to the net uptake of CO_2 during the measurement period (2423 nmol C m^{-2} s^{-1}) the influence is less than 2 % in Bosco Fontana. The daily average value of CO_2 gas exchange was -9.2 g C m^{-2}, similar to what observed by Wilson and Baldocchi (2001) over a mixed deciduous forest.

3.~~2~~3. Emission of terpenoids

The most abundant compound emitted by the Bosco Fontana forest was isoprene (protonated formula: $C_5H_9^+$), comprising over ~~65~~60% of the measured total ~~emission~~upward flux. It ~~has~~ had a clear diurnal cycle which follows the radiation. The maximum ~~emission~~upward flux (diurnal) at 20.6 nmol m^{-2} s^{-1} occurred just after midday. Figure ~~6b~~ 7b shows the wind rose for the isoprene flux. There are more isoprene emitting plants to the west of the site, indicated by the highest fluxes coming from this direction. Indeed, Acton et al. (2015) found that taking the contribution of the strong emitters in this wind sector into account improved the correlation between predicted and measured isoprene fluxes. Similar behavior can be seen from the wind rose of the isoprene concentrations, although the extent of the forest is smaller towards southwest~~SW~~, providing less opportunity for isoprene to accumulate during advection. From 21:00 to 05:00 the ~~emissions~~upward flux stayed below 0.1 nmol m^{-2} s^{-1}. The main sink of isoprene is oxidation due to reactions with OH during daytime. The calculated isoprene lifetime for daytime conditions in Bosco Fontana ~~is~~ was 2.2 h.

The fast oxidation, together with the relatively small extent of the woodland in a mixed agricultural landscape with relatively low isoprene emissions, explains why the diurnal concentration maximum of isoprene was only 2.8 ppb, even though the isoprene ~~emission~~upward flux wa~~i~~s dominating all other measured VOCs. Its daily average concentration was 1.3 ppb. The emission factors of isoprene and monoterpenes in Bosco Fontana, as well as the as the relative importance of pool and *de novo* emissions, are discussed in Acton et al. (2015). Isoprene's major source globally are forests (Guenther et al., 1995), oaks are known for being isoprene emitters (Rasmussen 1970) and dominate European isoprene emissions. Potosnak et al. (2014) measured a maximum isoprene emission of 217 nmol m^{-2} s^{-1} over an oak-dominated temperate forest in central Missouri.

2-methyl-3-buten-2-ol (MBO) can dehydrate in the proton transfer reaction and form isoprene (Fall et al., 2001, de Gouw and Warneke, 2006, Kaser et al. 2013). The influence on the isoprene signal depends on the MBO concentration and the settings of the PTR-ToF. The ~~influence~~ contribution of MBO to the isoprene signal in Bosco Fontana should be minor, as the major tree species are known to be isoprene or monoterpene emitter (~~Konig~~ König et al., 1995; Harley et al., 1999; Rosenstiel et al., 2002) as confirmed by the more specific leaf level measurements of Acton et al. (2015). However, a possible MBO source could be the understory of the forest.

In Bosco Fontana, monoterpenes have been the ~~fifth~~ seventh most emitted 'compound group'~~. With the PTR-TOF it is only possible to measure the sum of all monoterpenes, which had~~ with a maximum diurnal ~~emission~~upward flux of 0.7 nmol m^{-2} s^{-1}. Leaf-level measurements at Bosco Fontana presented by Acton et al. (2015) found the largest monoterpene emissions to be limonene originating from *Carpinus betulus* and *Corylus avellana* and to some extent *Comus sanguinea*, augmented with smaller emissions of α-pinene from *Q. robur* and *Acer campestre*, and β-pinene from *A. campestre* and *C. betulus*. Figure ~~6b~~ 7b shows the normalized wind rose of the monoterpenes ~~emissions~~upward flux (independent of the frequency of wind directions). The measurement site is very homogeneous, as no wind direction dependency on the monoterpenes flux was detected. This also holds for the monoterpene concentrations.

3.~~3~~4. MVK/MACR and their sources

MVK and MACR have the same elemental composition (protonated formula: $C_4H_7O^+$), and cannot be separated with our instrument settings. In Bosco Fontana, 3% of the total ~~emissions~~upward VOC flux ~~were~~ was due to MVK/MACR, which are both oxidation products of isoprene. To give an estimate of how much of the MVK/MACR flux is likely to have originated from atmospheric oxidation of isoprene below the measurement level z_m, we used two methods to estimate the flux divergence. The oxidation of isoprene is dominated by the reaction with the OH radical. The daytime maximum flux of isoprene oxidation products~~isoprene oxidation rates~~ between ground level and measurement height ~~are~~ were around 0.61 nmol m^{-2} s^{-1} (Eq.14) and 0.24 nmol m^{-2} s^{-1} (Eq.15) if the lower limit is the notional height~~ 0.24 nmol m^{-2} s^{-1} (Eq.15)~~. However, the result of the integration (Eq. 13) varies considerably depending on the integration domain and the assumed profiles.

Another approach to estimate the chemical degradation is to use the look-up tables for Flux-to-Surface-Exchange (F/E) ratios created using a stochastic Lagrangian transport model by Rinne et al. (2012). For the F/E ratio we use typical daytime values of friction velocity and chemical lifetime of isoprene. Depending on the assumed oxidant profile and leaf area index, ~~we have~~ F/E ratios rang~~ing~~ed between 0.97-0.95. Multiplying the isoprene ~~emission~~upward flux by F/E ratio leads to the oxidation ~~rates~~ fluxes between 0.6-1.0 nmol m^{-2} s^{-1}.

According to our calculations (Sect. 2.4), 35% of the oxidized isoprene molecules will create MVK or MACR molecules (for midday conditions). ~~The scatterplot between the concentration of isoprene and the MVK/MACR flux (Fig. 7a) shows a correlation coefficient of 0.65.~~ The scatterplot between the ~~If we compare the~~ measured MVK/MACR flux and ~~to~~ the calculated source of MVK/MACR by the oxidation of isoprene below the measurement height (Fig. 8). ~~, we get a correlation~~ shows a correlation coefficient of 0.81~~ (Fig. 7b)~~. Th~~e~~is correlation however, does not necessarily imply causality. The biogenic VOC emissions and concentrations are light dependent, as well as the concentration of OH radicals which may lead to correlations where causality does not exist.

The ~~one~~ hourly data in ~~both~~ the plot~~s~~ was separated into day and night by using a 200 µmol m^{-2} s^{-1} photosynthetically active radiation threshold. Then the $\frac{y}{x}$ ratios of the~~of Fig. 7a and Fig. 7b~~ daytime data were used to calculate the median and percentile ratios. ~~From the 25 and 75 percentiles ratios we estimated t~~The influence of the oxidation of isoprene to the measured MVK/MACR flux was estimated from the 25th and 75th percentiles ratios. If Eq. (14) ~~is~~ was used to calculate this influence, the oxidation products of isoprene ~~causes~~ vary between ~~11~~10% and ~~27~~30% of the MVK/MACR flux. If Eq. (15) ~~is~~ was used, the contribution of isoprene to the MVK/MACR flux ~~is~~ varied between 4% and 1~~1~~0%.

Comparing the results of the F/E calculations with the maximum diurnal MVK/MACR flux of 1.3 nmol m^{-2} s^{-1} ~~shows~~ suggested that a contribution of 16% to 27% of the MVK/MACR flux may originate from atmospheric chemistry. Overall the oxidation of isoprene may have an important influence (4% to ~~27~~30%) on the MVK/MACR flux, but fails to explain it fully.

Fluxes can also originate from direct MVK/MACR emissions from the plant as shown by Jardine et al. (2012). Other studies have shown also minor (Fares et al., 2015) or negligible (Karl et al., 2009; Karl et al., 2010) emission of MVK/MACR, however, in these studies there was a net uptake to the leaf. Part of the MVK/MACR concentration and fluxes may also be misattributed fragments from higher oxygenated hydrocarbons~~, which get destroyed inside the instrument~~ (Liu et al., 2013, Rivera-Rios et al., 2014). MVK and MACR have also been found to be formed from the decomposition of hydroxyl hydroperoxides (ISOPOOH) in the PTR-MS inlet. However, the ISPOOH precursor ISOPO2 will be effectively quenched by~~reacts readily with~~ NO. Therefore ~~and its~~the ISOPOOH concentration in polluted environments such as the Po Valley would ~~therefore~~ be expected to be very low, and consequently this artefact can be ruled out at this location. Additionally, an existing interference by ISOPOOH would most likely lead to a pretended MVK/MACR deposition, due to an expected downward flux of peroxides (Nguyen et al., 2015).

In general, a comprehensive theory of MVK/MACR emission and deposition is lacking, while in some environments (especially in the tropics) MVK/MACR are found to deposit fast, approaching the maximum rate permitted by turbulence (i.e. with a small canopy uptake resistance; cf Misztal et al., 2011, and references therein), whilst in other environments like at Bosco Fontana ~~emissions~~upward fluxes are observed.

3.~~4~~5. Emission of oxygenated VOCs

The second-most emitted compound was methanol (protonated formula: CH_5O^+), whose ~~net flux~~upward flux started at 08:00, later ~~in the day than the~~compared with the re~~st~~maining ~~of the~~ VOCs

~~emissions~~. It contributed ~~with 14~~15% to the total ~~emission~~upward flux (maximum ~~emission~~ at 14:30 with 4.4 nmol m^{-2} s^{-1}). Methanol is mostly emitted by plants e.g. by the plant growth metabolism (Wohlfahrt et al., 2015). From the wind rose in Fig. ~~6b~~ 7b it can be seen that the highest upward fluxes of methanol ~~emissions~~ originated from the west.

The third most emitted compound was acetone, which had a diurnal maximum ~~emission~~upward flux at 11:30~~, at~~ with 1.0 nmol m^{-2} s^{-1}. Its daily average contributed with over 3% to the total ~~emission~~upward flux (daily average). It has the same elemental composition as propanal. However, the contribution of propanal to the signal is normally less than 10% ~~to the signal~~ (de Gouw and Warneke, 2006). Acetone sources are ubiquitous: it can be emitted from several plants and trees (Geron et al., 2002; Fall 1999), ~~emitted~~ as well as from anthropogenic processes (Singh et al., 1994) or produced through secondary photochemical production (Goldstein et al., 2000).

The ~~emission~~upward flux of acetaldehyde peaked around 11:30 at 0.7 nmol m^{-2} s^{-1}. It is a hazardous air pollutant (EPA, 1994), and plays an important role in the formation of ozone, HO_x radicals (Singh et al., 1995) and PAN (Roberts, 1990).

The maximum ~~emission~~upward flux of acetic acid was at 11:30 at ~~0.5~~1.0 nmol m^{-2} s^{-1}. Its sources are manifold: it is emitted by soil and vegetation, from animal husbandry, it can be produced photochemically and it is also a combustion marker for biomass and fossil fuels (Chebbi et al., 1996).

~~Other reported sources of carbonyls are conifers (e.g. Janson et al., 1999; Rinne et al., 2007) and decaying vegetation (e.g. de Gouw et al., 2000; Karl et al., 2001; Warneke et al., 2002).~~ The C_6 green leaf volatiles (GLV; $C_6H_{13}O^+$) are emitted by damaged plants seconds after the damage occurred (Holopainen, 2004). They are found to be important in ‘plant communication’ and are used as ‘plant indirect defenses’ (Scala et al., 2013, and references therein). The emission of GLV accounted 1.2% of the total emission. Similar to the monoterpenes, a fragment of GLV ($C_6H_{11}^+$; Table 2) was also measured. But unlike monoterpenes, the behavior of the parental ion and fragment are very different. While $C_6H_{13}O^+$ has a downward flux/upward flux ratio of 0.3 (Sect. 3.6), the fragment’s downward flux/upward flux ratio is <1%. This leads to the assumption that the fragmentation pattern for the main GLVs measured in Bosco Fontana is different.

Ethanol participated with 1.2 % to the total upward flux. Ethanol is known to be emitted from different ecosystems, as shown in Park et al. (2013) and Kaser et al. (2013).

Other reported sources of carbonyls ~~are~~include conifers (e.g. Janson et al., 1999; Rinne et al., 2007) and decaying vegetation (e.g. de Gouw et al., 2000; Karl et al., 2001; Warneke et al., 2002).

The remaining compounds each contributed less than 1% to the total ~~emission~~upward flux.

3.~~5~~6. VOC deposition

~~For~~ In case of wet or dry deposition, the ambient concentration of the deposited compound plays an important role. Figure ~~8~~ 9 shows the total VOC concentration detected by the PTR-ToF and its diurnal behavior. The highest total VOC concentrations occur during the night, when the planetary boundary layer is shallower and the volume, into which the VOCs are emitted, is smaller. However, concentrations of biogenic VOCs (e.g. isoprene, monoterpenes) were much smaller during the night, reflecting a combination of smaller emissions and influences from air from outside the forest~~;~~ (the footprint for concentration measurements is much larger than the Bosco Fontana forest). By contrast, long-lived compounds, which can also be of anthropogenic origin, increase in concentration at night~~s~~. One of them, methanol, showed the ~~highest~~ largest concentration and ~~highest~~ biggest ~~deposition~~downward flux (Table 3). The wind rose for the methanol concentration is shown in Fig. ~~6b~~7b. ~~Highest~~ The largest concentrations were measured when the wind direction was northeast and southwest. The ~~deposition~~downward flux of methanol generally lasted from 01:00 to 08:00. The methanol concentration also peaked ~~D~~during this period~~ also highest concentrations were measured.~~, indicating~~It seems~~ that ~~methanol~~ the concentrations were considerably affected by horizontal transport or secondary production. Since the largest concentrations were measured ~~when~~ at the same time when downward fluxes were observed, the source must have been located outside of the flux footprint. Howerver, as the wind speed was below 2 m s^{-1}, a major source ~~for this compound must be located outside the forest but~~ is probably close to the measurement site. Overall methanol accounted for ~~83~~63% to the total ~~deposition~~downward flux~~ observed~~. The main sinks of methanol are reactions with OH and dry and wet deposition, which restrict the atmospheric lifetime of methanol to ~~seven~~ nine days (~~Jacob~~ Heikes et al., 200~~5~~2). Heikes et al. (2002) determined the average lifetime due to the gas reactions with OH to 18 days, while the lifetime with respect to deposition was calculated to be 24 days. Applying the same procedure for Bosco Fontana results in a deposition lifetime of 280 days, which reflects the different deposition velocities (V_d) used. For their estimate Heikes et al. (2002) used V_d = 4 mm s^{-1} while in Bosco Fontana, the average deposition velocity was an order of magnitude lower, 0.55 mm s^{-1}. As the measured downward flux is the sum of deposition and emission, just an upper limit of the deposition lifetime can be given. Additionally the ambient humidity during the campaign was on average 55%, which limits wet surfaces and thereby dry deposition. The global average also includes deposition over oceans, which is twice as fast as over land (Heikes et al., 2002). ~~The methanol deposition in the early mornings could be due to wet deposition on dew.~~ The deposition of methanol has been observed in other studies (e.g. Holzinger et al., 2001, Goldan et al., 1995, Riemer et al., 1998, ~~and Goldan et al., 1995~~, Rantala et al., 2015, ~~-~~Wohlfahrt et al., 2015). Laffineur et al. (2012) observed ~~very large~~considerable methanol uptake, which they suggest to be caused by adsorption/desorption to water films. In the bottom panel of Fig. ~~9~~ 10, the ambient, aerodynamic and dew point temperature~~ temperature and the dew point temperature are~~ are –shown. The colored ~~background~~ areas in the figure mark~~s~~ the standard deviation of the calculated temperatures. ~~when th~~On the onset of ~~e~~methanol ~~deposition~~downward flux periods ~~occurred~~ (~~as can be seen in the diurnal flux plot in~~Fig. 10 upper panel ~~Fig. 4~~), the dew temperature and aerodynamic temperature are closest to each other and the relative humidity is around 65%. The formation of dew is expected to happen during this time (01:00 to 06:00). Interestingly, the downward flux increases during the night and reaches a maximum between 07:00 and 08:00 when the relative humidity already decreased <60% and the difference between aerodynamic – and dew point temperature is around 10°C. After 08:00 the emissions dominate over the deposition and for the rest of the day the methanol flux is positive.

~~. The deposition occurs when the surface temperature was closest to the dew point.~~

Acetic acid showed the second highest ~~deposition~~downward flux, which contributed with more than ~~10~~16% to the total ~~deposition~~downward flux. It ~~has~~ had also the~~the third~~ second highest concentration (Table 3). ~~and~~ Its ~~a~~ lifetime is about~~of~~ 1.7 days in the boundary layer (Paulot et al., 2011).

With the elemental composition of $C_6H_{13}O^+$ (protonated) this C_6 green leaf volatile shows a higher downward flux (compare to its fragment $C_6H_{11}^+$), which explains 6% of the negative flux.

Ethanol had its maximum downward flux at 07:00 with -0.11 nmol m^{-2} s^{-1} and it explains 3.5 % of the total downward flux.

Next is acetone, which accounted for ~~2.3~~1.7% to the total ~~deposition~~downward flux. It ~~has~~ had the ~~second~~ third highest concentration (Table 3) and the tropospheric lifetime is reported to be 15 days (Jacob et al., 2002).

An unidentified compound with the mass 73.0255 amu caused 1.6% of the total downward flux, while ~~Minor deposition fluxes were calculated for MVK/MACR (1.1%), which can be affected by fragmentation (Sect. 3.4; Rivera-Rios et al., 2014), and methyl acetate (1.1%). T~~the remaining compounds each contributed with less than 1%. ~~to the total deposition.~~

4. Conclusions

During the Bosco Fontana campaign, up to 29 (depending on method and sigma threshold) compounds were found to have a detectable flux. The VOC exchange was dominated by isoprene which comprised over 65% of the total net flux (on a molar basis). The high isoprene flux influenced via atmospheric oxidation the MVK/MACR flux. The calculated chemical production was able to explain up to 30% of the measured MVK/MACR flux. Thus, the major part of the MVK/MACR flux remained unaccounted and further research is needed to identify its sources.

Methanol caused over 60% of the total downward flux, which happened during the early morning. The removal was assumed to be dry deposition to water films on surfaces (incl. dew) as the downward fluxes coincided with the calculated ratios of dew point to aerodynamic temperature approaching unity. The deposition lifetime of methanol was estimated to be long compared to the global mean, which might be explained by the dry conditions at Bosco Fontana during the measurement period.

Overall, five compounds caused over 90% of the total downward flux (-0.58 nmol m^{-2} s^{-1}) and seven compounds add up to over 90% of the total upward flux (10.4 nmol m^{-2} s^{-1}). The measured VOCs contribute with less than 2% to the net exchange of carbon by CO_2.

Comparing the results with the emissions from an orange grove (Park et al., 2013), our study found far fewer compounds that showed significant exchange. The used sigma criteria (3-10) for the compound with detectable flux classification had only a minor effect on total VOC upward and downward fluxes. The largest difference in the net VOC exchange between Bosco Fontana and the orange orchard was the dominance of isoprene upward flux at Bosco Fontana, while the fluxes of other major compounds were comparable between the two measurement sites.

The classical method, which searches for CCF maxima manually, detected over 80% of the upward flux, 49% of the downward flux and 84% of the net flux, compared with the automated method, which uses a routine to find masses with flux. Thus, this study recommends the automated method, as the fast analysis, objective criteria and better flux detection are valuable assets for calculating and classifying fluxes of several hundreds of different ion peaks.

~~During the Bosco Fontana campaign a total of twelve compounds with detectable flux were identified, for which a flux could be quantified, by using the automated method with compound filter. These compounds were dominated by isoprene, which comprised 65% of the total emission. We estimated the influence of the atmospheric oxidation of isoprene to the MVK/MACR flux. The calculated chemical production can explain up to 27% of the MVK/MACR flux. Thus, the major part of the MVK/MACR flux remains unaccounted for by this source.~~

~~The deposition of methanol was assumed to be due to dry deposition to leaf water layers (incl. dew) as deposition coincided with the calculated ratios of dew point to surface temperature approaching unity.~~

~~Using the data measured in Bosco Fontana, we compared the classical method to determine which compounds showed significant fluxes, with an automated approach (10 σ_{noise}). The results of the methods differed by 20% for the total emission and 41% for the total deposition. This indicates that 80% of the flux was covered by the classical method. The flux compounds identified ranged from 5~~

~~(classical method) to 48 (automated method with 3 σ_{noise}). With the automated method with compound filter (10 σ_{noise}) 12 flux compounds were identified. We recommend the automated method with compound filter, which combines the fast analysis and better flux detection, without the overestimation due to double counting.~~

Acknowledgements

We would like to thank Markus Müller for providing the PTR-ToF Data Analyzer and Heikki Junninen and the tofTools team for providing the tofTools. We are further grateful ~~to our colleagues from the Catholic University Brescia, and in particular Giacomo Gerosa and Angelo Finco, for the preparation of the tower and measurement infrastructure and~~ to the Corpo Forestale dello Stato for access to the site. Thanks to all participants of the Bosco Fontana campaign, especially to Joe Acton for discussing and comparing the fluxes measured with PTR-QMS and PTR-ToF, to Ben Langford and Mhairi Coyle for helping with the installation on the tower. The data for the annual mean temperature and precipitation (UDel_AirT_Precip) was provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/.

This research received funding from the EC Seventh Framework Programme (Collaborative projects "ECLAIRE", grant no. 282910, and “PEGASOS”, grant no. 265148) and from the Academy of Finland Centre of Excellence program (project number 272041).

References:

Acton, W. J. F., Schallhart, S., Langford, B., Valach, A., Rantala, P., Fares, S., Carriero, G., Tillmann, R., Tomlinson, S. J., Dragosits, U., Gianelle, D., Hewitt, C. N., and Nemitz, E.: Canopy-scale flux measurements and bottom-up emission estimates of volatile organic compounds from a mixed oak and hornbeam forest in northern Italy, Atmos. Chem. Phys. Discuss., 15, 29213-29264, doi:10.5194/acpd-15-29213-2015, 2015~~Acton, W. J. F., Schallhart, S., Langford, B., Valach, A., Rantala, P., Fares, S., Carriero, G., Tillmann, R., Tomlinson, S. J., Dragosits, Gianelle, D., U., Hewitt, C. N., and Nemitz, E.: Canopyscale flux measurements and bottom-up emission estimates of volatile organic compounds 5 from a mixed oak and hornbeam forest in northern Italy, submitted to Atmos. Chem. Phys Discuss., 2015~~.

Ammann, C., Brunner, A., Spirig, C., and Neftel, A.: Technical note: Water vapour concentration and flux measurements with PTR-MS, Atmospheric Chemistry and Physics, 6, 12, 4643-4651, 2006.

Andronache, C., Chameides, W. L., Rodgers, M. O., Martinez, J., Zimmerman, P. and Greenberg, J.: Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States, J. Geophys. Res., 99(D8), 16989–16999, doi:10.1029/94JD01027, 1994.

Baasandorj, M., Millet, D. B., Hu, L., Mitroo, D., and Williams, B. J.: Measuring acetic and formic acid by proton-transfer-reaction mass spectrometry: sensitivity, humidity dependence, and quantifying interferences, Atmos. Meas. Tech., 8, 1303-1321, doi:10.5194/amt-8-1303-2015, 2015.

Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M.E., Wirtz, K., Martin-Reviejo, M. and Pilling, M.J.: Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data, Atmospheric Chemistry and Physics 5, 623–639, 2005.

Boy, M., Mogensen, D., Smolander, S., Zhou, L., Nieminen, T., Paasonen, P., Plass-Dülmer, C., Sipilä, M., Petäjä, T., Mauldin, L., Berresheim, H., and Kulmala, M.: Oxidation of SO2 by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations, Atmos. Chem. Phys., 13:3865–3879, 2013.

Businger, J. A., and Oncley, S. P.: Flux measurement with conditional sampling, J. Atmos. Ocean. Tech., 7, 349-352, 1990.

~~Businger, J. A., Wyngaard, J. C., Izumi, Y. and Bradley, E. F.: Flux-profile relationships in the atmospheric surface layer, Journal of the Atmospheric Sciences 28: 181–189, 1971.~~

Chebbi, A.~~,~~ and Carlier, P.: Carboxylic acids in the troposphere, occurrence, sources, and sinks: A review, Atmospheric Environment, Volume 30, Issue 24, 4233-4249, ISSN 1352-2310, http://dx.doi.org/10.1016/1352-2310(96)00102-1, 1996.

Dalponte, M., Bruzzone, L. and Gianelle, D.: Fusion of hyperspectral and LIDAR remote sensing data for classification of complex forest areas, Geoscience and Remote Sensing, 46, 5, 1416-1427, 2008.

Damian, V., Sandu, A., Damian, M., Potra, F. and Carmichael, G. R. The kinetic preprocessor KPP – a software environment for solving chemical kinetics, Comput. Chem. Eng., 26:1567–1579, 2002.

Damköhler, G.: Der Einfluss der Turbulenz auf die Flammengeschwindigkeit in Gasgemischen, Zeitschrift für Electrochemie und Angewandte Physikalische Chemie, 46, 601–626, 1940.

de Gouw, J. A. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26: 223–257. doi: 10.1002/mas.20119, 2006.

de Gouw, J. A., Howard, C. J., Custer, T. G., Baker, B. M. and Fall, R.: Proton-transfer chemical-ionization mass spectrometry allows real-time analysis of volatile organic compounds released from cutting and drying of crops, Environmental science & technology, 34, 12, 2640-2648, 2000.

Dolman, A. J.: Estimates of roughness length and zero plane displacement for a foliated and non-foliated oak canopy, Agricultural and Forest Meteorology, 36, 241-248, 1986.

Derwent, R. G., Jenkin, M. E., Saunders, S. M., Pilling, M. J., Simmonds, P. G., Passant, N. R., Dollard, G. J., Dumitrean, P. and Kent, A.: Photochemical ozone formation in north west Europe and its control, Atmos. Environ, 37, 1983–1991, 2003.

~~Dyer, A. J.: A review of flux-profile relationships, Boundary-Layer Meteorology 7: 363 – 372, 1974.~~

EPA: Chemical Summary for Acetaldehyde, EPA 749-F-94-003a, Office of Pollution Prevention and Toxics, available at: http://onlinelibrary.wiley.com/doi/10.1002/9781118747926.app1/pdf (last access: 13 October 2015), 1994.

Fall, R.: Reactive hydrocarbons in the atmosphere, Academic Press, San Diego 41-96, 1999.

Fall, R., Karl, T., Jordan, A. and Lindinger, W.: Biogenic C5 VOCs: release from leaves after freeze–thaw wounding and occurrence in air at a high mountain observatory, Atmospheric Environment, 35, 22,3905 – 3916, 2001.

Fares, S., Paoletti, E., Loreto, F., and Brilli, F.: Bidirectional Flux of Methyl Vinyl Ketone and Methacrolein in Trees with Different Isoprenoid Emission under Realistic Ambient Concentrations, Environ Sci Technol, 49, 7735-7742, doi: 10.1021/acs.est.5b00673, 2015.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C.N., Lamb, B., Liu, S., Trainer, M., Westberg, H. and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, Global Biogeochem. Cycles, 6(4), 389–430, 1992.

Foken, T. and Wichura, B.: Tools for quality assessment of surface-based flux measurements, Agricultural and Forest Meteorology 78: 83–105, 1996.

Fuentes, J. D., Wang, D., Neumann, H. H., Gillespie, T. J., Den Hartog, G. and Dann, T. F.: Ambient biogenic hydrocarbons and isoprene emissions from a mixed deciduous forest. J. Atmos. Chem., 25, 67-95, 1996.

Fuentes, J. D., Gu, L., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J. W., Ciccioli, P., Lamb, B., Geron, C., Guenther, A. B., Sharkey, T. D. and Stockwell W.: Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review, Bull. Amer. Meteor. Soc., 81, 1537–1575, 2000.

Garland, J. A.: Dry Deposition of Sulfur-Dioxide to Land and Water Surfaces, P. Roy. Soc. A-Math. Phy., 354, 245–268, 1977.

Geron, C., Guenther, A. B., Greenberg, J., Loescher, H. W., Clark, D. and Baker, B.: Biogenic volatile organic compound emissions from a lowland tropical wet forest in Costa Rica, Atmospheric Environment, Volume 36, Issue 23, 3793-3802, ISSN 1352-2310, 2002.

Goldan, P. D., Kuster, W. C., Fehsenfeld, F. C. and Montzka, S. A.: Hydrocarbon measurements in the southeastern United States: The Rural Oxidants in the Southern Environment (ROSE) Program 1990, J. Geophys. Res., 100(D12), 25945–25963, doi:10.1029/95JD02607, 1995.

Goldstein, A. and Schade, G. W.: Quantifying biogenic and anthropogenic contributions to acetone mixing ratios in a rural environment, Atmospheric Environment, Volume 34, Issues 29–30, 4997-5006, ISSN 1352-2310, 2000.

Graus, M., Müller, M., and Hansel, A.: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, J. Am. Soc. Mass Spectr., 21, 1037–1044, 2010.

Guenther, A. B., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P., A global model of natural volatile organic compound emissions. J. Geophys. Res., 100(D5), 8873–8892, doi:10.1029/94JD02950, 1995.

Guenther, A. B., Greenberg, J., Harley, P., Helmig, D., Klinger, L., Vierling, L., Zimmerman, P. and Geron, C.: Leaf, branch, stand and landscape scale measurements of volatile organic compound fluxes from U.S. woodlands, Tree Physiol 16, 1-2, 17-24 doi:10.1093/treephys/16.1-2.17, 1996.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492, doi:10.5194/gmd-5-1471-2012, 2012.

Harley, P. C., Monson, R. K., and Lerdau, M. T.: Ecological and evolutionary aspects of isoprene emission from plants, Oecologia, 118, 2, 109-123, 1999.

Heikes, B.G., Chang, W.N , Pilson, M.E.Q., Swift, E., Singh, H.B., Guenther, A., Jacob, D.J.,. Field, B.D, Fall, R., Riemer, D. and Brand, L.: Atmospheric methanol budget and ocean implication, Global Biogeochemical Cycles, 16, 1133, 2002.

Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A. C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H.: Observation and modelling of HOx radicals in a boreal forest, Atmos. Chem. Phys., 14, 8723-8747, doi:10.5194/acp-14-8723-2014, 2014.

Herbig, J., Müller, M., Schallhart, S., Titzmann, T., Graus, M., and Hansel, A.: On-line breath analysis with PTR-TOF, Journal of Breath Research, 3, 027004, doi:10.1088/1752-7155/3/2/027004, 2009.

Holopainen, J. K.: Multiple functions of inducible plant volatiles, Trends in plant science9, 11, 529-533, 2004.

Holzinger, R., Jordan, A., Hansel, A. and Lindinger W.: Methanol measurements in the lower troposphere near Innsbruck (047°16′N; 011°24′E), Austria, Atmospheric Environment, 35, 14, 2525-2532, 2001.

Horst, T. W.: A simple formula for attenuation of eddy fluxes measured with first-order-response scalar sensors, Boundary-Layer Meteorology 82: 219–233, 1997.

Jacob, D. J., Field, B. D., Jin, E. M., Bey, I., Li, Q., Logan, J. A., Yantosca, R. M., and Singh, H. B.: Atmospheric budget of acetone, J. Geophys. Res.-Atmos., 107, 4100, doi:10.1029/2001JD000694, 2002.

~~Jacob, D. J., Field, B. D., Li, Q., Blake, D. R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H. B. and Guenther A. B.: Global budget of methanol: Constraints from atmospheric observations, J. Geophys. Res., 110, D08303, doi:10.1029/2004JD005172, 2005.~~

Janson, R., and De Serves, C. and Romero, R.: Emission of isoprene and carbonyl compounds from a boreal forest and wetland in Sweden, Agricultural and Forest Meteorology, 98, 671-681, 1999.

Jardine, K. J., Monson, R. K., Abrell, L., Saleska, S. R., Arneth, A., Jardine, A., Ishida, F. Y., Serrano, A. M. Y., Artaxo, P., Karl, T., Fares, S., Goldstein, A., Loreto, F. and Huxman, T.: Within-plant isoprene oxidation confirmed by direct emissions of oxidation products methyl vinyl ketone and methacrolein, Global Change Biology, 18: 973–984. doi: 10.1111/j.1365-2486.2011.02610.x, 2012.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, Atmos. Environ., 31:81–104, 1997.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Märk, L., Seehauser, H., Schottkowsky, R., Sulzer, P., and Märk, T. D.: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), Int. J. Mass Spectrom., 286, 122–128, 2009.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M. and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmospheric Measurement Techniques, 3, 4, 1039-1053, 2010.

Kaimal, J. C. and Finnigan, J. J.: Atmospheric Boundary Layer Flows: Their Structure and Measurement, Oxford University press, New York, USA, 1994.

Karl, T., Guenther, A. B., Jordan, A., Fall, R. and Lindinger, W.: Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting, Atmospheric Environment, 35, 491–495, doi:10.1016/S1352-2310(00)00405-2, Volume 35, Issue 3, 2001.

Karl, T. G., Spirig, C., Rinne, J., Stroud, C., Prevost, P., Greenberg, J., Fall, R., and Guenther, A.: Virtual disjunct eddy covariance measurements of organic compound fluxes from a subalpine forest using proton transfer reaction mass spectrometry, Atmos. Chem. Phys., 2, 279-291, doi:10.5194/acp-2-279-2002, 2002.

Karl, T., Guenther, A., Turnipseed, A., Tyndall, G., Artaxo, P., and Martin, S.: Rapid formation of isoprene photo-oxidation products observed in Amazonia, Atmos. Chem. Phys., 9, 7753-7767, 2009.

Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A., and Jardine, K.: Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation, Science, 330, 816 - 819, doi: 10.1126/science.1192534, 2010.

~~Karl, T., Guenther, A. B., Jordan, A., Fall, R. and Lindinger, W.: Eddy covariance measurement of biogenic oxygenated VOC emissions from hay harvesting, Atmospheric Environment, 35, 491–495, doi:10.1016/S1352-2310(00)00405-2, Volume 35, Issue 3, 2001.~~

Kaser, L., Karl, T., Guenther, A. B., Graus, M., Schnitzhofer, R., Turnipseed, A., Fischer, L., Harley, P., Madronich, M., Gochis, D., Keutsch, F. N., and Hansel, A.: Undisturbed and disturbed above canopy ponderosa pine emissions: PTR-TOF-MS measurements and MEGAN 2.1 model results, Atmos. Chem. Phys., 13, 11935-11947, doi:10.5194/acp-13-11935-2013, 2013.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): an overview on emission, physiology and ecology, Journal of Atmospheric Chemistry, 33, 1, 23-88, 1999.

König, G., Brunda, M., Puxbaum, H., Hewitt, C. N., Duckham, S. C. and Rudolph, J.: Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species. Atmospheric Environment, 29, 8, 861-874, 1995.

Kulmala M., Toivonen A., Mäkelä J. and Laaksonen A.: Analysis of the growth of nucleation mode particles observed in boreal forest, Tellus 50B: 449–462, 1998.

Laffineur, Q., Aubinet, M., Schoon, N., Amelynck, C., Müller, J.-F., Dewulf, J., Van Langenhove, H., Steppe, K., and Heinesch, B.: Abiotic and biotic control of methanol exchanges in a temperate mixed forest, Atmos. Chem. Phys., 12, 577-590, doi:10.5194/acp-12-577-2012, 2012.

Lamb, B., Westberg, H. and Allwine, G.: Biogenic hydrocarbon emissions from decidous and coniferous trees in the United States, J. geophys. Res., 90 (D1), 2380–2390, 1985.

Langford, B., Acton, W., Ammann, C., Valach, A., Nemitz E.: Eddy-covariance data with low signal-to-noise ratio: time-lag determination, uncertainties and limit of detection. Atmos. Meas. Tech. Discuss., 8, 2913-2955, 2015

Lawrence M. G: The Relationship between Relative Humidity and the Dewpoint Temperature in Moist Air: A Simple Conversion and Applications, Bull. Amer. Meteor. Soc., 86, 225–233, doi: http://dx.doi.org/10.1175/BAMS-86-2-225, 2005.

Lee, X., Massman, W., and Law, B.: Handbook of Micrometeorology: A Guide for Surface Flux Measurements and Analysis, Kluwer Academic Publisher, Dordrecht, 2004.

Liu, Y. J., Herdlinger-Blatt, I., McKinney, K. A. and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, Atmospheric Chemistry and Physics,13, 11,5715--5730, 2013.

Madronich, S.: UV radiation in the natural and perturbed atmosphere, in Environmental Effects of UV (Ultraviolet) Radiation, 17-69, CRC Press, Boca Raton, 1993.

Madronich, S. and Flocke, S.: The role of solar radiation in atmospheric chemistry, The Handbook of Environmental Chemistry, Vol. 2. Springer, Berlin, 1-26, 1999.

Mammarella, I., Launiainen, S., Gronholm, T., Keronen, P., Pumpanen, J., Rannik, Ü., and Vesala, T.: Relative humidity effect on the high-frequency attenuation of water vapor flux measured by a closed-path eddy covariance system, Journal of Atmospheric and Oceanic Technology, 26, 9, 1856-1866, 2009.

Misztal, P. K., Nemitz, E., Langford, B., Di Marco, C. F., Phillips, G. J., Hewitt, C. N., MacKenzie, A. R., Owen, S. M., Fowler, D., Heal, M. R., and Cape, J. N.: Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia, Atmos. Chem. Phys., 11, 8995-9017, doi:10.5194/acp-11-8995-2011, 2011.

Mogensen, D., Gierens, R., Crowley, J. N., Keronen, P., Smolander, S., Sogachev, A., Nölscher, A. C., Zhou, L., Kulmala, M., Tang, M. J., Williams, J., and Boy, M.: Simulations of atmospheric OH, O3 and NO3 reactivities within and above the boreal forest, Atmos. Chem. Phys., 15, 3909-3932, doi:10.5194/acp-15-3909-2015, 2015.

Monks, P. S., Granier, C., Fuzzi, S., Stohl, A.,Williams, M. L., Akimoto, H., Amann, M., Baklanov, A., Baltensperger, U., Bey, I., Blake, N., Blake, R. S., Carslaw, K., Cooper, O. R., Dentener, F., Fowler, D., Fragkou, E., Frost, G. J., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hansson, H. C., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I. S. A., Jenkin, M. E., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M. G., Lee, J. D., Liousse, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Moussiopoulos, N., Orlando, J. J., O'Dowd, C. D., Palmer, P. I., Parrish, D. D., Petzold, A., Platt, U., Pöschl, U., Prévôt, A. S. H., Reeves, C. E., Reimann, S., Rudich, Y., Sellegri, K., Steinbrecher, R., Simpson, D., ten Brink, H., Theloke, J., van derWerf, G. R., Vautard, R., Vestreng, V., Vlachokostas, C., and von Glasow, R.: Atmospheric composition change – global and regional air quality, Atmos. Environ., 43, 5268–5350, doi:10.1016/j.atmosenv.2009.08.021, 2009.

Moore, C. J.: Frequency response corrections for eddy correlation systems, Boundary-Layer Meteorology, 37, 17–35, 1986.

Müller, M., Graus, M., Ruuskanen, T. M., Schnitzhofer, R., Bamberger, I., Kaser, L., Titzmann, T., Hörtnagl, L., Wohlfahrt, G., Karl, T., and Hansel, A.: First eddy covariance flux measurements by PTR-TOF, Atmos. Meas. Tech., 3, 387-395, doi:10.5194/amt-3-387-2010, 2010.

Müller, M., Mikoviny, T., Jud, W., D'Anna, B. and Wisthaler, A.: A new software tool for the analysis of high resolution PTR-TOF mass spectra, Chemometrics and Intelligent Laboratory Systems, 127, 158-165, 2013.

Naik, V., Fiore, A. M., Horowitz, L. W., Singh, H. B., Wiedinmyer, C., Guenther, A., de Gouw, J. A., Millet, D. B., Goldan, P. D., Kuster, W. C., and Goldstein, A.: Observational constraints on the global atmospheric budget of ethanol, Atmos. Chem. Phys., 10, 5361-5370, doi:10.5194/acp-10-5361-2010, 2010.

Nemitz, E., Hargreaves, K. J., Neftel, A., Loubet, B., Cellier, P., Dorsey, J. R., Flynn, M., Hensen, A., Weidinger, T., Meszaros, R., Horvath, L., Dämmgen, U., Frühauf, C., Löpmeier, F. J., Gallagher, M. W., and Sutton, M. A.: Intercomparison and assessment of turbulent and physiological exchange parameters of grassland, Biogeosciences, 6, 1445-1466, doi:10.5194/bg-6-1445-2009, 2009.

Nguyen, T. B., Crounse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, P. Nat. Acad. Sci. USA, 112, E392-E401, doi: 10.1073/pnas.1418702112, 2015.

Nordbo, A., Kekäläinen, P., Siivola, E., Lehto, R., Vesala, T., and Timonen, J.: Tube transport of water vapor with condensation and desorption, Applied Physics Letters, 102, 2013.

Nordbo, A., Kekäläinen, P., Siivola, E., Mammarella, I., Timonen, J., and Vesala, T.: Sorption-Caused Attenuation and Delay of Water Vapor Signals in Eddy-Covariance Sampling Tubes and Filters, Journal of Atmospheric and Oceanic Technology, 31, 2629–2649, 2014.

Owen, P. R. and Thompson, W. R.: Heat transfer across rough surfaces, J. Fluid Mech., 15, 321–334, 1963.

Paasonen, P., Asmi, A., Petäjä, T., Kajos, M. K., Äijälä, M., Junninen, H., Holst, T., Abbatt, J. P. D., Arneth, A., Birmili, W., van der Gon, H. D., Hamed, A., Hoffer, A., Laakso, L., Laaksonen, A., Leaitch, W. R., Plass-Dülmer, C., Pryor, S. C., Räisänen, P., Swietlicki, E., Wiedensohler, A., Worsnop, D. R., Kerminen, V.-M. and Kulmala, M.: Warming induced increase in aerosol number concentration likely to moderate climate change, Nature Geosci. 6: 438–442, 2013.

Park, J.-H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J. and Holzinger R.: Active Atmosphere-Ecosystem Exchange of the Vast Majority of Detected Volatile Organic Compounds, Science, 9, 341 (6146), 643-647.doi:10.1126/science.1235053, 2013.

Paulot, F., Wunch, D., Crounse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J. W., Warneke, C., de Gouw, J. A., Dunlea, E. J., De Maziére, M., Griffith, D. W. T., Bernath, P., Jimenez, J. L. and Wennberg, P. O.: Importance of secondary sources in the atmospheric budgets of formic and acetic acids, Atmospheric Chemistry and Physics, 11, 2011.

Peräkylä, O., Vogt, M., Tikkanen, O.-P., Laurila, T., Kajos, M. K., Rantala, P. A., Patokoski, J., Aalto, J., Yli-Juuti, T., Ehn, M., Sipilä, M., Paasonen, P., Rissanen, M., Nieminen, T., Taipale, R., Keronen, P., Lappalainen, H. K., Ruuskanen, T. M., Rinne, J., Kerminen, V.-M., Kulmala, M., Bäck, J. and Petäjä, T.: Monoterpenes' oxidation capacity and rate over a boreal forest: temporal variation and connection to growth of newly formed particles, Boreal Env. Res. 19 supp. B, 293-310, 2014.

Petäjä, T., Mauldin, R. L. III, Kosciuch, E., McGrath J., Nieminen, T., Paasonen, P., Boy, M., Adamov, A., Kotiaho, T. and Kulmala, M.: Sulfuric acid and OH concentrations in a boreal forest site, Atmos. Chem. Phys. 9: 7435–7448, 2009.

Potosnak, M. J., LeStourgeon, L., Pallardy, S. G., Hosman, K. P., Gu, L., Karl, T., Geron, C. and Guenther, A. B.: Observed and modeled ecosystem isoprene fluxes from an oak-dominated temperate forest and the influence of drought stress, Atmospheric Environment, 84, 314-322, 2014.

Rannik, Ü.: On the surface layer similarity at a complex forest site, J. Geophys. Res., 103(D8), 8685–8697, doi:10.1029/98JD00086, 1998.

~~Rannik et al. 1998~~

Rantala, P., Taipale, R., Aalto, J., Kajos, M. K., Patokoski, J., Ruuskanen, T. M. and Rinne, J.: Continuous flux measurements of VOCs using PTR-MS — reliability and feasibility of disjunct-eddy-covariance, surface-layer-gradient, and surface-layer-profile methods, Boreal Env. Res. 19 (suppl. B): 87–107, 2014.

Rantala, P., Aalto, J., Taipale, R., Ruuskanen, T. M., and Rinne, J.: Annual cycle of volatile organic compound exchange between a boreal pine forest and the atmosphere, Biogeosciences, 12, 5753–5770, 2015.

Rasmussen, R. A.: Isoprene: identified as a forest-type emission to the atmosphere, Environ. Sci. Technol., 4 (8), pp 667–671, 1970.

Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kliendienst, T., Lonneman, W., Bertman, S., Shepson, P. and Starn, T.: Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States, Journal of Geophysical Research: Atmospheres, 103, D21, 28111-28128, 1998.

Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T.,Worsnop, D. R., Kulmala, M. and Donahue, N. M.: The contribution of organics to atmospheric nanoparticle growth, Nature Geosci. 5: 453–458, 2012.

Rinne, J. and Ammann, C.: Disjunct eddy covariance method, in: Eddy Covariance Handbook, edited by: Aubinet, M., Vesala, T., and Papale, D., Springer, New York, USA, ISBN 978-94-007-2350-4, e-ISBN 978-94-007-2351-1, doi:10.1007/978-94-007-2351-1, 291–307, 2012.

Rinne, J., Guenther, A. B., Warneke, C., de Gouw, J. A., Luxembourg, S. L.: Disjunct eddy covariance technique for trace gas flux measurements, Geophys. Res. Lett., 28, 3139–3142, 2001.

Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T. M., Hellén, H., Kajos, M. K., Vesala, T., and Kulmala, M.: Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling, Atmos. Chem. Phys., 7, 3361-3372, doi:10.5194/acp-7-3361-2007, 2007.

Rinne, J., Markkanen, T., Ruuskanen, T. M., Petäjä, T., Keronen, P., Tang, M. J., Crowley, J. N., Rannik, Ü., and Vesala, T.: Effect of chemical degradation on fluxes of reactive compounds – a study with a stochastic Lagrangian transport model, Atmos. Chem. Phys., 12, 4843-4854, doi:10.5194/acp-12-4843-2012, 2012.

Rivera-Rios, J. C., Nguyen, T. B., Crounse, J. D., Jud, W. St. Clair, J. M., Mikoviny, T., Gilman, J. B., Lerner, B. M., Kaiser, J. B., de Gouw, J., Wisthaler, A., Hansel, A., Wennberg P. O., Seinfeld, J. H. and Keutsch, F. N.: Conversion of hydroperoxides to carbonyls in field and laboratory instrumentation: Observational bias in diagnosing pristine versus anthropogenically controlled atmospheric chemistry, Geophys. Res. Lett., 41, 8645–8651, doi:10.1002/2014GL061919, 2014.

Roberts, J. M.: The atmospheric chemistry of organic nitrates, Atmos. Environ., 24A, 243–287, 1990.

Rosenstiel, T. N., Fisher, A. J., Fall, R. and Monson, R. K.: Differential accumulation of dimethylallyl diphosphate in leaves and needles of isoprene-and methylbutenol-emitting and nonemitting species, Plant Physiology, 129, 3, 1276-1284, 2002.

Ruuskanen, T. M., Müller, M., Schnitzhofer, R., Karl, T., Graus, M., Bamberger, I., Hörtnagl, L., Brilli, F., Wohlfahrt, G., and Hansel, A.: Eddy covariance VOC emission and deposition fluxes above grassland using PTR-TOF, Atmos. Chem. Phys., 11, 611-625, doi:10.5194/acp-11-611-2011, 2011.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds, Atmos. Chem. Phys., 3:161–180, 2003.

Scala, A., Allmann, S., Mirabella, R., Haring, M. A., and Schuurink, R. C.: Green leaf volatiles: a plant's multifunctional weapon against herbivores and pathogens, International journal of molecular sciences, 14, 9, 17781-17811, 2013.

Singh, H. B., O'Hara, D., Herlth, D., Sachse, W., Blake, D. R., Bradshaw, J. D., Kanakidou, M. and Crutzen P. J.: Acetone in the atmosphere: Distribution, sources, and sinks, J. Geophys. Res., 99(D1), 1805–1819, doi:10.1029/93JD00764, 1994.

Singh, H. B., Kanakidou, M., Crutzen, P. J. and Jacob, D. J.: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, Nature, 378, 50–54, 1995.

Taipale, R., Ruuskanen, T. M. and Rinne J.: Lag time determination in DEC measurements with PTR-MS. Atmospheric Measurement Techniques 3: 405–429 , 2010.

Tunved, P., Hansson, H.-C., Kerminen, V.-M., Ström, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P. P., Komppula, M. and Kulmala, M.: High natural aerosol loading over boreal forests, Science, 312, 5771, 261-263, 2006.

Vickers D. and Mahrt, L.: Quality Control and Flux Sampling Problems for Tower and Aircraft Data, J. Atmos. Oceanic Technol., 14, 512–526, 1997.

Warneke, C., Luxembourg, S. L., de Gouw, J. A., Rinne, J., Guenther, A. B. and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, J. Geophys. Res., 107(D8), D8, ACH-6, doi:10.1029/2001JD000594, 2002.

Webb, E. K., Pearman, G. I., and Leuning, R.: Correction of flux measurements for density effects due to heat and water vapour transfer, Q. J. Roy. Meteor. Soc., 106, 85–100, 1980.

Willmott, C. J. and Matsuura, K.: Terrestrial Air Temperature: 1900-2010 Gridded Monthly Time Series (Version 3.01), http://climate.geog.udel.edu/~climate/html_pages/Global2011/README.GlobalTsT2011.html, access date: 21.08.2015, 2012a.

Willmott, C. J. and Matsuura, K.: Terrestrial Precipitation: 1900-2010 Gridded Monthly Time Series (Version 3.01), http://climate.geog.udel.edu/~climate/html_pages/Global2011/README.GlobalTsP2011.html, access date: 21.08.2015, 2012b.

Wilson K.B. and Baldocchi D.D.: Comparing independent estimates of carbon dioxide exchange over 5 years at a deciduous forest in the southeastern United States, journal of geophysical research, 106, 167–34, 2001.

Wohlfahrt, G., Amelynck, C., Ammann, C., Arneth, A., Bamberger, I., Goldstein, A. H., Gu, L., Guenther, A., Hansel, A., Heinesch, B., Holst, T., Hörtnagl, L., Karl, T., Laffineur, Q., Neftel, A., McKinney, K., Munger, J. W., Pallardy, S. G., Schade, G. W., Seco, R., and Schoon, N.: An ecosystem-scale perspective of the net land methanol flux: synthesis of micrometeorological flux measurements, Atmos. Chem. Phys. Discuss., 15, 2577-2613, doi:10.5194/acpd-15-2577-2015, 2015.

Table 1: Comparison between the classical and the automated method for calculating VOC fluxes.

Step	Classical	Automated
'compound with exchange' detection:~~*Standard flux corrections*~~	~~*yes*~~	~~*yes*~~
CCF data used~~Calculate cross covariance function (CCF)~~	30 min~~yes~~	203·30 min~~yes~~
CCF preparation	none	average; absolute
amount of CCFs checked per compound~~Manual evaluation of CCFs (several 100)~~	>20~~yes~~	1~~no~~
detection of significant flux~~Average absolute CCFs~~	manual~~no~~	automated~~yes~~
threshold dependent results~~Data used for CCF plot and flux detection~~	no~~30 min~~	yes~~203*30 min~~
Maximum of found masses in literature [1]	10-20	ca. 500
flux data calculation:~~Threshold dependent results (σ_{noise})~~	~~no~~	~~yes~~
Lag time calculation	variable	constant; 2.6 s
CCF used for lag time	30 min smoothed	203·30 min
Wind vector rotation~~Filter results (fragments, isotopes, clusters)~~	2-d~~yes~~	~~no~~
QC: vertical rotation~~Work intensive~~	5°~~yes~~	~~no~~
QC: Stationary criteria~~Maximum of found flux-masses in literature~~	70%~~10-20~~	~~ca. 500~~
fluxes calculated from	30 min CCFs	

[1] The amount of compounds with exchange is dependent on many side specific factors (e.g. ecosystem, meteorological characteristics
)

Table 2: ~~Deposition~~Downward flux~~s~~ (~~D~~df) and ~~emissions~~upward flux (~~E~~uf) calculated with different methods. The individual compounds listed under automated are for a 10 σ_{noise} threshold, the remaining compounds (between 3 and 10 σ_{noise}) are summed up onder 'other'~~(*) shows the total E or D in nmol m^{-2} s^{-1}; (^{1}) F: fragment; WC: watercluster; CT: charge transfer; ($^{€}$) marks the calibrated compounds; (^{2}) C_6 green leaf volatiles (GLV) are calculated via the fragment $C_6H_{11}^+$; the fragmentation pattern and the sensitivity of hexanal were used.~~

possible compound	mass (prot.) Th	elemental composition	classical method		automated method	
			% of total downward flux (df) or upward flux (uf)~~% of total emission (E) or deposition (D)~~			
			~~D~~df (-0.28)*	uf~~E~~ (8.5)*	df~~D~~ (-0.~~47~~58)*	uf~~E~~ (~~10.5~~10.4)*
isoprene[c]~~isoprene[€]~~	69.0699~~69.0699~~	$C_5H_9^+$~~$C_5H_9^+$~~	0.2~~0.2~~	75.0~~75.0~~	0.0~~0.0~~	62.4~~61.2~~
methanol[c]~~methanol[€]~~	33.0335~~33.0335~~	$C_1H_5O_1^+$~~$C_1H_5O_1^+$~~	97.3~~97.2~~	18.4~~18.4~~	63.2~~77.1~~	14.8~~14.5~~
acetone[c]~~acetone[€]~~	59.0491~~59.0491~~	$C_3H_7O_1^+$~~$C_3H_7O_1^+$~~			1.7~~2.1~~	3.3~~3.3~~
MVK/MACR[c]~~MVK/MACR[€]~~	71.0491~~71.0491~~	$C_4H_7O_1^+$~~$C_4H_7O_1^+$~~	1.1~~1.1~~	3.9~~3.9~~	0.8~~1.0~~	3.0~~3.0~~
acetaldehyde[c]~~monoterpenes[€]~~	45.0335~~137.1325~~	$C_2H_5O_1^+$~~$C_{10}H_{17}^+$~~	~~0.2~~	~~2.6~~	0.2~~0.1~~	2.2~~2.1~~
monoterpenes[c]~~acetaldehyde[€]~~	137.133~~45.0335~~	$C_{10}H_{17}^+$~~$C_2H_5O_1^+$~~	0.2	2.6	0.1~~0.1~~	2.1~~2.2~~
acetic acid[1]~~acetic acid~~	61.0284~~61.0284~~	$C_2H_5O_2^+$~~$C_2H_5O_2^+$~~			16.7~~10.5~~	3.0~~1.5~~
acrolein[c]~~acrolein[€]~~	57.0335~~57.0335~~	$C_3H_5O_1^+$~~$C_3H_5O_1^+$~~			0.3~~0.4~~	0.8~~0.8~~
hydroxyacetone~~methyl acetate~~	75.0441~~75.0441~~	$C_3H_7O_2^+$~~$C_3H_7O_2^+$~~			0.8~~1.0~~	0.7~~0.7~~
hexanal F[2]~~butanone[€]~~	83.0855~~73.0648~~	$C_6H_{11}^+$~~$C_4H_9O_1^+$~~			0.0~~0.3~~	0.3~~0.7~~
C_8 GLV[2]	83.0855	$C_6H_{11}^+$			0.0	0.3
pentanal~~C_6 GLV F[2]~~	85.0648~~83.0855~~	$C_5H_9O_1^+$~~$C_6H_{11}^+$~~			0.1~~0.0~~	0.2~~0.3~~
unknown~~pentanal~~	101.0597~~85.0648~~	$C_5H_9O_2^+$~~$C_5H_9O_1^+$~~	1.2	0.1	0~~0.2~~	0~~0.2~~
other (18)					16.2	7.0
~~unknown~~	~~101.0597~~	~~$C_5H_9O_2^+$~~	~~1.2~~	~~0.1~~		

* shows the total uF or dF in nmol m^{-2} s^{-1};

[1] acetic acid was corrected for fragmentation (see Sect. 2.3.2)

[2] C_6 green leaf volatiles (GLV) are calculated via the fragment $C_6H_{11}^+$; the fragmentation pattern and the sensitivity of hexanal were used.

Table 3: ~~Deposited compounds~~Compounds with downward flux, their daily averaged: concentration, ~~the maximum diurnal deposition~~downward flux, ~~–~~deposition velocity ~~and~~ and their respective ~~lifetimes~~lifetimes. [a] ~~atmospheric lifetime according do Jacob et al. (2005);~~ [b] ~~lifetime in the boundary layer according to Paulot et al. (2011);~~ ~~[c] tropospheric lifetime according to Jacob et al. (2002).~~

compound	concentration [ppb]	~~deposition~~downward flux [nmol m^{-2} s^{-1}]	lifetime [days]	Deposition velocity [mm s^{-1}]
methanol	14.3	~~–2.7~~0.36	~~7[a]~~9[a]	0.56
acetic acid	~~2~~4.~~5~~9	~~–~~0.~~4~~10	1.7[b]	0.50
~~acetone~~	~~4.7~~	~~–0.1~~	~~15[c]~~	
C_6 GLV ($C_6H_{13}O_1^+$)	0.8	0.04	-	0.15
ethanol	0.6	0.02	2.8[c]	0.55
acetone	4.7	0.01	15[d]	0.05
73.0255	0.2	0.01	-	1.4

[a] atmospheric lifetime according to Heikes et al. (2002)

[b] lifetime in the boundary layer according to Paulot et al. (2011)

[c] atmospheric lifetime according to Naik et al. (2010)

[d] tropospheric lifetime according to Jacob et al. (2002)

Figure 1: Satellite picture (Imagery©2015 Cnes/Spot Image, DigitalGlobe, European Space Imaging, Landsat, Map data ©2015 Google) of the Bosco Fontana national park and the surroundings. The position of the flux tower is marked by a white cross and surrounded by the mean 80% of the flux footprint, which is represented by the white line (Acton et al., 2015)~~.~~ The dark green surrounding is the forest area of the national park.

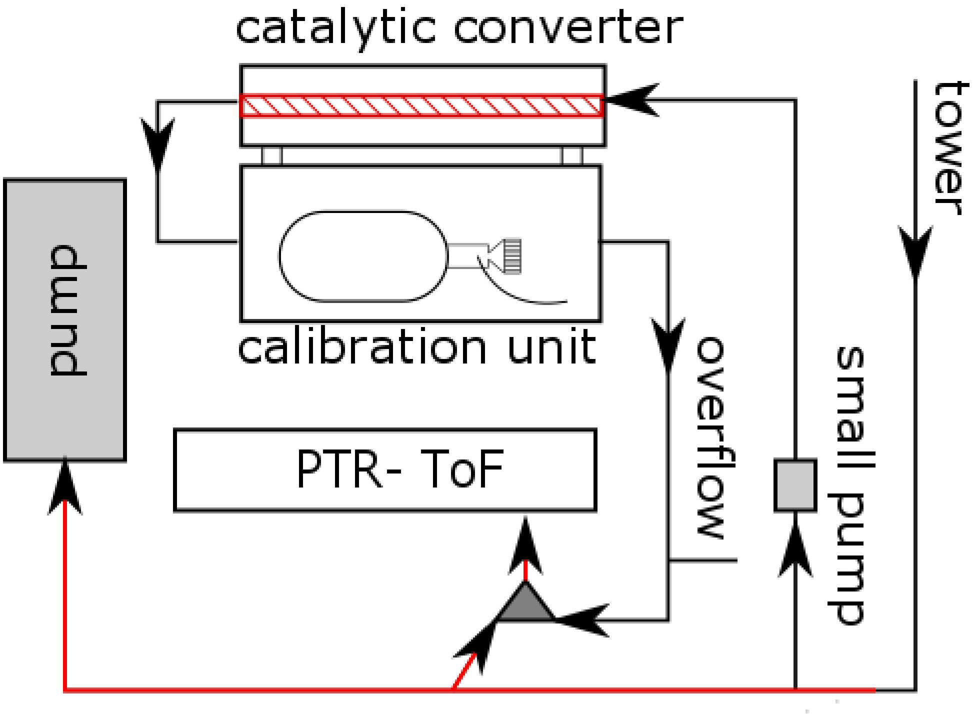

Figure 2: Schematic sketch of the inlet of the PTR-TOF used for the VOC measurements. Red lines indicade heated tubing.

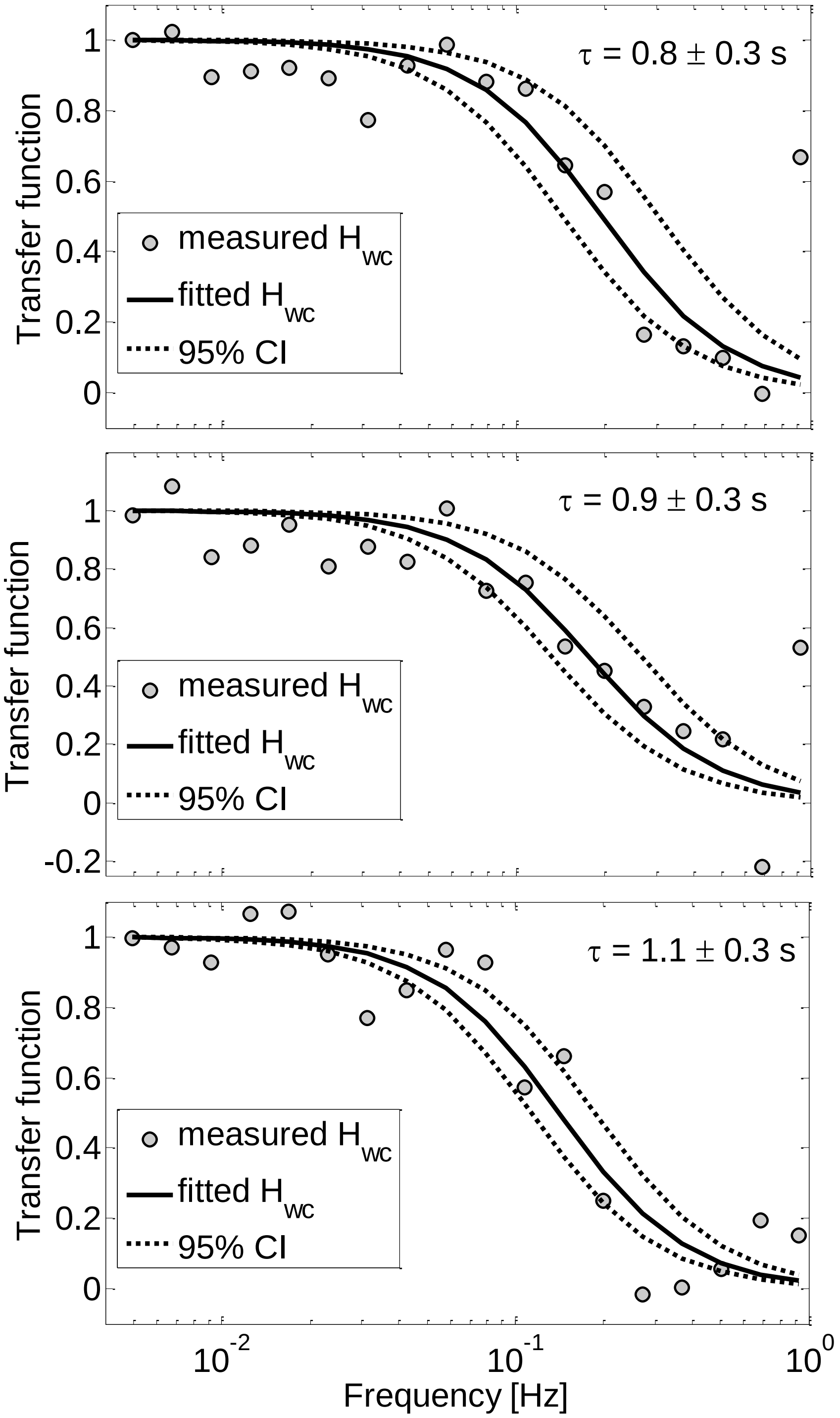

Figure 3: Transfer functions of $H_3O^+H_2O$ (37.0284 amu; top), $H_3O^+(H_2O)_2$ (55.039 amu; middle) and $C_5H_8H^+$ (69.0699 amu; bottom). The circles are the measurements, the solid black line the fitted transfer function and the dashed lines are the 95% confidence intervals. The response time of the measurement system, τ, was calculated by fitting Eq. 10 to the data.

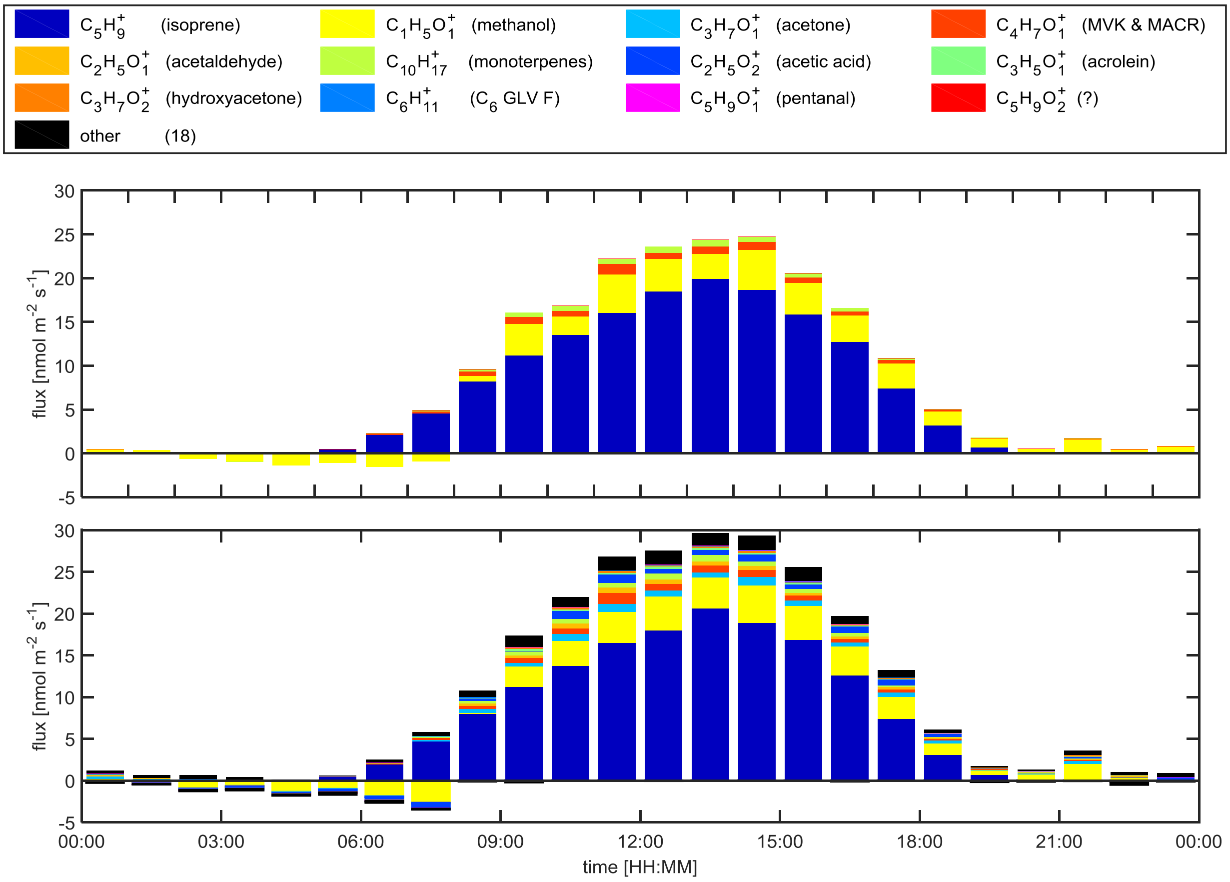

Figure 4: Diurnal flux plot of the classical method (top panel~~),~~) and the~~the~~ automated method (bottom panel). For the automated method, the 10 $\boldsymbol{\sigma}_{\mathbf{noise}}$ compounds are plotted individually, while the remaining 18 compounds, which passed the 3 $\boldsymbol{\sigma}_{\mathbf{noise}}$ threshold (see Table A1), are summed up and plotted as 'other'. ~~(mid) and the automated method with compound filter (bottom panel). The time is in CET wintertime. In each panel the 10 most abundend flux compounds are shown, the remaining compounds are summed up and plotted as 'other'. For the automated method (AM) there were 9 compounds summed up, for the automated method with compound filter (AM &CF) there were 2.~~ All individual flux compounds are listed in Table 2.

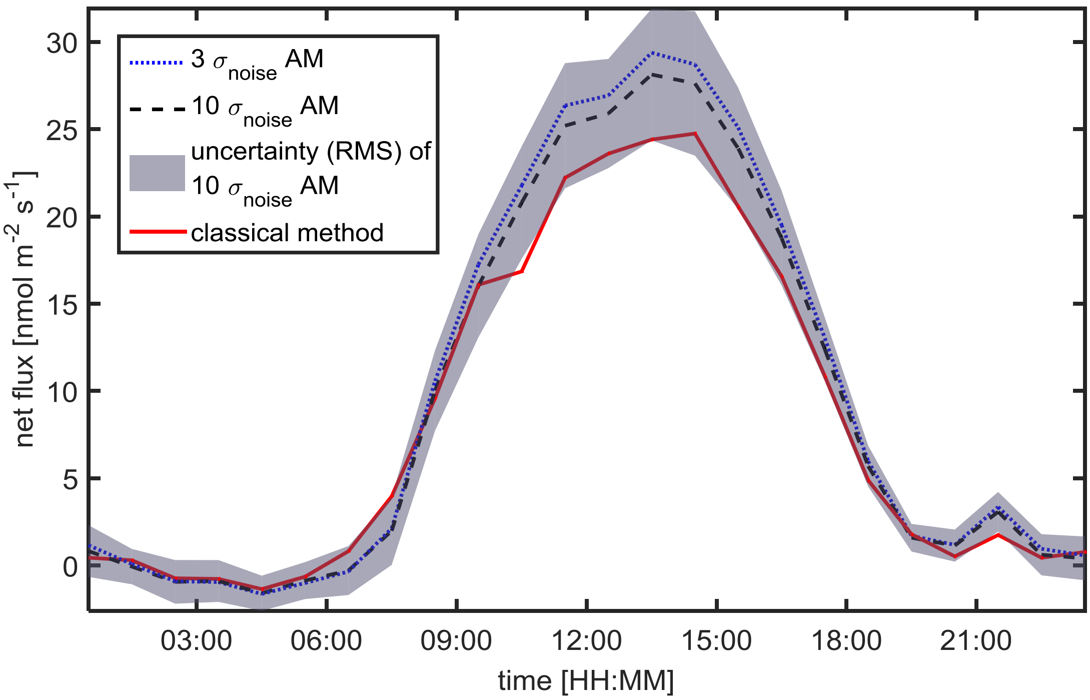

Figure 5: Diurnal ~~average~~net flux of the automated method (AM) with 3 and 10 σ_{noise} threshold for the flux calculation and the classical method.~~, the automated method with compound filter (AMCF) using a 10 σ_{noise} threshold,~~ The uncertainty (root mean square) was calculated for the automated method with 10 σ_{noise}.~~its uncertainty (root mean square) and the classical method.~~ The time is in CET wintertime.

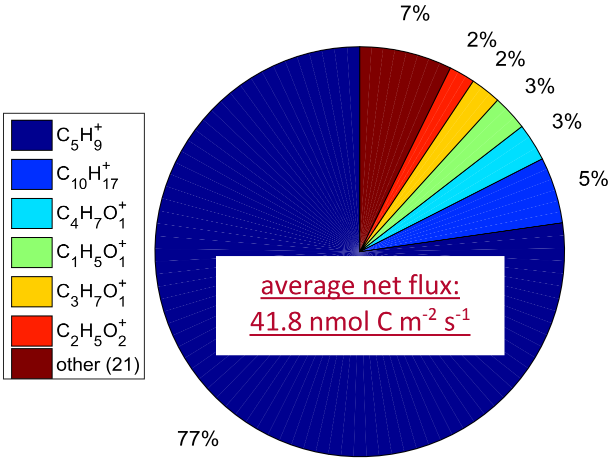

Figure 6: Average net flux of the major carbon emitters. Two masses were disregarded, as no matching elemental composition was found.

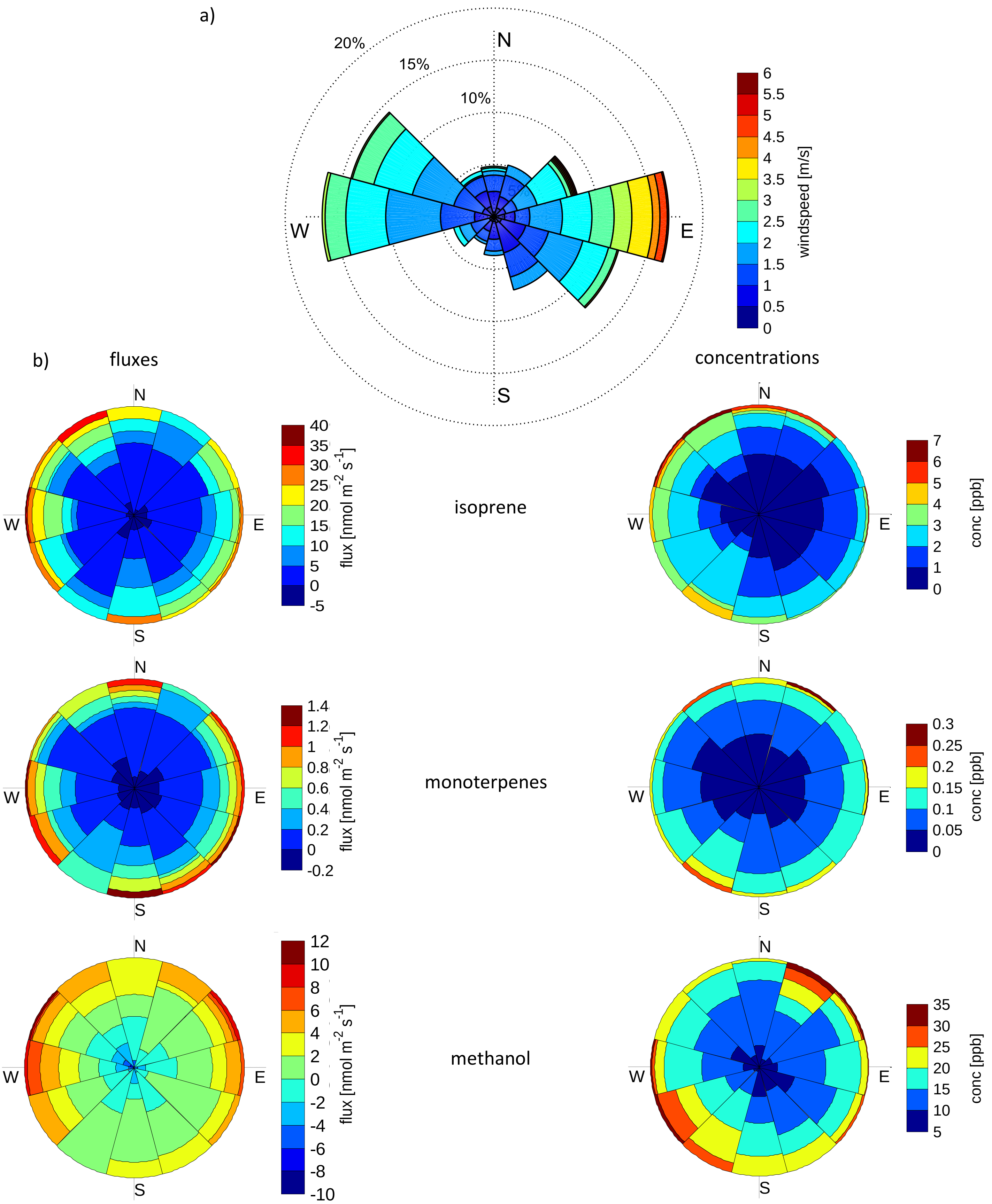

Figure ~~6~~7: a) wind rose of the wind speed. The percentages describe the how often the wind came from the selected wind direction. -b) Unscaled wind roses for fluxes (left) and concentrations (right) of isoprene (top), monoterpenes (mid), methanol (bottom).

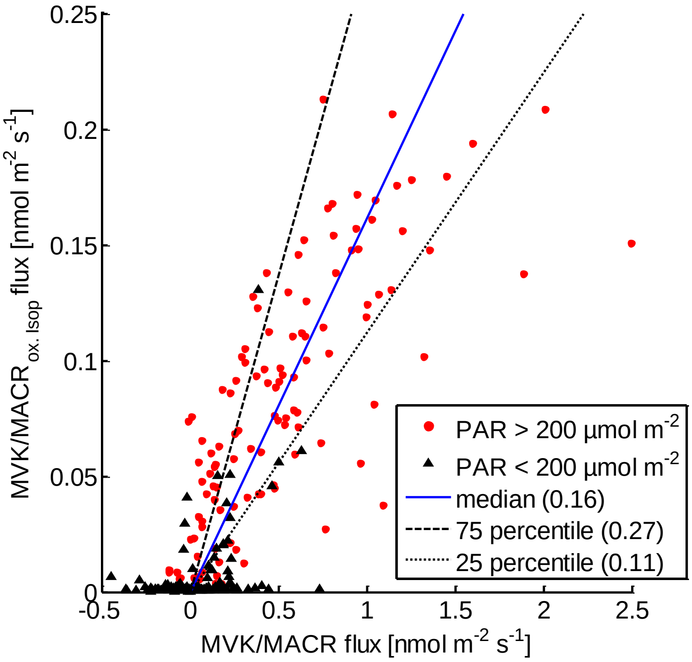

Figure ~~7~~8: Scatter plot~~s~~ of the ~~isoprene concentration and the MVK/MACR flux (a) and the~~ calculated MVK/MACR flux from oxidation of isoprene and the observed MVK/MACR flux~~ (b)~~. The correlation factor for the data is 0.81. The 1 h data are separated to day and night values by a 200 µmol m^{-2} photosynthetically active radiation (PAR) threshold. The $\frac{y}{x}$ ratios of the daytime data have been calculated~~ for the two figures, respectively.~~ to determine ~~From those ratios~~ the median, 25th and 75th percentiles. ~~have been calculated. The correlation factors for the day and night data are 0.65 in plot a) and 0.81 in plot b).~~ The MVK/MACR flux from oxidation of isoprene was calculated using Eq. 14.

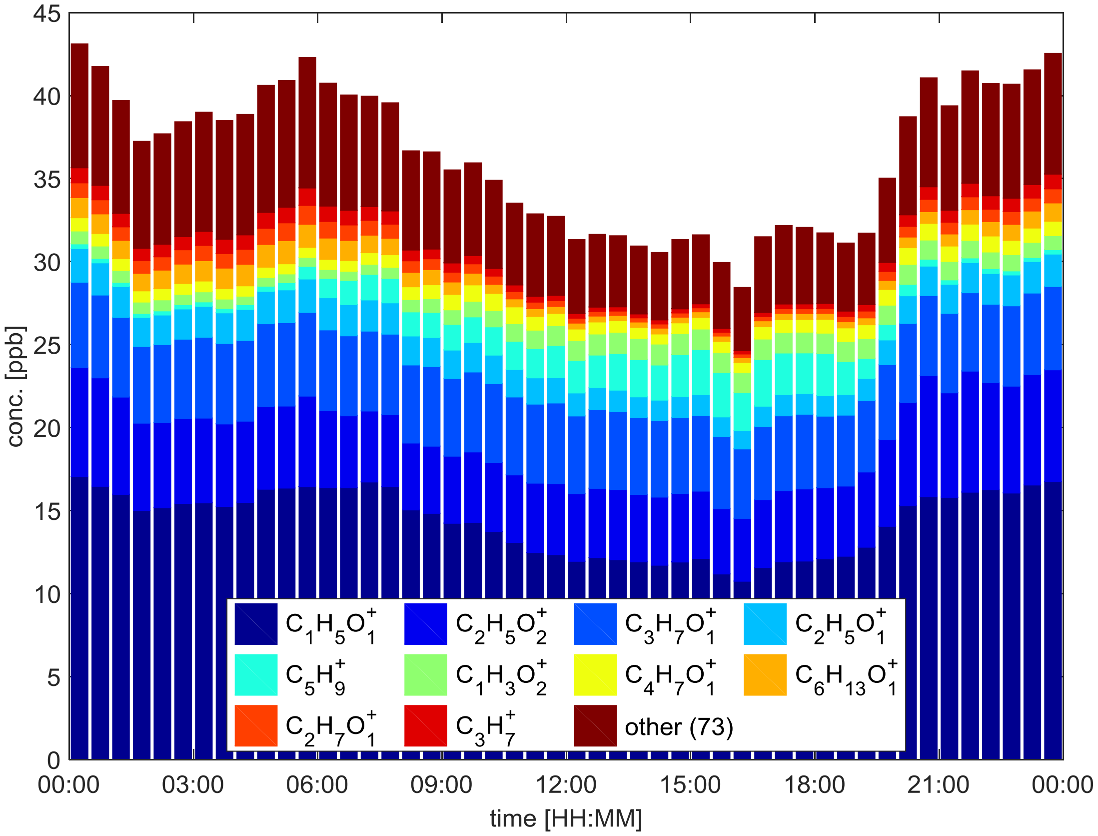

Figure ~~8~~9: Diurnal average of the total VOC concentration resolved with the PTR-ToF (filtered for fragments). The 10 most abundend flux compounds are shown, the remaining compounds are summed up and plotted as ‘other’.The time is in CET wintertime.

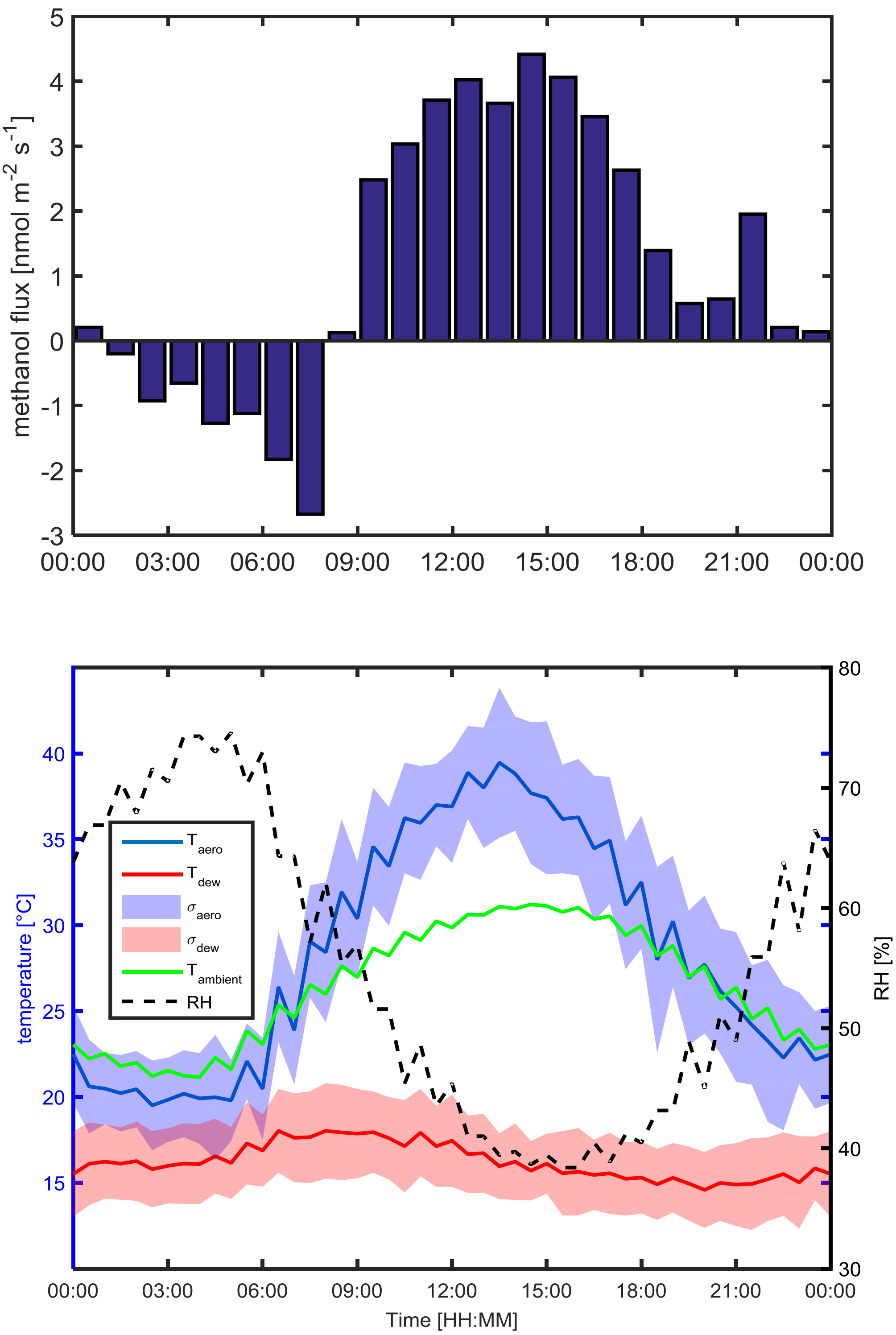

Figure ~~9~~10: ~~Time series~~Diurnal exchange of the methanol ~~flux~~ (top panel) and the calculated ~~surface~~ aerodynamical (T~~$_{surf}$~~$_{aero}$), ~~and~~ dew point (T$_{dew}$) and ambient temperature (T~~$_{dew}$~~$_{ambient}$; bottom panel). ~~The periods between 01:00 and 08:00 (methanol deposition from the diurnal plot, Figure 4) are highlighted with yellow~~The shaded blue and red area indicades the standart deviation of the calculated temperatures and the dashed line is the relative humidity.~~.~~

Appendix:

Table A1: Information about all measured 164 mass peaks in Bosco Fontana. The limit of detection is given for the calibrated masses. Masses with an F in the last column are filtered out as they were identified as fragments, clusters.

mass [amu]	elem. comp.	Background	sigma threshold	LOD (30min); Frag
21.0221		1	8.29	
27.0229	$C_2H_3^+$	1	-0.09	
28.0056	N_2^+	1	1.94	
29.0134	$H_1N_2^+$	1	35.03	
29.9974	$O_1N_1^+$	1	3.04	
31.0178	$C_1H_3O_1^+$	1	6.12	
31.9893	O_2^+	1	162.67	
32.9971	$H_1O_2^+$	1	3.42	
33.0335	$C_1H_5O_1^+$	0	45.69	38.5
35.0366	$H_5O_1N_1^+$	0	8.77	
36.0206	$H_4O_2^+$	1	1.98	
36.0444	$H_6O_1N_1^+$	1	19.26	
37.0284	$H_5O_2^+$	1	36.46	
38.0362	$H_6O_2^+$	1	159.67	
39.9629		1	1.42	
40.9710		1	1.74	
41.0386	$C_3H_5^+$	0	156.77	F
42.0100	$C_2H_2O_1^+$	0	-1.53	
42.0338	$C_2H_4N_1^+$	0	6.26	5.1
43.0178	$C_2H_3O_1^+$	0	10.57	F
43.0542	$C_3H_7^+$	0	5.13	
44.0138		0	1.74	
44.9971	$C_1H_1O_2^+$	1	2.63	
45.0335	$C_2H_5O_1^+$	0	15.53	13.2
45.9924	$O_2N_1^+$	1	3.27	
46.0287	$C_1H_4O_1N_1^+$	0	2.46	
47.0128	$C_1H_3O_2^+$	0	2.92	
47.0240	$H_3O_1N_2^+$	1	59.34	
47.0491	$C_2H_7O_1^+$	0	8.74	
48.0080	$H_2O_2N_1^+$	1	4.87	
49.0284	$C_1H_5O_2^+$	0	1.31	
49.9998	$H_2O_3^+$	1	-0.34	
51.0077	$H_3O_3^+$	1	5.73	
51.0441	$C_1H_7O_2^+$	0	26.53	F
51.9382		1	-1.63	
51.9944	$C_3O_1^+$	1	-0.68	
53.0022	$C_3H_1O_1^+$	1	-0.30	
53.0386	$C_4H_5^+$	0	3.59	
53.9394		1	-0.14	
55.0390	$H_7O_3^+$	1	167.77	
55.9377		1	2.88	
56.0468	$H_8O_3^+$	1	7.35	
57.0335	$C_3H_5O_1^+$	0	19.26	6.9

57.0699	$C_4H_9^+$	1	12.76	
57.9352		1	-0.86	
59.0491	$C_3H_7O_1^+$	0	15.82	6.1
60.0481		0	1.42	
61.0284	$C_2H_5O_2^+$	0	11.79	
62.0237	$C_1H_4O_2N_1^+$	0	0.84	
63.0263	$C_2H_7S_1^+$	0	1.60	
63.9852	$H_2O_1N_1S_1^+$	0	-1.30	
65.0233	$C_1H_5O_3^+$	0	5.84	
65.0584	$H_7O_1N_3^+$	0	1.59	
67.0542	$C_5H_7^+$	0	64.76	F
68.0621	$C_5H_8^+$	0	96.03	F
69.0699	$C_5H_9^+$	0	241.62	2.8
71.0491	$C_4H_7O_1^+$	0	39.95	4.7
71.0851	$C_5H_{11}^+$	0	7.47	
72.0875		0	6.68	
73.0255		0	3.63	
73.0473		0	0.73	
73.0648	$C_4H_9O_1^+$	0	9.64	2.1
74.0227		0	0.75	
75.0441	$C_3H_7O_2^+$	0	11.07	
75.9436	$C_1S_2^+$	1	0.51	
77.9424		1	-0.60	
79.0542	$C_6H_7^+$	0	3.44	2.5
80.9971	$C_4H_1O_2^+$	0	-0.80	
81.0335	$C_5H_5O_1^+$	1	10.76	
81.0699	$C_6H_9^+$	0	106.38	F
83.0523		0	1.47	
83.0855	$C_6H_{11}^+$	0	15.80	
85.0284	$C_4H_5O_2^+$	0	1.50	
85.0648	$C_5H_9O_1^+$	0	12.14	
85.1012	$C_6H_{13}^+$	0	1.30	
85.9471		1	1.27	
87.0441	$C_4H_7O_2^+$	0	1.58	
87.0804	$C_5H_{11}O_1^+$	0	1.61	
88.0763		0	1.14	
88.9555	$H_3O_1Cl_2^+$	1	0.42	
89.0233	$C_3H_5O_3^+$	0	3.58	
89.0597	$C_4H_9O_2^+$	0	0.99	
90.9487		1	7.58	
91.0567		0	1.16	
91.9457		1	1.79	
92.9480		1	2.59	
93.0369	$C_3H_9O_1S_1^+$	1	6.19	
93.0699	$C_7H_9^+$	0	1.79	0.7
93.9542	$C_1H_2O_1S_2^+$	1	-2.91	
95.0161	$C_2H_7O_2S_1^+$	0	-0.06	
95.0478	$C_4H_5N_3^+$	0	1.20	
95.0855	$C_7H_{11}^+$	0	8.87	F
95.9512	$O_4S_1^+$	1	1.38	

96.9961		0	1.10	
97.0284	$C_5H_5O_2^+$	0	3.04	
97.0634	$C_4H_7N_3^+$	0	2.96	
97.1012	$C_7H_{13}^+$	0	1.00	
98.0237	$C_4H_4O_2N_1^+$	1	-1.51	
98.0600	$C_5H_8O_1N_1^+$	0	1.43	
99.0077	$C_4H_3O_3^+$	0	0.34	
99.0441	$C_5H_7O_2^+$	0	6.23	
99.0804	$C_6H_{11}O_1^+$	0	6.69	
100.0393	$C_4H_6O_2N_1^+$	1	0.08	
100.0757	$C_5H_{10}O_1N_1^+$	1	-0.90	
101.0233	$C_4H_5O_3^+$	0	-1.69	
101.0597	$C_5H_9O_2^+$	0	5.07	
101.0961	$C_6H_{13}O_1^+$	0	3.11	18.7
101.9428		0	0.35	
102.0913	$C_5H_{12}O_1N_1^+$	0	0.57	
102.9468		0	-0.23	
103.0390	$C_4H_7O_3^+$	0	1.35	
103.0754	$C_5H_{11}O_2^+$	0	2.90	
103.9516	$H_5S_2Cl_1^+$	1	0.17	
105.9359		1	1.19	
106.9418		1	0.07	
106.9617		0	0.61	
107.0491	$C_7H_7O_1^+$	0	1.47	
107.0855	$C_8H_{11}^+$	0	0.58	0.4
107.9512	$C_1O_4S_1^+$	1	2.75	
108.9590	$C_1H_1O_4S_1^+$	1	2.88	
108.9920	$C_5H_1O_3^+$	1	-0.03	
109.0284	$C_6H_5O_2^+$	0	-3.77	
109.0648	$C_7H_9O_1^+$	0	2.71	
109.1012	$C_8H_{13}^+$	0	1.06	
111.0441	$C_6H_7O_2^+$	1	1.08	
111.0804	$C_7H_{11}O_1^+$	1	1.28	
111.1168	$C_8H_{15}^+$	0	-0.31	
111.9461	$O_5S_1^+$	1	-0.89	
113.0597	$C_6H_9O_2^+$	0	-0.83	
113.0947	$C_5H_{11}N_3^+$	0	2.37	
115.0096		1	1.31	
115.0363	$C_1H_3O_1N_6^+$	0	-1.02	
115.0754	$C_6H_{11}O_2^+$	0	2.18	
115.1117	$C_7H_{15}O_1^+$	0	-0.24	
116.9060	$C_1Cl_3^+$	0	-0.28	
117.9542	$C_3H_2O_1S_2^+$	1	-2.30	
118.9451		0	-3.19	
119.9512	$C_2O_4S_1^+$	1	-0.03	
120.9534		0	-1.06	
121.0648	$C_8H_9O_1^+$	0	0.10	
121.1012	$C_9H_{13}^+$	0	0.78	0.4
123.0441	$C_7H_7O_2^+$	1	0.20	
123.1168	$C_9H_{15}^+$	0	1.78	

123.9440		1	10.14	
124.9510	$C_1O_4N_1Cl_1^+$	1	-1.66	
125.9572		1	-0.85	
126.0159	$C_2H_6O_6^+$	1	1.45	
126.0557		1	1.71	
126.0957		1	0.30	
127.0390	$C_6H_7O_3^+$	0	1.84	
127.0754	$C_7H_{11}O_2^+$	1	-1.93	
127.1117	$C_8H_{15}O_1^+$	0	-0.12	
128.1107		1	-0.39	
130.9920		1	1.39	
135.0406		0	4.35	
137.0557		0	2.16	
137.1325	$C_{10}H_{17}^+$	0	115.45	0.5
138.0590		1	30.15	
140.0304		1	1.14	
140.0751		1	-1.76	
144.9606	$C_6H_3Cl_2^+$	1	0.69	
145.9685	$C_6H_4Cl_2^+$	1	-0.02	
180.9373	$Cl_3C_6H_4^+$	1	2.40	

Table A2: comparison of the detected compounds with flux in Bosco Bontana and their values at the orange grove (Park et al., 2013).

Elemental composition	mass [amu]	net (downward/ upward) flux (24h average) [nmol m-2 s-1]	
		this study	Park et al., (2013)[1]
$C_1H_5O_1^+$	33.0335	1.168 (-0.365/1.533)	1.655 (-0.102/1.757)
$H_5O_1N_1^+$	35.0366	0.061 (-0.002/0.064)	
$C_2H_4N_1^+$	42.0338	0.046 (-0.005/0.051)	
$C_3H_7^+$	43.0542	0.079 (-0.005/0.084)	0.075 (-0.001/0.076)
$C_2H_5O_1^+$	45.0335	0.228 (-0.001/0.229)	0.133 (-0.016/0.148)
$C_2H_7O_1^+$	47.0491	0.105 (-0.02/0.125)	-0.013 (-0.017/0.004)
$C_4H_5^+$	53.0386	0.008 (-0.001/0.009)	0.012 (-0.009/0.021)
$C_3H_5O_1^+$	57.0335	0.085 (-0.002/0.086)	0.033 (-0.016/0.049)
$C_3H_7O_1^+$	59.0491	0.335 (-0.01/0.345)	0.281 (-0.004/0.286)
$C_2H_5O_2^+$	61.0284	0.214 (-0.096/0.311)	0.413 (-0.005/0.418)
$C_1H_5O_3^+$	65.0233	0.03 (-0.001/0.031)	
$C_5H_9^+$	69.0699	6.466 (0/6.466)	0.025 (-0.001/0.025)
$C_4H_7O_1^+$	71.0491	0.311 (-0.004/0.315)	0.041 (-0.004/0.044)
C_5H_{11}+	71.0851	0.02 (-0.001/0.021)	0.006 (-0.005/0.011)
unknown	72.0875	0.015 (-0.002/0.016)	
unknown	73.0255	0.026 (-0.009/0.035)	
$C_4H_9O_1^+$	73.0648	0.075 (-0.002/0.077)	0.029 (-0.007/0.036)
$C_3H_7O_2^+$	75.0441	0.068 (-0.005/0.073)	
$C_6H_7^+$	79.0542	0.021 (-0.002/0.023)	0.016 (-0.002/0.018)
$C_6H_{11}^+$	83.0855	0.034 (0/0.035)	0.007 (-0.004/0.011)
$C_5H_9O_1^+$	85.0648	0.017 (-0.001/0.018)	0.008 (-0.005/0.013)
$C_3H_5O_3^+$	89.0233	0.011 (-0.001/0.012)	0.007 (-0.004/0.011)
$C_5H_5O_2^+$	97.0284	0 (-0.002/0.002)	0.007 (-0.005/0.012)
$C_4H_7N_3^+$	97.0634	0.003 (-0.001/0.004)	0.007 (-0.007/0.015)
$C_5H_7O_2^+$	99.0441	0.017 (-0.001/0.018)	0.008 (-0.004/0.012)
$C_6H_{11}O_1^+$	99.0804	0.014 (-0.001/0.014)	
$C_5H_9O_2^+$	101.0597	0.014 (-0.001/0.014)	0.004 (-0.003/0.008)
$C_6H_{13}O_1^+$	101.0961	0.091 (-0.037/0.128)	
$C_{10}H_{17}^+$	137.1325	0.219 (-0.001/0.219)	0.235 (0/0.236)[2]

[1] the presented data was calculated from Table S2 in the supplement.

[2] the fragments of monoterpenes were summed up to compare it with upscaled monoterpene signal from B.F.

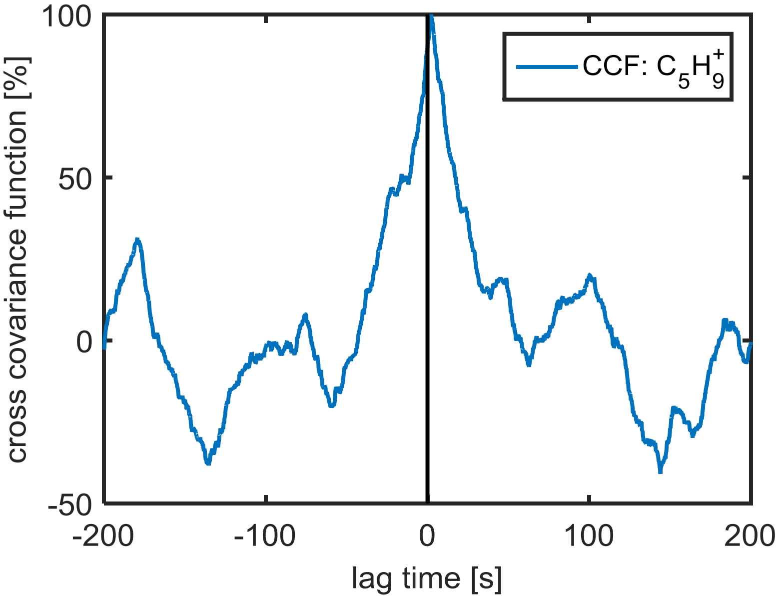

Fig A1: 30 min cross covariance function of $C_5H_9^+$ from the 15.06.2012 14:15. The function was normalized to the maximum. A clear maximum can be seen, slightly shifted to the right by the lag time.

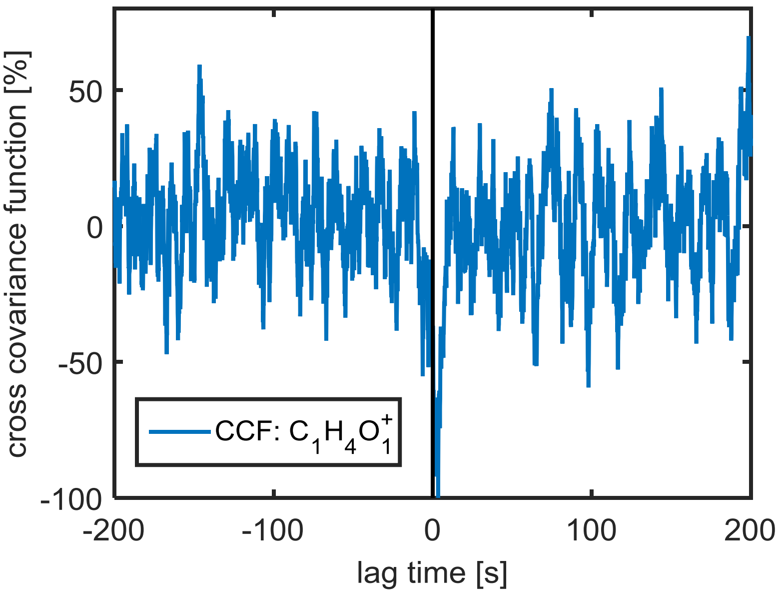

Fig A2: 30 min normalized cross covariance function of $C_1H_4O_1^+$ from the 22.06.2012 04:45. A clear minima can be seen, which defines downward fluxes.

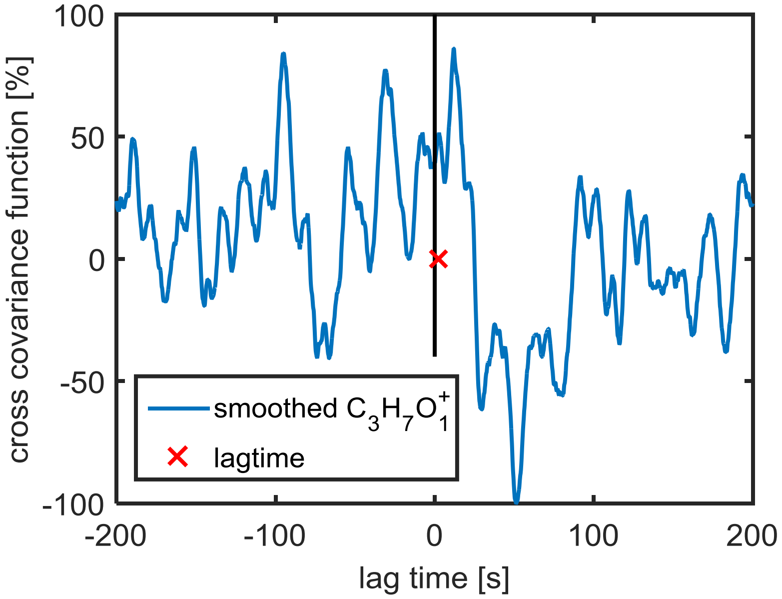

Fig S A3: Smoothed normalized CCF of $C_3H_7O_1^+$. The red cross marks the lagtime used in the original CCF (Fig A4) to find the flux value the allowed lagtime window is from 0 s to 5 s. In this specific CCF only a local maximum was found, as there is no clear maximum.

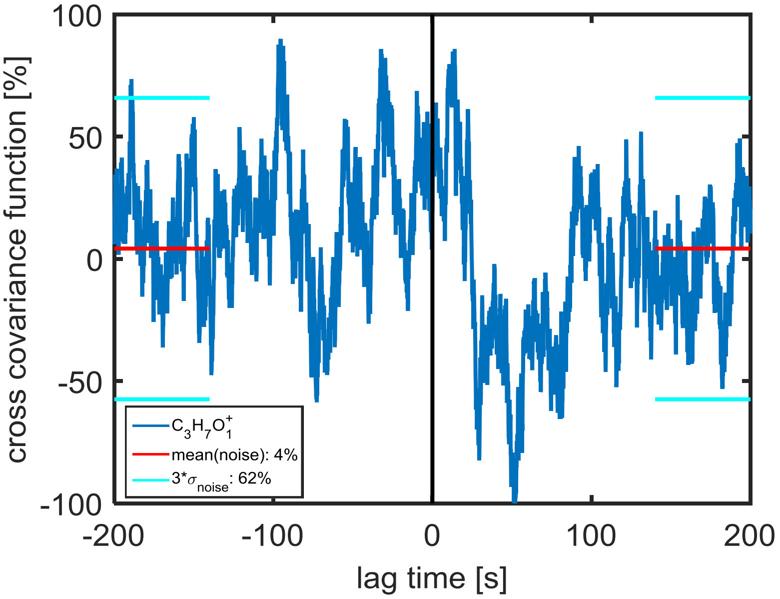

Fig A4: 30 min normalized cross covariance function of $C_3H_7O_1^+$ from the 15.06.2012 14:15. No clear maximum or minimum can be seen around 0 s lag time. The red lines at the corners of the plot indicate the average noise, while the cyan lines are the 3 σ_{noise} threshold (in the legend the 62% represents just the 3 σ_{noise}, while in the plot it is added to the mean noise).

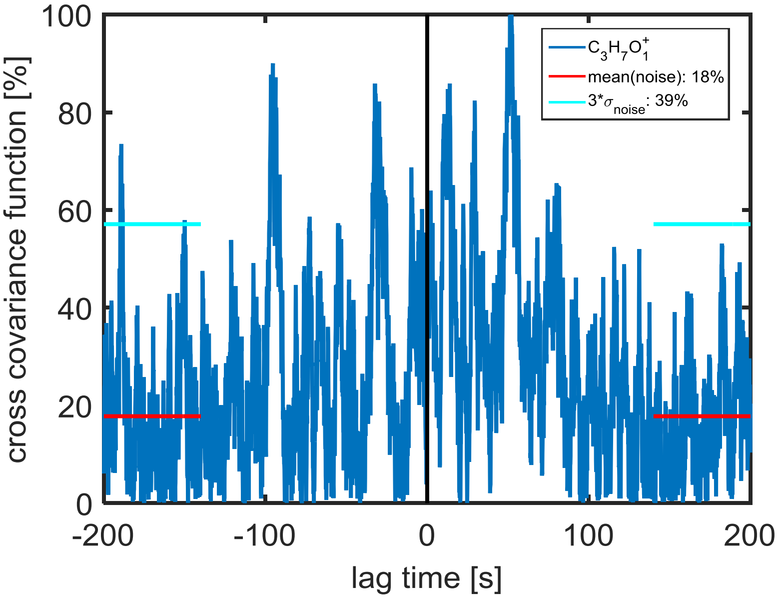

Fig A5: 30 min absolute normalized cross covariance function of $C_3H_7O_1^+$ from the 15.06.2012 14:15. The red lines at the corners of the plot indicate the average noise, while the cyan lines are the 3 σ_{noise} threshold (in the legend the 39% represents just the 3 σ_{noise}, while in the plot it is added to the mean noise). Taking the absolute of a CCF increases the mean value and thereby reduces the standard deviation of the noise (compare with Fig. A4)

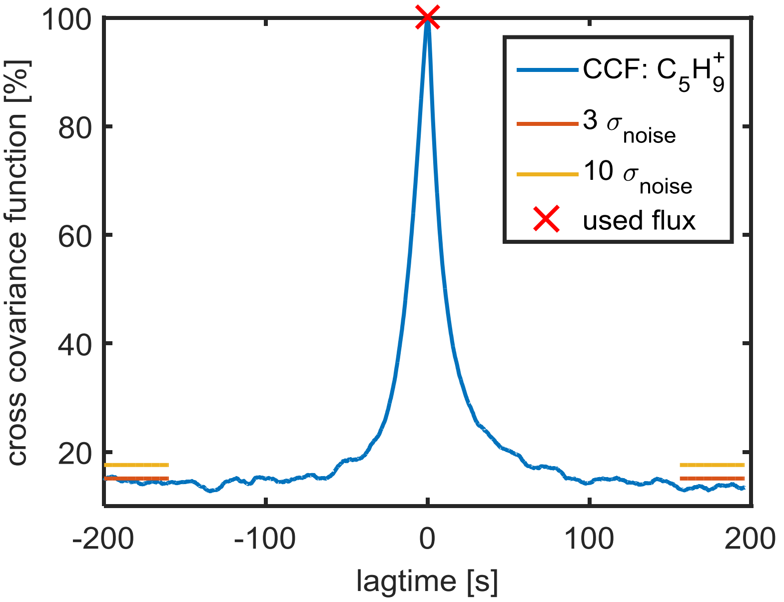

Figure A6: Averaged absolute CCF for $C_5H_9^+$. The used flux is well over the 10 σ_{noise} criteria.

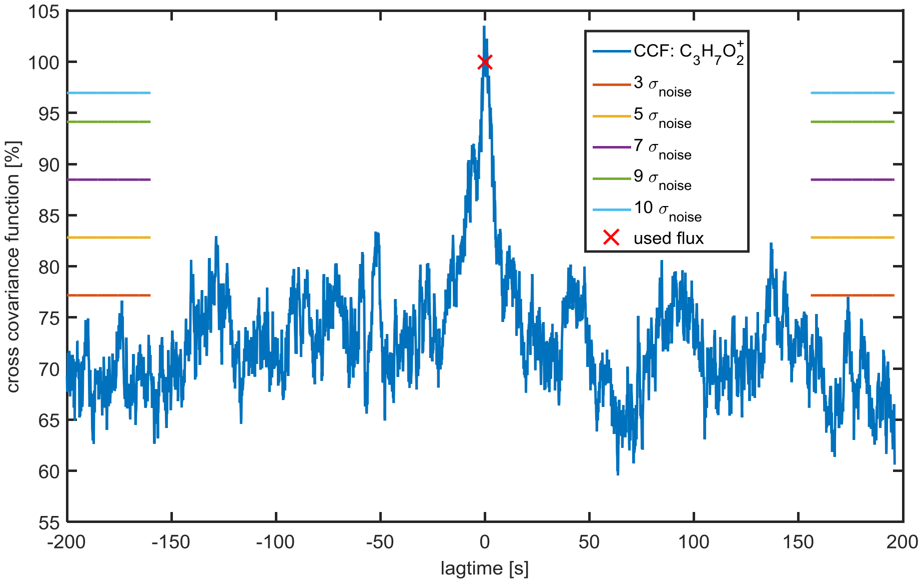

Figure A7: Averaged absolute CCF for $C_3H_7O_2^+$. Due to the constant lag time, not always the maximum of the CCF is used, as this would overestimate the flux. In this case the used value is actually a local minimum between two maxima.

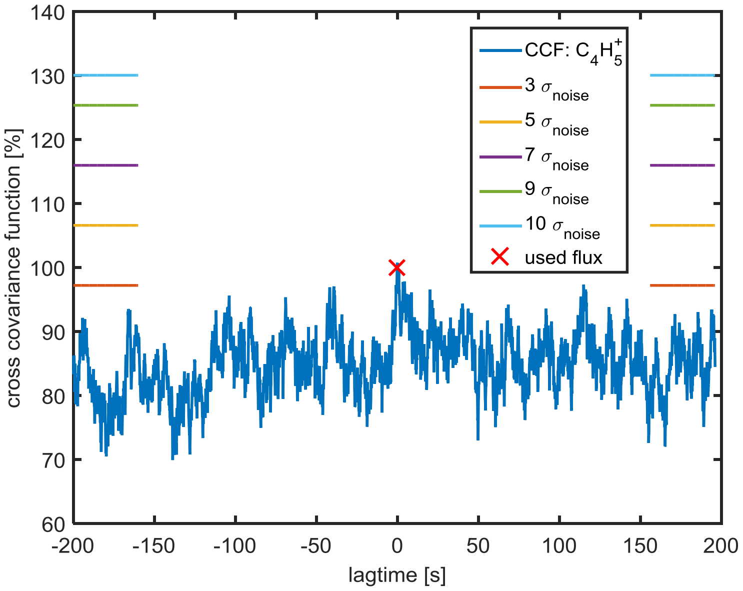

Figure A8: Averaged absolute CCF of $C_4H_5^+$, which fulfilled the 3 σ_{noise} criteria.

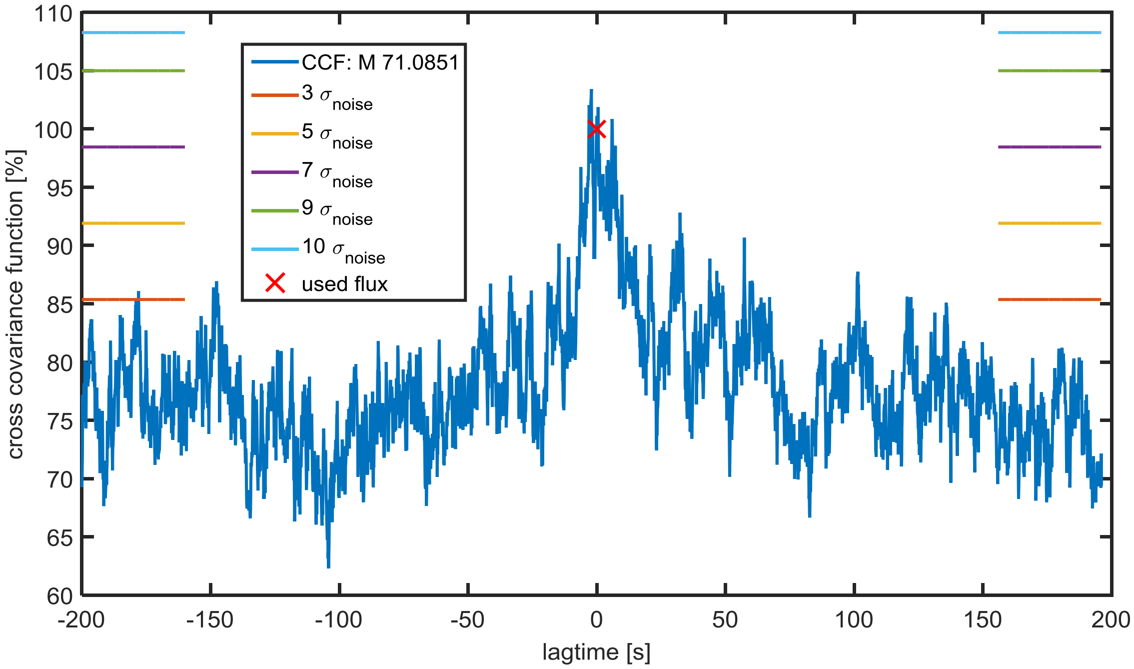

Figure A9: Averaged absolute CCF of mass 71.0851 (could not be identified), which fulfilled the 7 σ_{noise} criteria.