Specific comments referee #2

2.1 Study site: with the available data it must be possible to give percentages of the different tree species in the footprint. This would be an important piece of information for the result interpretation.

This precision was added right after the description of the footprint climatology:

“Within the 70% cumulative footprint, the distribution of tree species is dominated by Norway spruce (38%) and European beech (36%), followed by Silver fir (14%), Douglas fir (9%), and Scots pine (2%)”.

l. 259: according to Ionicon, negative peaks in IDA only occur when overfitting (e.g. the total peak area is already 102% with the first 7 peaks, so the 8th peak is made negative to get to 100%), so this points at a general problem in the data processing. This should be discussed here.

Due to statistical variability, small ion count rates can go below the baseline which leads to “negative counts” being associated with a peak. This issue is most common during zero measurements but is also more prevalent when looking at high sampling rates with inherently higher statistical uncertainties.

It is true however that negative peaks may show up during the peak fitting procedure in IDA due to overfitting of peak systems. Due to the high volume of data, we did not perform a manual check on all the signals which may induce some uncertainties. However, we estimate that the issue of negative peaks fitted in IDA is relatively small in our data processing workflow due to the mass selection strategy. If negative peaks occur close to a peak related to a protonated VOC, it will either expand the DBSCAN cluster or fall out of the neighbourhood. In the case that the peak occurs sufficiently close to the main signal to be considered part of its neighbourhood, the peak areas obtained from IDA will be added together and associated to the protonated VOC. This is expected to be a small effect and may even correct for minor uncertainties in the peak shape determined by IDA. If the negative peak does not occur sufficiently close to a protonated VOC to be considered in their neighbourhood, the peak is considered as “noise” and will not be processed. In the unlikely event that these “noise” peaks occur at a consistent location and are identified as a separate cluster by the DBSCAN algorithm, most (nearly all the data) will be negative and thus the cut on fraction of data above the limit of detection would lead to the non-consideration of the cluster in the final database.

To address the reviewer’s comment, the following sentence has been added to the manuscript: “This issue occurs especially during zero measurements and is more prevalent when considering data acquired at high sampling frequency, where statistical uncertainties are inherently higher”.

l. 397: the wood factory is only outside the 80% footprint, maybe even within the 90% or 95% footprint? - and definitely within the 99.99% footprint, so it is not a surprise that emissions from it can be measured

We thank the reviewer for this relevant remark. Referring to the wood factory as being outside the flux footprint was indeed inappropriate. Our intention was rather to emphasize that, although the factory generally lies outside the dominant flux footprint and is therefore expected to contribute only marginally, its influence on the measured fluxes was nonetheless significant, likely due to its strong VOC emissions relative to the surrounding biogenic sources.

A second hypothesis that may explain the observed impact relates to the advection of VOC-rich air masses emitted by the factory, which can lead to abnormally high concentrations at the tower and consequently to apparent downward fluxes.

These two explanations have now been incorporated into the manuscript as follows:

"Two mechanisms may account for the influence of the sawmill on local fluxes despite their relatively long distance from the tower (3 km). First, although the factory typically falls within an area with a low relative contribution to the measured flux compared with the surrounding forest, its clear influence observed in the fluxes suggests that the sawmill would constitute a strong VOC source. This influence is most evident at night, when more stable atmospheric conditions enlarge the flux footprint, thereby increasing the relative weight of the factory on the observed fluxes. A second explanation is that even when the factory lies in a region with very low contribution to the measured flux, VOC-rich air masses emitted by the factory may still be advected toward the tower. In such cases, the resulting high local concentrations can generate apparent downward fluxes, despite the source being located outside the main footprint area."

l. 399: at night, footprints are larger due to more stable conditions, so again it is not a surprise that influence from a larger area can be seen then

Indeed, this relevant comment has been considered and is now reflected in the revised text above.

l. 491: relative to what?

The term "relative" is used here to characterize non-calibrated ozone concentrations expressed in V, in opposition to "absolute" concentrations obtained from a calibrated instrument. This terminology was used in Muller et al. (2010).

To remove any misinterpretation, the sentence "Since the FOS analyser provides only relative ozone concentrations" becomes "Since the FOS analyser provides only voltages (V) proportional to the ozone concentrations".

l. 569: what brand/model of HPLC cartridges were used?

An error was present on this line. HPLC is indeed referring to the measurement method while DNPH (dinitrophenylhydrazine) cartridges were used. The sentence "VOCs adsorbed on TENAX-TA or HPLC cartridges were analysed by GC-MS and HPLC, respectively" becomes "VOCs adsorbed on TENAX-TA or DNPH cartridges were analysed by GC-MS and HPLC, respectively".

l. 621: not just fragmentation, also water clusters

Indeed, this has been added in the text. The sentence "It is important to note that compounds can give rise to signals at multiple ion masses, which may correspond either to isotopes associated with the chemical formula or to ion species resulting from the fragmentation of nascent, excited protonated molecules (i.e., fragment ions)" becomes "It is important to note that compounds can give rise to signals at multiple ion masses, which may correspond either to isotopes associated with the chemical formula, to ion species resulting from the fragmentation of nascent excited protonated molecules (i.e., fragment ions), or to protonated water-cluster adducts formed in the ionization region".

l. 628: is benzene really benzene or could it be a fragment e.g. of a phenolic plant emission?

According to the literature (e.g. Yuan B. et al., Chem. Rev. 117, 13187-13229, 2017) ions at m/z 79.054 (or at the isotope at m/z 80.058) are generally attributed to protonated benzene, but nascent excited protonated ethylbenzene may also partially fragment to this m/z (Alfons Jordan, personal communication). During the intense measurement campaign at the site (12-19 July 2022), an average [ethylbenzene]/[benzene] ratio of 12% was found, implying a potential ethylbenzene contribution to the protonated benzene signal of ca. 8%. We are not aware of fragmentation of phenolic compounds emitted by vegetation resulting in PTR-TOF-MS product ions at this m/z. However, as pointed out in the manuscript (l.626-627), disentanglement of the peak system at integer m/z 79 by IDA was difficult because of an important contribution of hydrated protonated acetic acid. At integer m/z 80, the peak related to the benzene isotope suffered less from this interference. Therefore, quantification of benzene was based on the ion signal at m/z 80.058.

l. 636: The fact that some compounds were not detected by the algorithm despite exhibiting diurnal trends, and others were detected but were considered insignificant by the authors, raises questions about the algorithm. Why could such mis-filtering happen and is there any way to improve the algorithm in that regard? In the end, if manual work is needed anyway, one could wonder why an algorithm is used at all.

The algorithm used to identify significantly exchanged compounds was initially developed at a stage where several hundred ions had to be processed simultaneously. Under such conditions, a systematic visual inspection of diel flux patterns for each ion would have been extremely time-consuming and, in practice, hardly feasible. The primary objective of the algorithm was therefore to provide an efficient and reproducible first-order screening of a large number of ions.

In a later step of the workflow, the application of the PAP software substantially reduced the number of ions to be analysed by retaining only mass-to-charge ratios for which peaks were regularly observed and generally above the limit of quantification. At this stage, the number of candidate ions became sufficiently small to allow a visual inspection of the algorithm's output. In the present study, the identification of significant VOC exchanges thus relies not only on statistical criteria such as flux detection limits used in the discussed algorithm, but also on the visual assessment of clear, consistent, and interpretable diel dynamics.

Overall, we consider that the algorithm performs well, as it agrees with the conclusions that would be drawn from visual inspection in most cases. However, as with many automated classification or filtering approaches, some degree of post-processing verification remains advisable, particularly for borderline cases. This additional step does not invalidate the usefulness of the algorithm but rather ensures the robustness of the final selection.

Finally, we note that this type of algorithm remains particularly valuable for studies dealing with a large number of ions, for which a fully manual/visual evaluation would again become impractical. As with other methods used to identify significantly exchanged compounds (see our response to the following comment), the algorithm involves user-defined choices (such as the percentage of significant half-hours within a day or the number of consecutive significant days) which directly influence the number of compounds retained. Consequently, some degree of subjectivity remains, and objectively improving such algorithms is inherently challenging.

l. 649: I think the authors should compare sensitivities/LODs or filtering criteria to find out if these could explain why more or less fluxes were considered significant in other studies.

We agree with the reviewer that this aspect could have been developed. A detailed comparison of filtering criteria has now been added in the text, as well as a quantitative comparison of flux signal-to-noise ratios across studies, that is illustrated in the Supplementary.

The following paragraphs were added in the manuscript:

"These large differences can be explained by the sensitivity of the PTR-ToF-MS instrument but also by the ecosystem type—for example, an orange orchard may emit substantially more VOCs than a temperate forest (Loubet et al., 2022). However, even for similar ecosystems and climatic conditions, Millet et al. (2018) reported six times more significant compounds than in the present study. This raises questions not only about instrumental performance, but also about the methodological choices involved in filtering ions to identify VOC exchanges.

Differences across studies already arise upstream of flux calculations, at the level of ion detection and selection. The number of ions identified by PTR-ToF-MS can vary substantially depending on how fragments, water clusters, isotopes, impurities, and other artefacts are filtered, a process that is often insufficiently described in the literature. In the present work, beyond an initial filtering of water clusters and isotopes, the application of the PAP software further reduced the ion list by retaining only mass-to-charge ratios for which peaks were regularly observed and generally above the limit of quantification.

At a later stage, when computing fluxes, additional methodological choices are introduced, particularly regarding the definition of a flux as being significantly different from zero. While most studies estimate the random flux error from the cross-covariance between vertical wind fluctuations (w′) and concentration fluctuations (c′) at large time lags—where the remaining covariance is attributed to noise (Langford et al., 2015)—the criteria used to extrapolate this assessment over an entire measurement period vary widely. Some illustrative examples are discussed below.

Loubet et al. (2022) computed an average random error following the recommendation of Langford et al. (2015), as the square root of the summed squared individual errors divided by the number of records. With this approach, the average random error decreases proportionally to 1/√n when averaging over n measurements. Consequently, the longer the measurement period, the more likely a compound's mean flux is to exceed its detection limit. Figure S15 compares the flux signal-to-noise ratio (SNR, defined as the mean flux divided by the average error) reported in several PTR-ToF-MS studies for a subset of masses calibrated in the present study. For consistency, the SNR shown for this work were computed using an average error calculated following Loubet et al. (2022). When averaging over our three measurement campaigns, the strong reduction in random error leads to SNR that exceed those found in all other studies. In contrast, the lower SNR in Park et al. (2013a), Ruuskanen et al. (2011), and Fischer et al. (2021) likely reflect the much shorter duration of their measurement periods. Applying the methodology of Loubet et al. (2022) to the present dataset would therefore lead to the conclusion that all 74 detected ions exhibit a mean flux significantly different from zero. However, this does not necessarily imply that the exchange of a given VOC displays a clear, consistent, or interpretable temporal pattern.

Several alternative approaches have been proposed to identify significant VOC exchanges. For instance, Ruuskanen et al. (2011) visually assessed the quality of the covariance function (presence of a distinct and well-defined extremum) for each ion. While this approach was feasible for their eight-day measurement period, it becomes impractical and excessively time-consuming for longer measurement campaigns. Similarly, Fischer et al. (2021) selected compounds based on their covariance with the vertical wind component, although the exact evaluation criteria were not detailed. A more formalised approach was introduced by Park et al. (2013a), who computed a mean absolute covariance function from individual half-hourly records and compared its peak value to the standard deviation of the covariance function at large lag times, assumed to represent random noise. This framework provides a direct way to extrapolate half-hourly significance assessments to longer time periods. However, unlike the algorithm applied in the present study, such methods may fail to detect compounds that exhibit significant exchanges only during limited or episodic periods.

Among the diversity of existing methods, it is also worth highlighting the approach developed by Millet et al. (2018), who estimated the flux detection limit using an internal standard (diiodobenzene), for which no biogenic exchange is expected. Any measured flux of this compound can therefore be attributed to instrumental or internal effects—primarily fluctuations in relative humidity—and used to define a general detection limit.

Overall, the choice of detection and significance criteria has a direct and often dominant impact on the number of VOCs reported as being exchanged by an ecosystem (Schallhart et al., 2016; Jensen et al., 2018). The wide diversity of methodologies currently in use makes quantitative comparisons across studies challenging. We therefore advocate for the development of more unified algorithms and community standards for PTR-ToF-MS flux analyses."

l. 654: in what way were trunk flux dynamics more difficult to assess, can you give an example?

First, the temporal resolution of TRUNK fluxes was lower (about one half-hour every 2 hours). In addition, their magnitude was lower and more erratic, so clear diel patterns were more difficult to observe for TRUNK fluxes. To express this, the sentence "No visual inspection was applied to adjust this list, as the TRUNK flux dynamics were more difficult to assess visually" becomes "Considering their lower temporal resolution (about one half-hour every 2 hours), and less pronounced flux dynamics, no visual inspection was applied to adjust this list"

l. 654: why are acetic acid and its fragment listed separately? If acetic acid was calibrated with a gas standard on the parent mass, the fragment should be omitted to avoid double counting; otherwise why are the two not added up?

Based on the reviewer's comment, and to avoid confusion with double counting of acetic acid, we decided to only keep m/z 61.028 in Table 3 of the manuscript for quantification.

However, both the ion signals at m/z 43.018 and m/z 61.028 were kept in the Supplementary Table S3, together with their associated sensitivities, and in the database. The sensitivities were not obtained from calibrations with an acetic acid standard, but from the calculated H_3O^+/acetic acid reaction rate constant and from the average ratio of ambient m/z 43.018 to m/z 61.028 transmission-corrected normalized count rates over the entire measurement period. Variations in the ratio of acetic acid concentrations based on m/z 61.028 ions to concentrations based on m/z 43.018 could point to potential contributions of other compounds to these ion species and therefore indirectly provide extra information. That's why we kept them in the database. Adding up the two ion signals for acetic acid quantification could have been an option, but this would probably not have increased the accuracy, and it stands in contrast to the concept of the attribution of VOC concentrations to single m/z ratios used in the PAP software. This can be considered for future versions of the data processing chain but is currently out of scope.

Fig. 6., Table 3, treatment of fragments of gas standard-calibrated compounds: for example, why are mass 81 and mass 137 considered separately? If the monoterpenes were calibrated on the parent mass, then including the mass 81 fragment leads to double counting of a certain fraction of the monoterpene flux and concentration. The same is true for the mass 41 isoprene fragment.

Similar as for acetic acid, we removed m/z 81.070 and 41.039 from Table 3 to avoid confusion related to double counting of the sum of monoterpenes and isoprene, respectively, but kept the information in the Supplementary Table S3 and in the database. Changes in ratios of monoterpene concentrations based on the ion signals at m/z 81.070 and m/z 137.132 could potentially provide indirect information on the emission of stress-related compounds (Simpraga M. et al., 2011) by the ecosystem or variations in ambient monoterpene distribution leading to slightly different m/z 81.070 and m/z 137.132 ion intensity ratios. Isoprene concentrations based on the ion signal at m/z 41.039 should moreover be considered as an upper limit as several compounds may contribute to this m/z, as indicated in the Supplementary Table S3.

As a result of the comment of the reviewer, all m/z values for which compound quantification could give rise to double counting are now removed from Table 3. These include m/z 41.039, 43.018, 71.086, 81.070, 93.070, 101.096, 115.112, 121.101 and 149.132.

Table 3 (some of these points are also relevant for the supplementary list of detected ions):

- Please mark the compounds that were calibrated with a gas standard and thus have higher certainty than the others.

Compounds calibrated with a gas standard are now identified in italic, as mentioned in the table caption.

- When you report the seasonal mean mixing ratios, it would also be interesting to show the standard deviations.

The standard deviation around the 24h mean mixing ratio is now given for each season.

- The mass 151.112 could also be an oxygenated monoterpene like thymol, carvol or similar, why is the fragment of pinonaldehyde considered as the likeliest in table 3?

Because GC-MS measurements during the IMP 2022 campaign indicated that alpha-pinene is the most abundant monoterpene, it is expected that pinonaldehyde will be present as it is a known OH-initiated oxidation product of alpha-pinene. Parameters for quantification from first principles are available for this compound, and nascent excited protonated pinonaldehyde is known to strongly fragment to m/z 151.112. At present we have no indication of the presence of specific oxygenated monoterpenes resulting in ion species at that m/z, but this can be investigated in future GC measurements at this site.

- water clusters should not be ignored. I assume that “ethanediol” is more likely acetaldehyde + H2O, and “propanediol” is more likely acetone + H2O. Please check through correlations with the parent mass.

We thank the reviewer for their thorough and pointed remark. By checking the correlations, we can indeed see strong links between the acetaldehyde and acetone signals and those associated with their potential water clusters. Additionally, because both acetaldehyde and acetone are present in the calibration standard, we can estimate the effect of acetaldehyde and acetone on the m/z 63.044 and 77.060, respectively, by considering the ratio of their signals in tc-ncps during calibrations. During a more intensive calibration with respect to relative humidity, we noted that up to 3.5 % of the signal calculated at the parent masses was found at their respective water cluster masses. During the campaign, this ratio was typically 2—5 %. As such, we have concluded that the reviewer is correct in their assessment and decided to omit these masses from the data as we do not aim to report water clusters.

l. 709: “xylene” and “trimethylbenzene” sound unlikely to be emitted from a forest. Mass 121.101 could be a fragment of sesquiterpenes, and mass 107.09 a fragment of limonene, see Kari et al.: PTR-ToF-MS product ion distributions and humidity-dependence of biogenic volatile organic compounds, International Journal of Mass Spectrometry, 430, 87–97, https://doi.org/10.1016/j.ijms.2018.05.003, 2018.

This reference had not been considered when consolidating Table S3 in the Supplementary Material. The entries corresponding to m/z 107.086 and 121.101 have been updated to indicate a potential contribution from monoterpene and sesquiterpene fragmentation, respectively.

As Table 3 in the manuscript focuses on m/z values and associated compounds for which non-negligible fluxes have been observed, m/z 107.086 and 121.101 were not included, since xylene and trimethylbenzene are unlikely to be emitted by the ecosystem. Fluxes at these m/z values could arise from contributions of monoterpene and sesquiterpene fragments, potentially leading to “double counting” of fluxes.

Despite this potential biogenic contribution, considering xylenes and trimethylbenzene as major contributors to the ion signals at these m/z ratios remains reasonable in terms of concentrations. At line 709, the reference to xylene and trimethylbenzene is provided when discussing their diel concentration patterns, which were similar to the one of NOx. This indicates that a mesoscale contribution from distant sources is possible, and therefore we chose to retain the reference to both xylene and trimethylbenzene. The sentence has been reformulated to emphasize the potential and uncertain attribution of each ion mass.

General answer based on above comments from the reviewer

Two comments from the reviewer lead to an update of the numbers of (VOC-related) ions reported in the manuscript at the beginning of Section 3.2.1. The first modification concerns the removal of m/z 63.044 (ethanediol) and m/z 77.060 (propanediol) from the list of 76 detected m/z values, as we decided not to include water clusters in this list. These two ions are therefore excluded from the reported database and from all results. The second modification involves m/z 107.086 and m/z 121.101, which are likely fragments of monoterpenes and sesquiterpenes, respectively, and were removed from the list of unique m/z used for VOC flux quantification. In addition, we noticed that m/z 80.058 (benzene isotope) had been unintentionally omitted from the list of unique ions used for VOC quantification. This correction has also been applied to the manuscript.

After implementing these modifications, the following numbers were adapted in the manuscript:

- the 76 ions detected by the DBSCAN algorithm become 74 ions (removal of 2 water clusters at m/z 63.044 and 77.060)
- the 65 unique ions used for the quantification of VOCs become 62 ions (removal of 2 water clusters at m/z 63.044 and 77.060, removal of MT fragment at m/z 107.086 and SQT fragment at m/z 121.101, addition of benzene isotope at m/z 80.058)
- the 60 ions previously reported as exhibiting significant exchange are no longer referred to. When discussing significant fluxes, multiple ions associated with the same VOC are now directly removed, so that each VOC is represented by a single ion.
- the 51 significantly exchanged VOCs become 48 VOCs (removal of 2 water clusters at m/z 63.044 and 77.060 + SQT fragment at m/z 121.101)

l. 781: It has been reported in other studies that the fraction of carbon allocated to VOCs increases under stress (e.g. Peñuelas, J. and Llusià, J.: BVOCs: plant defense against climate warming?, Trends in plant science, 8, 105–109, https://doi.org/10.1016/S1360-1385(03)00008-6, 2003.). How did this fraction change during the heatwave in 2022?

A heatwave was officially recorded in Belgium in 2022 from 9 to 16 August. Due to instrumental issues, VOC flux measurements were available only for part of this period. Under the high temperatures recorded in August 2022, the relative carbon allocation to VOCs reached its highest values (~0.6%), a pattern that also appeared at the end of June 2023. The increase in carbon allocation to VOCs during the heatwave, however, was not much higher than during other warm periods, and overall BE-Vie is known to be only weakly affected by heat stress (e.g. based on past net CO_2 exchange measurements). Seasonal variability in the carbon allocation to VOCs was nevertheless evident, with summertime maxima, consistent with previous observations in other ecosystems (Sharkey and Loreto, 1993; Peñuelas and Llusià, 1999, 2001).

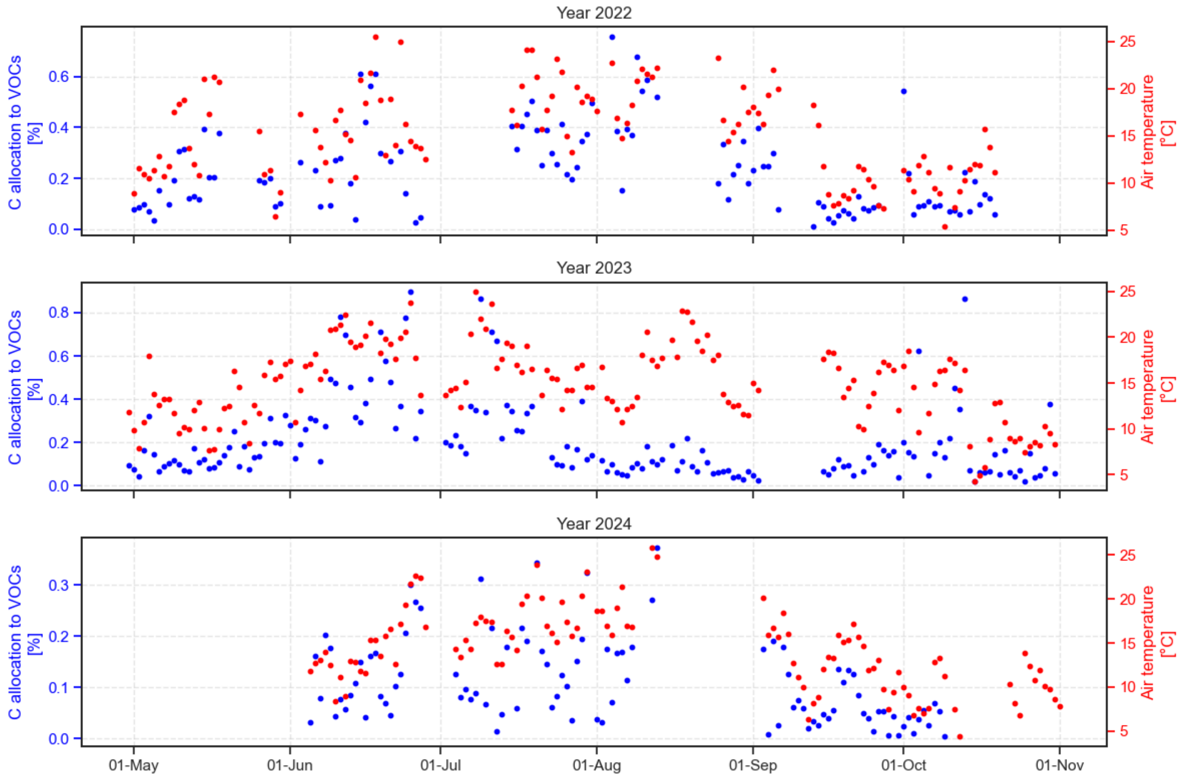

Fig. Seasonal evolution of total VOC emission relative to photosynthetic carbon fixation (left y-axis) and air temperature (right y-axis). Each point represents the daily median value of both variables.

The following sentences were added in the manuscript to summarize this small analysis: "This fraction was highest in summer (daily median of up to 0.9%) and lowest in autumn and winter (daily median of 0.1%, data not shown here), consistent with observations reported for other vegetation types (Sharkey and Loreto, 1993; Peñuelas and Llusià, 1999, 2001). This summertime increase has previously been attributed to a potential acclimation strategy to cope with stressful conditions under high temperature and irradiance. The fraction of carbon allocated to VOCs was highest during the heatwave event encountered at BE-Vie, although not significantly higher than during the rest of the summer."

l. 830: I think the main point from Millet et al. was that deposition fluxes have lower individual contributions, that is why there are more species needed to explain e.g. 90% of the deposition flux.

The previous formulation did not imply that directly. The sentence "This confirms the observation by Millet et al. (2018) that the total deposition flux is composed of a larger number of contributing species" becomes "This confirms the observation by Millet et al. (2018) that the total deposition flux is composed of a larger number of species with lower individual contributions".

l. 865: Was there any influence of rain events or soil moisture seen on the TRUNK emissions? Emission bursts of VOCs from soil after wetting have been reported in several studies, e.g. Bourtsoukidis, et al.: Strong sesquiterpene emissions from Amazonian soils, Nature communications, 9, 2226, https://doi.org/10.1038/s41467-018-04658-y, 2018.

Based on a preliminary analysis, TRUNK net fluxes tended to decrease and become negative during and shortly after rain events, indicating enhanced depositions under wet conditions. No subsequent re-volatilization or moisture-induced emissions are clearly observed in our dataset, in contrast to Bourtsoukidis et al. (2018).

The increase of VOC below-canopy deposition during wet conditions is particularly important for more soluble VOCs, but this is out of the scope of the present manuscript and will constitute a dedicated publication.

l. 946: It looks like the O3 deposition was larger when ozone concentrations were larger. Is this relevant besides stomatal aperture?

The deposition of ozone, as for many gases, is generally understood as being proportional to the concentration gradient between the atmosphere and the sink (stomata, leaf, ground surfaces, etc.) and governed by a series of resistances. Among the different uptake pathways, the stomatal one usually dominates ozone deposition, and stomatal aperture is therefore a major controlling factor. Under heatwave conditions, two contrasting responses are typically expected: on the one hand, ambient ozone concentrations tend to increase (as observed here), while on the other hand stomatal conductance often decreases as a protective response to heat stress. Our flux measurements indicate that ozone uptake increased during this period, suggesting that stomatal regulation played a relatively minor role compared with the strong enhancement of ambient ozone levels.

An additional hypothesis, which was not discussed in the manuscript, concerns a shift from predominantly stomatal to non-stomatal uptake. This mechanism has recently been proposed and evaluated under field conditions. Juráň et al. (2025) showed that during drought, non-stomatal ozone fluxes compensated for reduced stomatal uptake in a temperate Norway spruce forest. The increased contribution of non-stomatal deposition was attributed mainly to reactions on leaf cuticles and soil particles, and to a lesser extent to chemical loss through reactions with VOCs.

In response to the reviewer’s comment, the paragraph has been revised to account for two complementary explanations for the enhanced ozone uptake during the heatwave: (i) elevated ozone concentrations which offset the decrease in stomatal conductance, and (ii) a greater relative contribution of non-stomatal deposition pathways.

l. 1026: it is not clear which kind of remote sensing measurements are available. They should be made available with a doi, like the rest of the data.

Remote sensing measurements are described twice in the manuscript. Table 1 provides a concise overview of the instruments and the quantities retrieved, specifying that tropospheric columns and vertical profiles of HCHO, NO_2 and aerosols were obtained. Table S1 then offers additional detail by listing the specific instrument used (SkySpec Compact, Airyx), the measurement principle (MAX-DOAS), and the acquisition frequency. At present, the remote sensing dataset from BE-Vie has not yet been published nor archived in a formal database, and no DOI is therefore available. As stated in the manuscript, however, the dataset can be obtained upon request from its originator.

Technical comments referee #2

L. 8 abstract: „processing pipeline“ sounds to figurative and can be confused with an actual pipeline, I would just say software

“Using a PTR-ToF-MS and a dedicated open-source processing pipeline” becomes “Using a PTR-ToF-MS and an open-source data-processing workflow”

l. 91: “same two levels” – which ones?

The same two levels refer to the point (i) before (above the canopy and at ground level). This was adapted to avoid any confusion: “30-minute fluxes of BVOCs and O3 above the canopy and at ground level”.

l. 93: I assume you mean vertical profiles of turbulence measured by anemometers (“profiles of anemometers” sounds wrong)

Indeed, this was adapted as suggested.

l. 145: “absolute and stable” needs to be explained. It became clearer to me later in the text when the other ozone instrument was introduced, but at this point it was not clear

“The T400 instrument was used to obtain absolute and stable measurements of ozone” becomes “The T400 instrument was used to deliver calibrated concentrations of ozone”.

l. 176: what material was the pump membrane? PFA? Otherwise the ozone might react with the membrane?

The membrane of the pump is coated with PTFE to avoid chemical loss. This is now added in the text.

l. 220: you can make clear here already that the PAP software is available and cite it here

The link to PAP software is now given directly when presented, along with a doi:

“The PAP software is publicly available (https://github.com/bverreyk/PeakAreaProcessing, Verreyken et al. (2025a)) and a general overview of its main processing steps is given below.”

Fig. 7: Nice way of presenting the data, but way too small to make out anything useful from it.

We were not entirely certain which specific aspect of Fig. 7 the reviewer found too small. To improve clarity, we have increased the size of all labels and adapted the colormap to ensure accessibility for readers with colour-vision deficiencies, as requested by the editor. We have also enlarged Fig. 7 in the revised manuscript.

Fig. 8: the colors of mass 137 and of “other > 0” look the same in print.

The editor indicated that Fig. 8 was not adapted for readers with colour vision deficiencies. Colours were adapted and the categories “other > 0” and “other < 0” are now represented with a hatched texture to be easily distinguished from other categories.

Specific comments referee #3

Line 7: While mentioned in the title, it would be a slight improvement to the Abstract if the type of forest - "mixed temperate" - investigated is mentioned earlier in the abstract text (perhaps near where the ICOS Vielsalm station is introduced), rather than at the end.

We added this important precision in the abstract, as suggested by the reviewer: “We conducted a three-year field campaign (2022—2024) at the Integrated Carbon Observation System **mixed temperate** forest station of Vielsalm (BE-Vie)”.

Line 27: There are many different types of forest ecosystems, it would be an improvement to have a more additional introduction material regarding what is known about the BVOC emissions from the type of temperate mixed forest that the study site represents.

We agree with the reviewer that the introduction would benefit from explicitly highlighting the role of mixed temperate forests in global BVOC emissions. The following paragraph was added in the introduction.

“Within forests, Guenther et al. (2012) estimated that broadleaf deciduous temperate trees rank third in isoprene emissions, contributing 35.4 Tg year^{-1}, compared to 244 and 178 Tg year^{-1} for tropical evergreen and deciduous forests, respectively. Similarly, needleleaf evergreen temperate trees are the third largest monoterpene emitters, with 7.38 Tg year^{-1}, behind tropical evergreen and deciduous forests (82.9 and 45 Tg year^{-1}, respectively). These estimates suggest that temperate forests composed of mixed deciduous and needleleaf species deserve particular attention in future studies of BVOC fluxes.”

Line 38: cite reference(s)

A reference to Clifton et al. (2020), a review paper on O_3 deposition has been added.

Line 41-42: For a long time MT emissions from coniferous trees/plants were treated as temperature-dependent only. Perhaps highlight this in the text or include additional references here regarding early research of temperature-dependent MT emissions from coniferous forests.

MT emissions where indeed primarily modelled as temperature-dependent only. This information is present in Guenther et al. (1995), but our formulation did not explicitly mention that Guenther et al. (1995) modelled MT emissions based on temperature only. To clarify this, the sentence “Early research primarily focused on isoprene and monoterpenes—the two most widely emitted isoprenoids globally (Guenther et al., 2012)—whose fluxes were long considered exclusively upward, driven by light and temperature (Guenther et al., 1995)” becomes “Early research primarily focused on isoprene and monoterpenes—the two most widely emitted isoprenoids globally (Guenther et al., 2012)—whose fluxes were long considered exclusively upward, with isoprene emissions driven by light and temperature and monoterpene emissions by temperature alone (Guenther et al., 1995)”.

Line 50: The deposition loss of organic vapors lead to a reduced availability of these vapors to contribute to the formation and growth of SOA - not the direct removal of already-formed SOA particles themselves. I would suggest rephrasing this sentence. (double-check)

We agree with the reviewer that the original wording could be ambiguous. We therefore revised the sentence to clarify that deposition affects SOA formation through the removal of condensable organic vapours rather than the direct removal of particulate SOA.

Line 54: You should cite multiple sources/examples for your claim that emissions are typically simulated by MEGAN - conceivably there are other model tools that have been created over the years

We agree with the reviewer that several models exist to simulate biogenic emissions. Our intention was not to imply that MEGAN is the only available tool, but rather to refer to one of the most widely used frameworks. We therefore slightly revised the wording to avoid any implication of exclusivity. The sentence "Emissions are typically simulated using the MEGAN model" becomes "Emissions are often simulated using the MEGAN model, one of the most widely used biogenic emission models", and references to a few representative studies using MEGAN have been added to the manuscript.

Line 60: This section neglects the role that turbulence and mixing has in in-canopy exchange processes.

We agree that turbulent mixing plays a key role in in-canopy exchange by controlling residence times and thus the extent of chemical processing. We have therefore clarified this interaction in the revised text, as in this sentence: "VOCs can be lost between their point of release and the atmosphere above the canopy, **where chemical processing depends strongly on turbulent mixing and residence times within the canopy**".

Line 76: Gradient and profile -based flux estimates have also been used in the past as well (e.g., Rantala et al. 2014 and references therein).

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 Environ. Res., 19, 87-107, 2014.

We thank the reviewer for this reference. Gradient and profile-based flux measurements have now been mentioned in the manuscript with a reference to Rantala et al. (2014).

Line 91: two measurement heights? Please state them here in the text.

The same two levels refer to the point (i) before (above the canopy and at ground level). This was adapted to avoid any confusion: "30-minute fluxes of BVOCs and O3 above the canopy and at ground level".

Line 103: It also provides an opportunity to investigate the role of turbulent mixing. mixing times would be particularly important for short-lived compounds such as SQT, which react quickly with ozone.

The concept of turbulent mixing is already discussed earlier in the Introduction. In the current section, the term in-canopy chemistry is intended to implicitly account for turbulent mixing, as chemical processing depends on the residence time of compounds within the canopy. Therefore, we believe that this aspect is already captured in the existing text and does not require additional modification.

Line 114: In addition to this description, provide some information regarding the most common understory vegetation species.

The following sentence was added in the text: "Besides tree saplings, the understory vegetation is very sparse and is mainly composed of mosses (~ 76% of the understory vegetation in dry weight), shrubs (~ 15%, mainly Vaccinium myrtillus [L.] and Rubus species), and ferns (~ 8%)".

Line 114-115: Add a sentence that states the typical forest canopy height h. This is important for footprint estimation and in-canopy estimation of sources and sinks from concentration+sonic profile data. I cannot seem to find the canopy height listed anywhere in the manuscript.

We thank the reviewer for this suggestion. Mean tree heights are now reported from the last extensive tree inventory (2019) for each tree species as well as the overall mean tree height (26 m).

Figure 2: It would be useful if the setup schematic representation include some kind of indication of the forest canopy height. This would also illustrate which portions of the setup are above canopy and which are in-canopy. It would also be useful to add a height scale/reference of some kind to the schematic of the profile setup, as this would provide a point of visual reference for the vertical location of the various components of the tower setup relative to the forest's vertical canopy structure. You state the height of several components in the text but do not illustrate these heights in the figure.

We agree with the reviewer that the figure would benefit from greater clarity by including indications of canopy and concentration profile heights. The figure has been updated to show the height of each sampling point, and two tree illustrations have been added to indicate which levels are above and which are below the mean canopy height.

Line 139: State the typical residence time of sample air in the tower's Teflon tubing (travel time from tower inlet to PTR-ToF). How does this time compare (though not necessary to state/add in text) with the lagtimes determined during EC flux analysis? (This is somewhat related to the comment at Line 303)

As a first-order estimate, the residence time is expected to be around 10 s. While this information is already provided at line 310, it has been added at line 139 to present it directly to the reader.

Line 157-158: As noted earlier, it is useful and relevant addition to provide some information regarding the most common understory plant species at the study site.

The sentence has been revised to read: “a small part of this space is occupied by young woody vegetation, shrubs, mosses and ferns.”

Line 163-164: As previously noted, this height information should be illustrated in the Figure 1 setup representation as well.

The heights of sampling points have been added in Figure 2 (experimental set-up).

Line 177: To ambient atmospheric pressure or just into the operational pressure range needed by the T400 to function properly (not necessarily the same)? Please clarify

The additional KNF pump was used to return air at ambient atmospheric pressure, which falls within the pressure range required by the T400. Strictly speaking, the air is not brought to exactly 1 atm, but rather to the ambient atmospheric pressure inside the shelter. For clarity, the term “atmospheric pressure” was replaced by “local atmospheric pressure”.

Line 203: Please provide a citation regarding the EVR.

The following reference was added in the manuscript:

Piel, F., Müller, M., Winkler, K., Skytte af Sätra, J., and Wisthaler, A.: Introducing the extended volatility range proton-transfer-reaction mass spectrometer (EVR PTR-MS), Atmos. Meas. Tech., 14, 1355–1363, https://doi.org/10.5194/amt-14-1355-2021, 2021.

Line 207: A frequent "internal" mass scale calibration. Be sure to distinguish in the text between internal calibrations and external calibrations (i.e., VOC gas cal. standard from a bottle).

The word “internal” was added, as suggested by the reviewer.

Line 240-241: Is the transmission curve of this Ionicon PTR-ToF-MS linear with m/z in the range of 21.022 to 180 m/z? For Tofwerk's Vocus PTR-ToF-MS, the transmission curve can also be closely fit with a sigmoidal function. It would be useful to see the transmission results plotted for an example calibration run (perhaps such a Figure would be a useful addition to the Supplement). Is the transmission above 180m/z relatively close to unity?

The transmission of the PTR-ToF-MS was not linear across the m/z range from 21.022 to 180.937. A linear interpolation was applied between measured points. For m/z above 180.937, a plateau is not reached, and the transmission at higher m/z values is assumed equal to that at m/z 180.937 due to lack of direct information. This introduces larger uncertainties for high masses, but in practice, only m/z 205.195 (sesquiterpenes) was retained by the PAP software above m/z 180.937. For information, the concentration of sesquiterpenes at m/z 205.195 was quantified from the kinetic approach and therefore already carries a higher uncertainty compared to m/z calibrated from a gas standard.

Concerning the transmission results suggested by the reviewer, we refer the reviewer to Fig. S2, which presents the transmission curves obtained during calibration runs in 2022, 2023, and 2024. A direct reference to this figure was also added in the manuscript.

Line 218: You should provide a software reference for the IDA software in your reference list.

The following reference was added in the manuscript:

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, https://doi.org/10.1016/j.chemolab.2013.06.011, 2013.

Line 219: If one is available, you should provide a reference in the reference list for the PAP software as well.

The reference of PAP software is now given directly when presented, as well as within the “Code and data availability” section: https://github.com/bverreyk/PeakAreaProcessing, Verreyken et al. (2025a)

Line 231: I assume steps i, ii, and iii relate directly to the description of DBSCAN in Ester et al., 1996)? Otherwise, please provide some additional information/background regarding these steps or provide references that describe it.

The paper by Ester et al. (1996) describes the development of the DBSCAN algorithm. In the present study, this algorithm was applied to the mass-to-charge ratio space defined by the IDA peak-finding algorithm from the different IDA analyses to create m/z clusters. In a later stage, which is specific to this study, clusters were filtered based on criteria i, ii, and iii. The choice of these steps was made by the authors of the present study, with the objectives of ensuring peak stability, significance of concentrations, and interpretability of the data, as detailed in the manuscript.

Line 258: Provide a reference for this statement here.

We are not entirely certain which specific concept the reviewer is referring to when suggesting the addition of a reference. If the comment pertains to the determination of peak area precision, further details about error quantification are provided in the Supplementary Material. If, instead, it refers to the fact that peak areas obtained using IDA are inherently baseline-subtracted, we have added a reference to Müller et al. (2013) in the manuscript and in the Supplementary Material.

Line 277-279: You should cite relevant references for each of these methods/steps, or provide a general example reference at the end of the first sentence.

A reference to Aubinet et al. (2012), a widely recognized standard reference in the field, has been added.

Line 280: I would suggest an alternative word choice here, using "by" to replace "under" or "under low", as the wording here may suggest that only EC fluxes during low/negligible turbulence conditions were kept - EC flux analysis typically performs most poorly when there is little mixing, such as during stable nighttime conditions.

For clarity, the sentence has been modified to “EC fluxes are commonly filtered **to remove data collected** under low-turbulence conditions”.

Line 290: Why was the planar fit method not applied to both the TOP and TRUNK systems?

In general, we rather opt for the double rotation method because it is applied at the flux-averaging time scale, does not require long, stationary datasets, and is well suited to conditions with variable wind direction and stability. As explained in the manuscript, however, the double rotation did not provide satisfactory results for the TRUNK system, under low turbulence conditions. In that case, the planar fit method was therefore applied.

Line 303: As part of the VOC/ozone flux data collection, were the computer clocks for the sonic anemometer's datalogger and the PTR/ozone instrument synchronized in some way? This is a relevant consideration for lagtime analysis during long campaigns (weeks to months). If so, this should be noted in the text for this section. If not, given the multi-year length of observations, was clock desynchronization observed during the lagtime analysis (seems likely given duration of observations). How was clock-desync considered and/or handled? The latest version of innFLUX has a workflow step as part of the lagtime analysis where the clock drift can be fitted using regression and corrected for.

We agree with the reviewer that the synchronisation of logging systems is crucial for EC measurements and was not covered in the manuscript.

The following paragraphs were added/adapted at the beginning of the “Lag time determination” section:

“In EC measurements, the lag time represents the time delay between instantaneous measurements of the vertical wind component *w* and the tracer concentration *c*, arising, among other factors, from differences in electronic signal processing, spatial separation between wind and scalar sensors, and air transport through sampling lines (Aubinet et al., 2012). When *w* and *c* are recorded on separate data logging systems, it is therefore good practice to regularly synchronise their internal clocks in order to minimise clock drift, which would otherwise introduce an additional temporal offset between the two time series.

In the present set-up, *w* and *c* were recorded on two distinct laptops, which were frequently synchronised using a GPS time reference (MR-350, GlobalSat WorldCom Corporation, Taipei Hsien, Taiwan). However, while the computers themselves remained synchronised, the internal data acquisition system (DAQ) of the PTR-ToF-MS relied on a separate internal time axis, which exhibited a non-linear time drift, the origin of which could not be fully identified. As a consequence, the timestamps assigned to the mass spectra by the DAQ progressively became de-synchronised from the sonic anemometer time series. To overcome this issue, the evolution of this drift was monitored during each field campaign and used to correct for the DAQ-related time drift during post-processing. In addition, the DAQ was regularly restarted during the campaigns in order to minimise the accumulation of this time drift.

After correction for the DAQ-related time drift, the lag time between *w’* and *c’* was determined by maximizing their covariance within a physically plausible window (11–15 s) for each flux window and each m/z. If the maximum covariance occurred at the edge of the window, a fixed lag of 13 s was assigned. [...]”

Line 311-314: Could you explain this more? The innFLUX paper seems to indicate that time variability in flow rates could create a problem for this approach in the case of very weak flux signals.

We are not entirely certain which specific issue in the innFLUX paper (Striednig et al., 2020) the reviewer is referring to. In that study, Striednig et al. (2020) explain that estimating the time lag as the local extremum of the raw covariance function may lead to flux over- or underestimation, because the extremum can be strongly influenced by statistical noise, particularly for measurements with a low signal-to-noise ratio. To mitigate this issue, the authors propose estimating a single lag time from a subset of the data with high signal-to-noise ratio and applying it to the remaining dataset. However, this approach may result in flux underestimation when the actual lag deviates from the assumed single lag.

As an alternative, Striednig et al. (2020) suggest smoothing the covariance function to reduce the influence of statistical noise while still allowing for time-varying lag determination. They nonetheless point out that, even with smoothing, the identification of a meaningful extremum can become unreliable when fluxes are close to zero, potentially leading to inappropriate flux estimates.

We believe that the reviewer may be referring to this difficulty in identifying a well-defined extremum of the covariance function for a given averaging interval. In practice, when fluxes are very small, a non-physical extremum is often detected at the boundary of the physically plausible lag window (11-15 s in the present study). In such cases, the time lag is set to the nominal lag value. As also discussed in Striednig et al. (2020), these situations primarily occur when fluxes are close to zero. We consider that, under such conditions, any resulting error in lag estimation is expected to have only a minor impact on the associated flux, given its already very small magnitude.

Line 322: Are there any references motivating this approach which you can cite? If so please cite them.

The following references were added in the text:

Aubinet, M., Grelle, A., Ibrom, A., Rannik, , Moncrieff, J., Foken, T., Kowalski, A., Martin, P., Berbigier, P., Bernhofer, C., Clement, R., Elbers, J., Granier, A., Grünwald, T., Morgenstern, K., Pilegaard, K., Rebmann, C., Snijders, W., Valentini, R., and Vesala, T.: Estimates of the Annual Net Carbon and Water Exchange of Forests: The EUROFLUX Methodology, vol. 30 of Advances in Ecological Research, pp. 113–175, Academic Press, https://doi.org/https://doi.org/10.1016/S0065-2504(08)60018-5, 1999

Wintjen, P., Ammann, C., Schrader, F., and Brümmer, C.: Correcting high-frequency losses of reactive nitrogen flux measurements, Atmospheric Measurement Techniques, 13, 2923–2948, https://doi.org/10.5194/amt-13-2923-2020, 2020.

Line 351-352: last access date here may be required - "(https://github.com/icos-etc/RFlux; last access: day month year)". The toolbox that was adapted will also require a reference in the reference list.

As the toolbox is directly linked to and described in Vitale et al. (2020), which is cited in the manuscript, we consider that an additional reference to the toolbox in the reference list is not required.

Line 402: formaldehyde may not be the best example to include for a PTR, due to its back reaction with water vapor and humidity dependence. As a suggestion, if humidity variability was a significant factor during these plume events, perhaps "such as methanol and acetic acid" for this portion of text, with formaldehyde and additional complications discussed separately, may be more appropriate.

We agree with the reviewer that changes in the concentrations and fluxes of formaldehyde during plume events may be influenced by variations in relative humidity. As our analysis did not investigate this aspect in detail, we have revised the sentence to refer only to methanol and acetic acid, as suggested by the reviewer.

In Loubet et al. 2022 (cited in the text's flux analysis section with respect to WPL corrections), formaldehyde is noted to have large deposition, yet the authors choose not to further discuss it in detail since the uncertainties in its concentration measurement, especially in response to water vapor, were deemed too large to provide consistent measurements.

It seems that formaldehyde should also be handled here with caution as well.

We acknowledge the uncertainties associated with formaldehyde flux measurements due to back reactions with water vapor in the PTR-ToF-MS instrument. We considered that addressing this issue properly requires a dedicated discussion, which is provided in Section 3.4.1, where some VOC fluxes are discussed individually. The conclusion of this discussion is consistent with Loubet et al. (2022): formaldehyde fluxes should be considered with caution and treated as a first rough approximation. In Section 3.2.2, by contrast, we aimed to provide a general overview of the typical concentrations and fluxes of VOCs detected at BE-Vie, without discussing each compound in detail at this stage.

Line 445: Why was the GEddySoft Software not used here as well for ozone fluxes?

At the beginning of the simultaneous ozone and VOC flux measurements, GEddySoft was still under development and therefore not available for flux computation. To ensure the proper functioning of the ozone setup, we quickly calculated ozone fluxes using EddyPro, which was available and with which we were already familiar. Since EddyPro projects had already been parameterized for ozone flux computation, we chose not to recompute the ozone fluxes once GEddySoft became stable and ready for use.

Line 668: Sesquiterpenes etc are also, generally, emitted at lower rates than MT and Isoprene.

We consider that the impact of VOC emission on ambient concentrations is already discussed at l. 672: “Local emissions also influence this pattern, as suggested by the circle sizes. Most of the strongest emissions correspond to ions with m/z values below 80, while heavier compounds tend to show weaker emissions”.

Line 659-660: The level of detection (3xSD) and level of quantification (10xSD) are different - did you detect any compounds with greater m/z than SQT which did not meet the level of quantification? i.e., did you observe any oxygenated SQTs, heavier photooxidation products, etc., in your measurements?

There was a stable cluster identified in the 2024 campaign that can be related to $C_{15}H_{24}O$. However, this cluster was not selected for further quantification because the signal was not sufficiently significant according to the criteria used in the present study. Moreover, as there were no clusters with the same mass identified in the campaigns for 2022 and 2023, we do not consider this for the current work. In the future, we may revisit the dataset with alternative methods to tease out additional information in specific case studies but for this general overview, it is considered out of scope.

Line 670: While a general trend, not strictly true for all compounds.

We agree that this is indeed a general trend. To account for this, the sentence has been revised to: “This pattern largely reflects the tendency for heavier compounds to exhibit lower volatility.”

Figure 6: Note: See also comments for Table 3.

Figure 6 needs to be revised to either report only identified VOCs (51 reported in the Abstract) or (alternatively) by only reporting ion signal on the y-axis (and by cutting the dot-size representation of EC signal strength or attempting to present it via alternative units, for example based on passing the cps timeseries through EC flux analysis). The former seems likely to be the more practical approach.

This comment, together with several of the following ones, highlights a lack of clarity regarding how protonated compounds and fragment ions are treated in the manuscript. To address this issue, we first clarify here the overall approach now beign used in the manuscript. The specific points raised by the reviewer are then addressed individually under each corresponding comment.

In total, 74 m/z values were retained by the DBSCAN algorithm, including both protonated compounds and fragment ions. No water clusters or isotopes were considered, with the exception of m/z 80.042 (protonated benzene isotope), which provides improved quantification of benzene (as discussed in the manuscript). Both protonated compounds and fragment ions are reported in Table S3 and in the online database, as temporal variations in their relative abundances can reveal shifts in chemical processes, ionization conditions, or source contributions.

However, as now explicitly stated in the manuscript, in the analyses and figures presented in the Results section, the ion signal at only one m/z value (either of the protonated VOC or of a fragment, depending on which one has the highest proton transfer/fragment yield - see Table S3) was taken into account for quantification of each VOC to avoid double counting and redundancy. This resulted in a list of 62 VOC species that were considered in Table 3.

Among the 62 detected VOCs, 48 were found to be significantly exchanged at the TOP system based on the three-step comparison with flux limits of detection.

To help the reader reconcile the different numbers presented at the beginning of Section 3.2.1, we added the following sentence after describing the different ways of counting VOC-related ions: “In summary, the DBSCAN algorithm retained 74 m/z values corresponding to 62 VOCs, of which 48 showed significant exchange”.

We also draw the reviewer’s attention to the fact that all the numbers reported above were updated following the comments of Reviewer 2. Specifically, m/z 63.044 and 77.060, previously assigned to ethanediol and propanediol, respectively, were more likely acetaldehyde and acetone water clusters and were therefore removed from the list of 74 m/z values. In addition, m/z 107.086 and 121.101, potentially corresponding to MT and SQT fragments, respectively, were not considered in the list of 62 unique VOCs. Finally, the protonated benzene isotope at m/z 80.058 had been omitted from the previously reported lists and has now been included.

Regarding the reviewer’s specific comment, Figure 6 was updated to represent only single VOCs by removing duplicate signals associated with fragment ions or protonated compounds.

In the current version of the figure, mean VOC mixing ratios (y-axis) are compared to m/z (x-axis) for the 76 detected ions. Due to fragmentation and other related signals, this means that these 76 correspond to an inherently smaller number of VOCs: 76 VOC-related ions -> 60 VOCs + fragments (based on Table 3) -> 51 VOCs. In practice, only these 51 identified VOCs represent "real" ecosystem VOC concentrations and fluxes - how are the others converted from cps to mixing ratios here (and subsequently, to fluxes)? For the fragments (9), are they being used to determine the parent VOC concentration (with the figure essentially showing double-counting of certain VOCs?). What about the 16 other signals? This is not made clear in the figure nor its caption, which appears to host multiple instances of double-counting for the fragments (if converted to mixing ratios based on parent VOC ion mass). Of the eight ions featured as the most exchanged, at least two of them are double-counted (isoprene and MT). This ambiguity should be eliminated.

As explained above, Figure 6 has been revised to include only the 62 detected VOCs, regardless of whether their fluxes are significant or not. The purpose of this figure is to illustrate the diversity of the detected VOCs, without addressing flux significance at this stage. To clarify the number of VOCs shown in Figure 6, both the sentence introducing the figure (“The mass range of the ion species used for quantification of the 62 detected VOCs, as well as the range of their average mixing ratios and mean absolute fluxes, are illustrated in Fig. 6”) and the figure caption (“Mean mixing ratio of the 62 detected VOCs over the whole campaign (in log scale) as a function of the mass-to-charge ratio (m/z) of the ion species used for their quantification”) were revised accordingly.

In addition to the ions displayed in Figure 6, we clarify here how VOC concentrations and fluxes associated with fragment ions are reported. For fragment ions corresponding to VOCs not included in the calibration standard, VOC mixing ratios were quantified using the kinetic approach, following the same methodology as for protonated compounds, by computing a sensitivity that accounts for the fragment yield (see Section S2.1.3). VOC fluxes associated with fragment ions and expressed in carbon units were calculated by accounting for the carbon mass of the corresponding parent VOC. This methodological detail has been added to the manuscript at the beginning of Section 3.2.2.

Finally, we recall that within the list of 62 VOCs, each compound may be quantified either using the ion signal corresponding to the protonated compound or to one of its fragment ions. As stated in the manuscript, “to ensure the best possible quantification, we used the ion signal at the m/z associated with the highest H_3O^+/VOC product ion yield.”

Table 3: One (potentially) significant qualitative issue with this table is the inclusion of parent ion fragments (9) with VOC fluxes and concentrations. The fragment ions are generated within the PTR instrument and are artifacts of the measurement. Just from a reading of Table 3 and the table caption, it is not clear whether you are reporting the parent VOC concentration & flux based on the fragment ion signal (i.e., simply providing another determination of the parent VOC conc. & flux based on the fragment), or for the fragment itself (i.e., converting from cps to mixing ratio based on the fragment’s mass). The latter would be a significant issue (though from a reading of Figures 8 & 9, this does not appear to be the case). Therefore the reporting of fragments here, and how they are used to get to a mass mixing ratio (similarly for flux), needs to be clarified.

Table 3 has also been revised to report only one ion per VOC. The caption now explicitly states that “only the 48 VOCs exhibiting significant exchange are reported and listed in descending order of flux magnitude.” The use of the term *VOCs* rather than *VOC-related ions* emphasizes that multiple ions corresponding to the same VOC are not counted separately.

While Table 3 no longer contains duplicate ions (i.e., multiple ions corresponding to the same VOC), this does not imply that fragment ions are omitted. Fragment ions are not considered artefacts but rather an additional means of quantifying a given VOC. In Table 3, as discussed in the manuscript, the ion signal at the m/z associated with the highest H_3O^+/VOC product ion yield was used. Whenever a fragment ion is used for quantification, this is clearly indicated in the “tentative attribution” column, as explained in the caption: “For VOCs quantified based on their fragment ion, the chemical formula of the protonated compound is indicated.” The integer mass of the parent VOC is also reported in Table S3 for each VOC.

As noted in the above comment, for VOC fluxes quantified from fragment ions in mass units, “molar fluxes were converted to mass units using the molar mass of the corresponding VOC,” as now detailed at the beginning of Section 3.2.2.

If the former (i.e., double-reporting certain VOC concentrations and fluxes), I would suggest reorganizing the table and clarifying in the caption text that the fragment rows are merely providing another estimate of the parent VOC’s concentration and flux. While this double-accounting of parent VOC conc. and fluxes is quite interesting for its own merits (and may provide indirect qualitative information about the state of the PTR instrument and chemical speciation of a VOC - for example the MTs, due to the differing fragmentation rates among MT compounds, since the external mass calibration is based on a single MT compound), another (quick) solution would be to simply remove these fragment rows from the table.

We have reorganized Table 3, not by removing fragment ions, but rather by removing duplicates, as already discussed.

There is no ascending/descending ordering to the m/z values of the table rows. What is the logic behind the ordering in which ions are presented in Table 3, Eddy-covariance signal strength? The rows could also be sorted by m/z, or the property by which rows are ordered could be included as an additional column.

The caption of Table 3 indicates that the ions are listed in descending order of flux magnitude. We chose this ordering rather than sorting by m/z to directly highlight the VOCs with the largest exchange.

Line 680-681: These cycles also reflect changes in atmospheric conditions, such as diurnal changes in atmospheric turbulent stability and boundary layer behavior. Stable nighttime conditions and low boundary layer height can cause an emitted compound to accumulate to high concentrations (for example, can be the case for MT emission from needle-storage at night). This should be noted here as well.

The impact of atmospheric stability within the boundary layer is already discussed later in the manuscript, particularly in the interpretation of nighttime concentrations. We nevertheless agree that this process can be mentioned among the factors explaining the observed concentration profiles at the beginning of this section. Accordingly, the first paragraph of Section 3.3 has been revised to read:

"These exhibit pronounced cycles, albeit with differing phases and amplitudes, likely reflecting distinct sources, sinks, and reactivity. In addition, these patterns are modulated by atmospheric stability within the boundary layer, which influences vertical mixing and the vertical distribution of compounds. Their vertical concentration profiles may therefore help identify sources and sinks at different heights, as well as the role of boundary-layer dynamics."

Line 697: Also seen in the vertical ozone profile for boreal forest BVOC measurements presented in Petersen et al. 2023.

We thank the reviewer for this reference which was added in the manuscript.

Line 821: Given the additional complications with formaldehyde, perhaps this should be pointed out in the methods section as well.

In the Materials and Methods section, we aimed to remain as holistic as possible with respect to PTR-ToF-MS signal processing and flux calculation, by describing procedures that are generally applicable to all measured VOCs. Issues related to compound-specific interferences, such as those affecting formaldehyde due to back reactions with water vapour, were therefore not detailed at this stage. Instead, these aspects are addressed in the Results and Discussion section, where the behaviour and uncertainties of individual VOCs can be discussed more in detailed, and when possible, supported by the observations. We consider that maintaining this separation between general methodology and compound-specific discussion ensures consistency with the treatment adopted for other VOCs throughout the manuscript.

Figure 8: Panel labeling: there is no mention in the figure caption regarding the meaning of the figure labeling (a, b, c, d, etc.). Since a Figure caption outlines the visual elements of a figure, the general logic behind the order of panel labeling should be indicated as well.

To be efficient with caption space, I would suggest modifying the caption's first sentence to something like "Seasonal evolution of VOC fluxes measured by the TOP system over the years (a-e) 2022, (f-k) 2023, and (l-o) 2024.".

We thank the reviewer for this suggestion that was implemented and improve the clarity of the Figure and its caption.

Small suggestion: If the m/z legend can be divided into two columns (6-by-2 or 2-by-6) and placed into the space available in the lower-left corner, the entire figure (including text) can be made larger (i.e., more reader-friendly)

We thank the reviewer for this suggestion. This has been implemented and does indeed improve the readability of our figures.

Figure 9: Similar to comment for Figure 8, please indicate in the Figure 9 caption the meaning behind the panel labeling (a, b, c, etc.) - for example "(a-f) 2023 and (g-h) 2024".

Figure 9 caption was adapted accordingly.

Line: 878 Given the discussed year-to-year differences in the select VOC fluxes presented in section 3.4.2 and the availability of tree species distribution data around the site, the text here (for example, at lines 889-895) can be improved by providing some information about the approximate percentages of the different tree species that fall within each of the yearly footprint climatologies. In the final paragraph of section 3.4.2, the use of species maps such as Figure 1 with flux footprint analysis to better attribute observed fluxes is discussed, but an attempt (even if very simplified) with the readily available Figure 1 data was never made here.

We agree with the reviewer that besides a visual inspection of Figure 1 on which the description of isoprene vs. monoterpenes emissions is based on, percentages of tree species within the footprint would better serve our purpose here. To this end, we calculated the percentages within the 70% footprint (area with a high contribution to fluxes, and where the tree inventory is nearly complete) and reported them in the text below, which was adapted:

"In 2022, winds predominantly originated from the south-west sector, where beech was the dominant tree species, accounting for 62% of the vegetation within the 70% flux footprint (followed by 24% of silver fir; Fig. 1). Measurements conducted in 2009 at the same site by Laffineur et al. (2011) identified beech as the main monoterpenes emitter among the species present at BE-Vie. The higher monoterpenes emissions in 2022 appear to support this finding. In contrast, in 2023, winds mainly originated from the north-east sector, which was dominated by Norway spruce, representing 61% of the vegetation within the 70% flux footprint, followed by Douglas fir (17%)."

Beyond this first-order, footprint-based quantification, a more detailed analysis could indeed further refine the attribution of the observed VOC fluxes to specific tree species. For example, flux footprints could be computed at the half-hourly scale, and for each footprint the corresponding tree species composition could be quantified. The resulting time-resolved species distributions could then be directly related to the measured fluxes. While such an approach would provide valuable additional insight, it would require a substantially more complex analysis framework and therefore lies beyond the scope of the present study.

Line 973-975: Some brief additional description/info is required here to link the Abstract text with that of the conclusion. In the Abstract, it states that 51 significantly exchanged VOCs were identified. Yet, here in the conclusion it simply states the study identified "60 significantly exchanged ions, among 76 VOC-related signals". The intended meaning for the number of significant exchanges involved is somewhat unclear (i.e., a loose end) – ions, VOC-related signals or VOCs? Since Figure 6 indicates that there were 76 detected ions with significant exchange - I assume the 60 refers to the number of significant EC signals from the processed ion timeseries data. How does this 60 relate to the 51 described in the abstract - are some of the described exchanged ions not VOCs, etc? It appears so. Table 3 also includes 60 m/z ions with attributed formulae, but also includes ion fragments (9).

We consider that this comment synthesises several aspects already addressed in the previous comments.

In the initial version of the manuscript, 51 significantly exchanged VOCs were reported in the Abstract, while 60 significantly exchanged ions were mentioned in the Conclusions. We agree with the reviewer that, although these numbers referred to different groupings (with or without double counting of ions related to the same compound), using different values could lead to confusion.

To resolve this issue, we decided to consistently report the number of VOCs rather than VOC-related ions throughout the manuscript. Accordingly, the sentence in the Abstract was revised to: "Using a PTR-ToF-MS and an open-source data-processing workflow, we identified 48 significantly exchanged VOCs." The corresponding sentence in the Conclusions section now reads: "The processing of VOC data resulted in the identification of 48 significantly exchanged VOCs among 74 VOC-related signals."

We also recall that Figure 6 was revised to display concentrations and fluxes for the 62 detected VOCs, irrespective of the significance of their fluxes, which differs from the 74 VOC-related signals. Similarly, Table 3 was adapted to report concentrations and fluxes only for the 48 VOCs exhibiting significant exchange.

Since the number of significantly exchanged VOC compounds is one of the core results of your study, please clarify the final accounting regarding the total number of significantly exchanged VOC compounds (51) here in the conclusion via a sentence, etc.

In the Conclusions, the sentence was revised to "The processing of VOC data resulted in the identification of 48 significantly exchanged VOCs among 74 VOC-related signals, based on a single representative ion m/z per VOC and fluxes frequently exceeding the detection limit."

Table S2: In the Supplement's Table S2 caption, for the gas standard calibration bottles used, please provide the name of the calibration standard manufacturer

The reference to the gas standard calibration bottles has been added in Table S2 caption.

Figure S14: Panel labeling (same comment as for Figure S15 and Figure 8 in the main text): Please indicate in the Figure S14 caption the meaning behind the panel labeling (a, b, c, etc.)

Figure S14 caption was adapted as suggested.

Figure S15: Panel labeling (same comment as for Figure 8 in the main text): there is no mention in the figure caption regarding the meaning of the figure labeling (a, b, c, d, etc.). To be efficient with caption space, I would suggest modifying the caption's first sentence to something like "Seasonal evolution of VOC fluxes measured by the TOP system over the years (a-e) 2022, (f-k) 2023, and (l-o) 2024.".

Figure S15 caption was adapted as suggested.

Table S3: The total number of presented VOC-related ions in the table should be mentioned in the table caption.

This number was added in Table S3, as well as Table 3 (reported mean fluxes and concentrations for significant VOCs).

For Table S3, the Limit of Detection (LoD) should be presented as a table column if possible. Were the LoD values relatively stable throughout the multiyear campaign? If not, then please include min/max or mean ± SD, etc., for the LoD values if possible.

We thank the reviewer for this suggestion. The following column was added to Table S3: "3-year average limit of detection with the associated standard deviation from 1 min concentrations"

Technical comments referee #3

Line 8: Commenter 2 suggests replacing "pipeline" with "software". I would suggest either this, "workflow", or "workflow software", as it cannot be confused with a physical object but still conveys the meaning that the analysis was carried out through a series of steps which carried out specific tasks/objectives as part of the full analysis.

We thank the reviewer for this suggestion.

“Using a PTR-ToF-MS and a dedicated open-source processing pipeline” becomes “Using a PTR-ToF-MS and an open-source data-processing workflow”.

Line 200: Analyzer or instrument? Here, combined with its use at Line 205, the use of the term is somewhat confusing/fluid. I would suggest "PTR-ToF-MS" or "PTR-ToF-MS instrument".

We understand the potential confusion when mapping line 200 with line205, and opted for “PTR-ToF-MS instrument” for clarity.

Line 205: Spectrometer? Here the ToF appears to be discussed independently of the whole PTR-ToF-MS instrument.

We understand the potential confusion and replaced “analyser” by “spectrometer”.

Line 207: Provide manufacturer information if available - company name + location, etc.

The manufacturer was added in the manuscript (Ionicon Analytik GmbH, Innsbruck, Austria)

Line 283: I believe it is spelled "innFLUX". After reviewing the original paper and code repository documentation, it appears that the first letter of the term is only capitalized in the title (it's first word) of that paper.

We thank the reviewer for this correction, which has been implemented in the manuscript.

Line 444: "larger" or "greater"?

We thank the reviewer for this comment. However, as we could not ascertain which word is being referred to at line 444, we were not able to incorporate a change.

Line 595: Requires a last access date and a reference in the reference list.

The last access was added, as well as a reference to the Python package in the reference list.

Line 627: phrasing should be checked here - benzene itself is not an isotope.

The sentence has been adapted into “One notable exception is protonated benzene (m/z 79.054), whose peak is entangled with that of protonated hydrated acetic acid (m/z 79.039). This entanglement is reduced for the ^{13}C isotopes of these ion species (at m/z 80.042 and 80.058, respectively) due to the relatively higher abundance of the protonated benzene isotope. As a result, only the protonated benzene isotope signal was considered for benzene quantification, eliminating any risk of double counting.”

Line 610: Phrasing - all deciduous trees, or just European beech? "(i.e., Fagus sylvatica)" might work better here. Consider also using the common name, as the latin name has already been introduced in the site description section.

As European beech is by far the dominant deciduous tree species at BE-Vie, “deciduous trees” was replaced by “beeches”. In line with the reviewer’s recommendation, Latin names were replaced by vernacular names throughout the manuscript, except at their first occurrence.

Line 685: Perhaps it would be more appropriate to say for example "reaffirms", etc. Also, it should be made clear that these observations apply to tropospheric ozone.

The verb “confirms” was replaced by “supports”, and it was specified that we are here discussing tropospheric ozone.

Line 689: "cessation of photochemistry" - with sunset (i.e., loss of solar radiation). The sentence text could be improved somewhat by adjusting the phrasing, since there is substantial time between mid-afternoon and sunset.

The sentence has been revised to clarify that the decline in ozone concentrations after the mid-afternoon peak occurs as photochemical production decreases with declining solar radiation, rather than abruptly ceasing. This better reflects the temporal evolution between the afternoon maximum and sunset.

Line 750: "transport's"

A word was missing in the sentence highlighted by the reviewer. The sentence now becomes:

“Source apportionment studies can identify the impact of specific sources on local concentrations by using positive matrix factorisation (Song et al., 2024), by looking at **how** meso-scale transport affect**s** the concentration dataset (Simon et al., 2023), or by using a combination of both (Verreyken et al., 2021)”

Supplement section 2.1.3: The Dusanter reference appears twice in the reference list (the entries for Dusanter S. et al. 2025a & 2025b are identical). The first name initial should also be omitted when citing (i.e., "Dusanter et al., 2025").

We thank the reviewer for this remark. We confirm that both references are identical, and the reference list was adapted accordingly.

Figure S15 caption: There is a font/text rendering issue with the symbols here - it states for emission ”other ¿ 0” and for deposition ”other ¡ 0”. I assume it is meant to be ”other > 0” and ”other < 0”, respectively.

We thank the reviewer for highlighting this issue which has now been resolved.

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