RESPONSE TO THE REVIEWERS (ACP-2020-595)

We thank the reviewers for their encouraging comments and their careful reading of the manuscript. We have addressed each one of the points raised, and have altered text, figures and tables wherever appropriate. We look forward to having the editor's approval to submit a revised manuscript to be considered for final publication in ACP.

The referees' comments followed by our responses (R) are below.

**Juho Aalto (Referee #1)**

Seco et al. provide high-quality measurement data representing very relevant study object, VOC emissions from subarctic peatland and lake. Given how rare such datasets are, the results are obviously worth reporting, though the shortness and temporal limitedness of the data set apparent limitations concerning the data analysis and conclusions.These limitations should not be considered as weaknesses of the manuscript – they are more common features that should be taken into account, than any reason for rejection.

Overall, the manuscript fulfills the review criteria of ACP. The scientific question is well within the scope of ACP, both the data and conclusions are mainly valid, as well as the measurement and data analysis methods. The manuscript itself is mostly well structured and clearly expressed. There are some minor issues in the manuscript that may need to be reconsidered; those issues will be listed in my detailed comments.

Within the following section, I'll go through my main concerns regarding the data analysis and conclusions. Please note that many of my comments are more suggestions and questions aiming to clarify the results, than sound challenging based on solid scientific evidence. Chances are that many of the aspects pointed out by me have already been taken into consideration during the data analysis and manuscript compilation. In that case, I'd like you to once more consider each aspect, in order to ensure that the data analysis and conclusions are balanced and comprehensive.

R: We are glad that the referee considers our dataset and manuscript worthy of publication and thank him for his time in reviewing our work.

The obvious scientific highlight of the manuscript is the high temperature sensitivity of isoprene emissions from subarctic fen. The finding is rather exceptional and has potentially important implications, in so far as it requires and deserves extra careful consideration and special scrutiny. Regarding the analysis and conclusions reported

in the manuscript, most of my concerns are either directly or indirectly related to this temperature sensitivity finding.

Conducting any scientific measurements is always by nature imperfect. To analyze something like temperature response of VOC flux, one has to take into consideration at least five aspects: 1) VOC flux per se, as a natural phenomenon, 2) Temperature per se, 3) Assumed relationship between T per se and VOC flux per se, 4) Measured estimate of VOC flux, and how complete or incomplete view that gives for VOC flux or emission per se, and finally, 5) Measured T, and its' ability to describe the thermal conditions relevant for VOC flux or emission. Failing with any of these aspects causes the risk that the analysis and conclusions on temperature response will be partly or fully misleading or incomplete.

I find no special need to believe that there would be any major shortcomings in the VOC flux measurement results of the manuscript. They also likely represent reality with reasonable accuracy, so aspects #1 and #4 should be in order. Also, it can be quite safely assumed that T response follows some exponential form – that is so common feature in this field – so also the aspect #3 can be left above suspicion. That leaves us with aspects #2 and #5, T per se and measured T as an estimate of that.

The obvious merit of the manuscript is that it includes both air T and surface T as estimates for thermal conditions relevant for VOC flux. However, I suggest that a little bit more attention would be paid on discussing, how completely or incompletely these estimates are able to reflect the true thermal conditions controlling VOC (isoprene) sources. How sensitive these T measurements are to fail in producing accurate and precise description on relevant thermal conditions? Please note, that for example figure 5 gives the impression that if there is rather minor tendency to underestimate high surface temperatures and overestimate low surface temperatures, that would likely have a major impact on detected T response. I have no specific reason to believe that there would be such tendencies for under-/overestimation, but it's especially important to take even the slightest chance for those into account when exceptional T sensitivity is proposed.

R: It is true that a minor tendency to underestimate the high surface temperature and overestimate low surface temperatures could change the $Q_{10}$ of the temperature response. It is also true that our surface temperature readings were taken at the ICOS station, several hundred meters from the footprint of our measurements, but that is the only (and therefore, the best) vegetation surface temperature dataset we could obtain. We did measure with thermal cameras closer to our EC tower but, unfortunately, they were not functioning during the short time span when the BVOC fluxes were functioning. Furthermore, it seems reasonable that the diurnal profile of surface temperature at the ICOS station would not differ much from the temperatures in our footprint area, located within the same mire complex. With that said, we also agree with the reviewer in that there is no reason to believe that the surface temperatures would have such tendencies of under- and overestimation.

In the manuscript, G93 emission model is applied for analyzing the isoprene fluxes. The core assumption is fairly expressed: it is assumed that the fen vegetation is a single big leaf. This assumption is of course inevitable, because there is lack of any other proper way to conduct model analysis on such flux data. However, it includes also significant limitations, mainly because of the inability of unshaded PAR measurement and single T measurement to reflect the true thermal and light conditions controlling VOC sources. Again, these limitations doesn't mean that one shouldn't use the model approach; one should just keep in mind that these limitations may complicate drawing the conclusions.
Although the fen surface vegetation is structurally very simple when compared to for example forest canopy, it still includes self-shading, causing full continuum from full light to totally shaded parts within the shallow layer of vegetation. This degree of self-shading varies significantly depending on the angle of incoming radiation and/or proportion of diffuse radiation on total radiation. Therefore, any above-surface PAR measurement is judged to fail in fully describing the light conditions within the surface vegetation layer. Similarly, there is T gradient within the vegetation layer, which can't be properly described by air T measurement or even surface T measurement. Again, I have no specific reason to believe that your results would be untypically imprecise or inaccurate in this sense. Based on results presented in the manuscript, it's more and more obvious that models like G93-approach, especially CLxCT as such but also any form of T dependency, works best with simple structures, such as tree leaves. However, when they are applied for more complex structures such as surface vegetation layer, they struggle if the gradients in light and T environment are not described in detail. It's not that G93 or any other model or dependency description would be useless when used with 'single big leaf assumption' in case of complex structures, it's just that special caution is required when relevant findings are tried to distinguish among the features of model, assumptions and incompleteness of recorded environmental drivers. This is not stated as a challenge for the manuscript, but it's more to encourage you to once more consider, which of the conclusions based on findings and features presented for example in figures 5 and S5 are well-founded, given the limitations of 'single big leaf assumption' with complex vegetation structure.
R: A similar 'big-leaf' analysis with the G93 algorithms was published several years ago for a *Sphagnum*-dominated fen in Southern Finland (Haapanala et al 2006). In that case, the authors tried to run a modification of the G93 model by simulating different light penetration inside the 2.5 cm deep active moss carpet. They concluded that there was no substantial improvement and that it was better to use the original G93 algorithm. Of course, the canopy of our fen was taller and more open than a moss carpet, because it was dominated by tall graminoids, and thus more prone to light and temperature differences at different levels.
First, we decided to keep the G93 in its original, simple form, not only because it is simpler and easier to calculate (therefore it is arguably better because it requires less "specialized" input data) but also because it allows better comparison with other studies that used the same approach in other ecosystems, such as the abovementioned fen in Finland. Second, if the surface temperature (and PAR) values that we used represented only the highest temperatures (and PAR) of the canopy, found only at the very top of the canopy, then we could assume that the canopy as a whole would experience lower temperatures (and PAR) due to self-shading closer to the ground. However, the ecosystem-scale isoprene fluxes we measured already represented the mix of the fluxes of the different levels the whole canopy. Considering these facts in Fig. 5, the resulting modified figure would be that the ecosystem isoprene fluxes would remain in place but the corresponding leaf (surface) temperatures, or at least the highest temperatures, would become lower than they are currently shown. Thus, the temperature dependency of isoprene fluxes would either remain the same (with fluxes starting to rise at lower temperatures than currently shown) or be even steeper than currently shown in Fig. 5. Nevertheless, in this case, the vegetation surface temperature sensor measured the temperature averaged over its field of view, where there were sunlit and shaded regions. All these facts suggest that the high temperature response seems to be a robust finding. Of course, future research could try to disentangle the contribution of the different layers of the canopy to the ecosystem isoprene flux.

From results and discussion as well as from figure S5 one gets the impression that light is not the primary control of fen isoprene fluxes. However, based on figures 2 and 3 there is remarkable similarity between PAR and fen isoprene flux. Or to be exact, at first glance there is similarity, but with a closer look there is also distinctive differences. First, before noon there is little variation in isoprene flux whereas during afternoon hours there is more variation. There is no similar bimodality in PAR recordings, but in air T there is some bimodality (figure 2), so it's obvious that thermal conditions have some effect on this difference between the different degree of variation in isoprene flux during morning hours and afternoons. Also, during morning hours PAR typically reaches value of 400 µmol m-2 s-1 soon after 6 o'clock in morning (which I believe should correspond to CL=0.8, after which the isoprene fluxes tend to differ from zero, figure S5), but the detected isoprene fluxes in figure 3 differ from zero only some hours later. Overall, it would be very interesting to understand why the dynamics in fen isoprene fluxes differ between morning hours and afternoons. Would there be any chance to deepen the analysis in this sense? Also, do you have any guess why PAR=400 µmol m-2 s-1 looks like a threshold value for fen isoprene flux? What does that value for detected PAR would mean in regard to light conditions within the surface vegetation layer?

R: These are all interesting questions; unfortunately, the present dataset does not encourage partitioning (morning/afternoon) given the limited amount of data points available. Future datasets with higher data availability may be used to investigate these suggestions.

Detailed comments:

L34-56: This paragraph has all the right ingredients, but I felt that it's somehow difficult to follow. Please consider at least dividing it to two or more paragraphs (for example cut it from L45); or any other way to make this paragraph just a bit more easier to follow.

R: Following the suggestion, we have divided the paragraph into two, cutting from line 45.

L126: Use of the term 'teflon' here and elsewhere in the manuscript. Please consider if the term could be removed. Originally, it's commercial brand-name. It's scientifically inexact, because nowadays it can refer to practically any fluoropolymer. And the exact name of your tube material is already mentioned in the same sentence.

R: We have now removed the term 'teflon' in this sentence and replaced it with PFA in the following sentence, the only two places where it appeared in the original manuscript.

L126: Please mention inner diameter instead of outer diameter, because the inner diameter is more relevant for the context.

R: We have now added the internal diameter of the tube: 1/4''.

L168: Was the T/RH probe equipped with radiation shield? Was it passively or actively ventilated? These details matter when one tries to judge how well the recorded T represents air T per se.

R: The temperature probe was equipped with a radiation shield that was passively ventilated. We have now added this information to the manuscript.

L230: This sentence is missing context. Emission from where? Please rephrase to clarify the context.

R: We have now given context and rephrased. The new sentence reads:

> Research on isoprene emissions from plant leaves has established that the instantaneous isoprene emission rate depends on the short-term (seconds to hours) light and temperature conditions (Monson et al., 2012).

L254-255: Would there be difference in these Q10 values between morning hours and afternoon hours? Based on figure 3, there may be different type of response to environmental conditions between morning hours and afternoon hours. I understand that the lack of data points having high PAR somewhat limits partitioning this dataset between morning hours and afternoon, but what if you include also data with PAR just below 1000 µmol m-2 s-1, let's say starting from 900 or 800 µmol m-2 s-1? Using PAR=800. . . . . .1000 µmol m-2 s-1 shouldn't be a problem, because at 800 µmol m-2 s-1 the CL is already > 0.96. These are suggestions that not necessarily lead to any reasonable result, but in case you haven't considered them earlier, they would potentially be interesting. Or what do you think, wouldn't it be even more unexpected if there is difference in T sensitivity between morning hours and afternoon?

R: Again, the morning/afternoon partitioning is an interesting question but this dataset is not the most appropriate for these kind of partitioning given the low number of available isoprene flux observations (half-hour data points with PAR ≥ 800 µmol $m^{-2}$ $s^{-1}$ and concurrent surface temperature readings were only 35 and 31, respectively, for morning and afternoon). Nevertheless, it could very well be that there are differences along the day in the response to environmental variables, as some studies have found an influence of the circadian rhythm on isoprene emission fluxes (Hewitt et al, 2011). However, this needs more data for the analysis.

Following the reviewer suggestion, we have tested the temperature response with data points measured at PAR ≥ 800 µmol $m^{-2}$ $s^{-1}$, and included the following discussion in the appropriate section of the manuscript:

> For our calculation, we used only emission data points for which light was not a limiting factor (i.e. PAR ≥ 1000 µmol $m^{-2}$ $s^{-1}$) to avoid interference from the correlation between light and temperature when fitting the temperature response. The $Q_{10}$ of isoprene emission in response to vegetation surface temperature was 14.5 and the $Q_{10}$ in response to air temperature was much higher, 131 (Fig. 5). Including in our calculation emission data points measured at PAR ≥ 800 µmol $m^{-2}$ $s^{-1}$ increased the number of data points involved (from 52 to 66 at PAR ≥ 1000 and ≥ 800 µmol $m^{-2}$ $s^{-1}$, respectively) at the expense of potential light-response interference, although according to the G93 model the light-response effect would be small ($C_L$>0.96 at PAR=800 µmol $m^{-2}$ $s^{-1}$). The lower-PAR $Q_{10}$ for the surface temperature was 10.3, still above the range 3-6 of the G93 and other biogenic models. The $Q_{10}$ for the air temperature was 18.6, much lower than for the higher PAR, probably due to the less direct relationship of isoprene emissions with air temperature. Altogether, these calculations suggest a robust, strong response of isoprene fluxes to temperature.

L256-273: In this paragraph some very interesting points are raised. Could you consider to give recommendations for the community considering this issue? Maybe underline in the conclusions how important it is to measure T accurately, precisely and with such methods that it represents the true thermal conditions controlling the VOC production and release processes? The results and findings of the manuscript clearly support this kind of remark. Or should this be a topic for a follow-up article?

R: This is an important point and thus we have included the following text in the “concluding remarks”:

> Our measurements also displayed the disparity between the temperature of the air and that of the vegetation surface, the latter being several degrees warmer during daytime (Figs. 2 and 5). Consequently, it is advisable that future VOC studies measure accurately and precisely the vegetation temperatures that represent the thermal conditions controlling the VOC production and release processes. Furthermore, while we do not suggest taking these $Q_{10}$ values as true coefficients to be directly implemented into modelling, it is worth mentioning that care should be taken when applying $Q_{10}$ values in models. Otherwise, a mismatch could translate into erroneous results, for instance when using a $Q_{10}$ derived from the response to air temperature in models that drive VOC emissions with leaf temperature and vice versa.

L294: I have nothing to contest; it’s clear that biomass growth is a classical source of methanol. However, according to the figure S1, leaf expansion period has already ended before the mid-July measurement period. This methanol flux after the leaf expansion period is not surprising, because based on my own experience with boreal forest methanol emission continues throughout growing season (for example Aalto et al., 2014). I’d like to see more observations about cases when methanol emission is not clearly linked with biomass growth; here you would have chance to present one such case. Otherwise the community will keep repeating this Hüve et al. (2007) finding as the only relevant source for methanol emissions for another 13 years. I believe it’s true finding but I also believe that it’s not the whole truth.

R: We agree that methanol is emitted throughout the growing season. Indeed, our July measurements correspond to a period when leaf expansion was not at its seasonal strongest time. We showed in Fig. 3 that methanol emission fluxes in July described a diurnal cycle, and we commented (lines 280-281) also that Holst et al (2010) reported methanol fluxes at the same fen several years ago also outside of the peak in leaf expansion (in August, even later than our measurements). Furthermore, we mentioned (L285-287) a reference to other studies of methanol fluxes that are not restricted to the leaf expansion (Wohlfahrt et al 2015). Therefore, in our original manuscript, we did not imply that the only source of methanol is biomass growth. That paragraph gave a hint to the reader of the multiple and complex controls on the emissions of these non-isoprenoid VOCs, other than light and temperature. Nevertheless, it is true that methanol is typically emitted in higher amounts during leaf elongation, as shown for boreal forests in Aalto et al (2014) as well.

We have now expanded that section, which now reads:

> Methanol can be emitted constitutively by plants throughout their growing season, with increased release linked to leaf expansion (Aalto et al., 2014; Hüve et al., 2007) and emission bursts elicited by herbivore feeding (Peñuelas et al., 2005a). Methanol emissions have also been associated with soils. For example, methanol was one of the main compounds released from subalpine forest floor (Gray et al., 2014) and thawing permafrost (Kramshøj et al., 2018).

L330-340: Were the depositions rates tested against relative humidity? At least in case of acetaldehyde it could be interesting. It's very likely that the potential effect of RH on these deposition rates returns to T (due to autocorrelation of T and RH), but there are chances that it could be vice versa: high humidity could be the main driver, instead of T itself. I don't ask you to add anything regarding RH, but just to consider by yourselves, would accounting RH make sense for the analysis.

R: We have checked the relationship of RH with the deposition rates of these carbonyl compounds. In the case of acetone, the relationship resembled very much that of temperature, with higher deposition rates matching the lower RH values expected for those higher temperatures. Thus, higher RH did not drive deposition of acetone. Acetaldehyde deposition, just like with temperature, did not show a clear relationship with RH. The strongest deposition rates were broadly scattered around 70-90% RH but with most of the near-zero fluxes at around RH of 85-100%, so again there was no clear relationship to RH.


References:

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**Anonymous Referee #2**

In their manuscript, "Volatile Organic Compound fluxes in a subarctic peatland and lake," Seco et al. present the results of flux measurements of volatile organic compounds (VOCs) at a subarctic fen and lake. The methods used are sound and are explained clearly and thoroughly. The results are important in that they provide one of the few measurements of VOC fluxes from these types of biomes in an understudied geographical region. The observations show that the fen is a source of many VOCs, particularly isoprene, and that the isoprene temperature response is stronger than is often assumed based on lower latitude data. Conversely, the lake appeared to be a sink of acetone and acetaldehyde. Overall, the study is of high quality and I recommend publication following minor revisions as described below.

R: We thank the referee for his/her effort in reviewing and are glad of his/her positive opinion of the manuscript.

As the authors point out, the results show that (1) there is a large difference between the air temperature and vegetation surface temperature and (2) VOC emissions are extremely sensitive to temperature in this region. This is an important finding that can be used to improve model estimates of VOC emissions at high latitudes. It also suggests the importance of accurately measuring the temperature. I would suggest that the authors discuss in more detail the uncertainties associated with the temperature measurement method, how it compares with contact measurements of vegetation surfaces (or cite appropriate references). They should also discuss the uncertainty introduced by using a surface temperature measurement obtained some distance from the flux measurement site. Given these uncertainties, what is the uncertainty in the calculated Q10 values?

R: We agree that it is important to accurately measure the temperature of the ecosystem that we are studying. That is why we have included a reminder in the "concluding remarks" section of the article (see response to reviewer #1 regarding lines L256-273).

We have also added more information on the measurement of the vegetation surface temperature in the "methods" section of the manuscript, which now reads:

> We used the vegetation surface temperature, retrieved with an infrared radiometer (SI-111, Apogee Instruments, Logan UT, USA), from the nearby ICOS (Integrated Carbon Observation System) Sweden measurements within the same Stordalen Mire complex (Fig. 1). A technology used for

> decades (Fuchs and Tanner, 1966), the infrared radiometer measured non-invasively the vegetation surface temperature integrated over its field of view (4.8 $m^2$). Even though these radiation readings took place a couple of hundred meters away from our flux footprint, it was the best available proxy of the temperature experienced by the vegetation surface of the fen. Indeed, previous studies have shown that solar radiation can warm Arctic plants several degrees above their surrounding air temperature (Lindwall et al., 2016a; Wilson, 1957).

Regarding the uncertainty of the $Q_{10}$ values, assuming that the measured temperature (either air or surface temperature) has a precision of 1% –as indicated by the sensor manufacturers– and that it is accurate, then most of the uncertainty in the $Q_{10}$ coefficient comes from the isoprene mixing ratios –which have 15% uncertainty. We have now also calculated the $Q_{10}$ values using more data than we did in the first version of the manuscript (see our answer to reviewer #1 regarding lines L254-255), which illustrates that our $Q_{10}$ coefficients shows some degree of variability, but they always corroborate a higher sensibility to temperature than current emission models. Lastly, we must add that our study was not designed to determine the $Q_{10}$ values as such and that they should not be taken as an absolute truth. Instead, we use the $Q_{10}$ values to highlight the strong temperature dependence of our fen.

Lines 266-269: "Indeed, the response of our isoprene emissions to air temperature was even steeper (Q10 = 131; blue triangles in Fig. 5) than to surface temperature, which could translate into increased modelled isoprene emissions if implemented in models that do not calculate the vegetation temperature but instead use air temperature to drive biogenic VOC emissions." This sentence is overly long and while I understand what the authors are trying to say, it's not stated very clearly. I suggest separating into two sentences (replace the comma with a period), and rephrasing the second part of the existing sentence. In particular, the authors should more specifically state how the implementation of the Q10 result in models would lead to increased modelled isoprene emissions. It seems like an error would arise if there was a mismatch between the Q10 value and the temperatures used (i.e., using the high Q10 from air temp, but using leaf surface temps in the model, or vice versa) and the direction of the error would depend on the sense of the mismatch (Q10(air) + Tsurf vs. Q10(surf) + Tair). Please restate to improve clarity.

R: We agree that this sentence is not well stated. Now, we have removed the second part from this section of the manuscript and rewritten the main idea in the "concluding remarks" (see our answer to reviewer #1 regarding lines L256-273).

Lines 335-337: "Air temperature also influenced the flux of these two carbonyl VOCs. Acetone deposition was more intense at higher air temperatures, in July, when its mixing ratios were also higher (Fig. 6)." The authors state that air temperature "influenced the flux of these two carbonyl VOCs," but it seems like this could be simply correlation rather than causation. The difference in flux between the two time periods (July and September) happens to coincide with a change in temperature, but also with a difference in mixing ratios. Also, the sense of the relationship is opposite in the two cases, with acetone deposition being higher at higher T, whereas acetaldehyde deposition is higher at lower T. Is there a mechanistic explanation for this? If not, and the relationship with temperature may not be causal, I would suggest rewording to clarify this.

R: We agree that the text needs to be clarified. Our intention was just to state the relationship with temperature observed from the plots in Fig. 6. It is known that atmospheric mixing ratios can drive the flux direction to/from water of these water soluble short-chain oxygenated VOCs, and the relationship with temperature may just be a coincidence. We have now reworded this paragraph; this is the final text:

> There was a correlation of the acetaldehyde and acetone deposition rates with their corresponding atmospheric mixing ratios (Fig. 6), with increasing deposition at higher mixing ratios, resulting in average deposition velocities of -0.23 ± 0.01 and -0.68 ± 0.03 cm $s^{-1}$ for acetone and acetaldehyde, respectively. The high water solubility of these short-chain oxygenated VOCs helps their deposition from the air to the water, and may partly explain the correlation of the deposition rate with their atmospheric mixing ratios (Fig. 6). The flux of these two carbonyl VOCs showed a relationship to air temperature as well, that might very well be coincidental and dependent on atmospheric mixing ratios. Acetone deposition was more intense at higher air temperatures, in July, when its mixing ratios were also higher (Fig. 6). In contrast to acetone, acetaldehyde did not present a clear relationship with air temperature but its strongest deposition rates occurred at air temperatures below 3 ºC, concurrent with higher mixing ratios (Fig. 6).

Lines 357-358: “Instead, average methanol fluxes showed both net deposition and emission along the day during both seasons.” How statistically significant is this conclusion? From Figure 3, it appears that the blue shaded region representing +/- 1 standard deviation overlaps 0 for most if not all data points (possibly excepting the last July data point, which I believe represents only a single measurement for that time window). Given the relatively sparse data and indicated standard deviations, wouldn’t it be more accurate to say that the results indicate little to no flux (emission or uptake) of methanol to/from the lake?

R: We concur with the reviewer and have modified that sentence to:

> Instead, average methanol fluxes showed little to no flux, either deposition or emission, along the day during both seasons.

Lines 395-396: “. . .similar to our July average of 4.7 ± 3.1 μmol m-2 day-1 (Table 1).” Referring back to lines 318-320, which state, “In particular, compounds such as DMS and monoterpenes had mean daily fluxes dominated by one or two hourly average data points that were not actually hourly averages, since they were based on only one measurement during that hour (i.e. data points without shading in Fig. 3).” along with the data shown in Figure 3, there appear to be two time periods with large positive fluxes representing single measurements. How were the daily averages calculated? Were they an average of all measurements equally weighted, or an average of the hourly averages? If the latter, that would give disproportionate weight to the high “hourly averages” that represent single data points. Please clarify in the text.

R: The daily averages were calculated as an average of the hourly averages. The reason is that, for each VOC species, the number of available data points at each hour was variable among the 24 hours of the day. Giving an equal weight to each data point would give a disproportionate weigh to the values of the hours with more data, which tend to be the central parts of the day due to better turbulence conditions and clearer VOC fluxes, or those hours that saw more frequently the wind blowing from the right direction. The downside is that an “average” from a single data point that is disproportionately different from the other data points can distort the daily average. This is just what we discussed in lines 318-320 of the preprint. We have now clarified the calculation of the daily averages by including the following text in the caption of Table 1:

> These daily averages were calculated from the hourly averages shown in Figs. 3 and 4.

My last few comments regarding the lake fluxes suggest that the authors should consider alternate ways of analyzing and presenting the lake data to increase the statistical robustness of the results. For example, instead of hourly averages, they could consider averaging over 2 or 3 hour time periods to increase the number of data points in each time period and improve the statistics, perhaps allowing for more definitive conclusions.

R: That is a good suggestion and we tried this approach with the lake monoterpenes and DMS in July. Averaging over 2 hours did only slightly change the trace shown in Fig.3 and the daily average was practically the same given the high uncertainty of the original daily averages shown in Table 1. This is understandable because there are few points measured during the hours surrounding the “outliers” too, so the effect of the “outliers“ is still apparent in the new averages. Averaging over 3 hours made the daily pattern more constant (but with high standard deviation and of course less time resolution), which may better reflect the real flux behavior or not, because we do not know what is the real flux behavior.

Therefore, we decided to keep the original hourly averages for these two compounds, like all the other reported VOCs and environmental variables, instead of obscuring a few high values by averaging with neighboring data points. We maintained the same cautionary comment in the text (lines 318-320 in the original preprint), so the reader can have a better idea of the available data and their shortcomings.

Minor grammatical changes:

Lines 270-273: “At the same Stordalen wetland as our study, Holst et al. (2010) found a steep temperature response to air temperatures above 15 _C, in agreement with our results (Fig. 5). Nevertheless, our high Q10 values corroborate that Arctic vegetation can have a stronger temperature sensitivity compared to plants from lower latitudes, which underpinned the most used biogenic emission models (Guenther et al., 2006), as already suggested from previous high-latitude studies (Holst et al., 2010; Kramshøj et al., 2016; Lindwall et al., 2016b, 2016a; Rinnan et al., 2014).” The second sentence is overly complicated. It obscures the important point that the high Q10 found in this study differs from model values based on lower latitudes. I would suggest rearranging the two thoughts into different sentences. Also, “underpinned” should be “underpin”. E.g., “At the same Stordalen wetland as our study, Holst et al. (2010) found a steep temperature response to air temperatures above 15 _C, in agreement with our results (Fig. 5) and other high-latitude studies (Holst et al., 2010; Kramshøj et al., 2016; Lindwall et al., 2016b, 2016a; Rinnan et al., 2014). Our high Q10 values corroborate that Arctic vegetation can have a stronger temperature sensitivity compared to plants from lower latitudes, which underpin the most used biogenic emission models (Guenther et al., 2006)."

R: We have improved the readability of these sentences following the reviewer's advice.

Lines 364-365: "Nevertheless, our available data showed maximum hourly average net emissions of 1 nmol m-2 s-1, being the daily average net rate of 0.24 ± 0.12 nmol m-2 s-1 (equivalent to 20 ± 10 μmol m-2 day-1; Table 1)." The wording of this sentence is awkward and confusing. Assuming I'm interpreting the authors' intent correctly, I would suggest replacing "being" with "and", e.g., "Nevertheless, our available data showed maximum hourly average net emissions of 1 nmol m-2 s-1, and a daily average net rate of 0.24 ± 0.12 nmol m-2 s-1 (equivalent to 20 ± 10 μmol m-2 day-1; Table 1)."

R: We have improved the readability of these sentences following the reviewer's advice.

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# Volatile Organic Compound fluxes in a subarctic peatland and lake

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**Abstract**

Ecosystems exchange climate-relevant trace gases with the atmosphere, including volatile organic compounds (VOCs) that are a small but highly reactive part of the carbon cycle. VOCs have important ecological functions and implications for atmospheric chemistry and climate. We measured the ecosystem-level surface-atmosphere VOC fluxes using the eddy covariance technique at a shallow subarctic lake and an adjacent graminoid-dominated fen in Northern Sweden during two contrasting periods: the peak growing season (mid July) and the senescent period post-growing season (September-October).

In July, the fen was a net source of methanol, acetaldehyde, acetone, DMS, isoprene, and monoterpenes. All of these VOCs showed a diel cycle of emission with maxima around noon and isoprene dominated the fluxes (93 ± 22 µmol $m^{-2}$ $day^{-1}$, mean ± SE). Isoprene emission was strongly stimulated by temperature and presented a steeper response to temperature ($Q_{10}$ = 14.5) than that typically assumed in biogenic emission models, supporting the high temperature sensitivity of arctic vegetation. In September, net emissions of methanol and isoprene were drastically reduced, while acetaldehyde and acetone were deposited to the fen, with rates of up to -6.7 ± 2.8 µmol $m^{-2}$ $day^{-1}$ for acetaldehyde.

Remarkably, the lake was a sink for acetaldehyde and acetone during both periods, with average fluxes up to -19 ± 1.3 µmol $m^{-2}$ $day^{-1}$ of acetone in July and up to -8.5 ± 2.3 µmol $m^{-2}$ $day^{-1}$ of acetaldehyde in September. The deposition of both carbonyl compounds correlated with their atmospheric mixing ratios, with deposition velocities of -0.23 ± 0.01 and -0.68 ± 0.03 cm $s^{-1}$ for acetone and acetaldehyde, respectively.

Even though these VOC fluxes represented less than 0.5% and less than 5% of the $CO_2$ and $CH_4$ net carbon ecosystem exchange, respectively, VOCs alter the oxidation capacity of the atmosphere. Thus, understanding the response of their emissions to climate change is important for accurate prediction of the future climatic conditions in this rapidly warming area of the planet.

## 1 Introduction

Arctic climate is warming twice as fast as the global average (Post et al., 2019). This is due to a number of climate system feedbacks, including albedo change due to retreating snow cover and sea ice, and the forest cover expansion to the open tundra (Overland et al., 2014; Post et al., 2009). Northern ecosystems are known to exchange climate-relevant trace gases with the atmosphere, not only long-lived greenhouse gases such as carbon dioxide ($CO_2$) or methane ($CH_4$) but also hundreds of different volatile organic compounds (VOCs) that are a highly reactive part of the carbon cycle (Rinnan et al., 2014). Trace gases originate from sources as diverse as soils, peats, vegetation and lakes, and currently several of them show a trend towards greater emission rates with climate warming (Kramshøj et al., 2019; Lindwall et al., 2016a; Wik et al., 2016). At the same time, the warming-induced expansion of woody shrubs into tundra ecosystems (Myers-Smith and Hik, 2018) could enhance the photosynthetic uptake of $CO_2$ and offset concurrent increases in heterotrophic respiration (Mekonnen et al., 2018). Indeed, $CO_2$ and $CH_4$ have been extensively surveyed in high latitudes due to a potential increase in their atmospheric concentrations and connected climatic effects as permafrost thaws (Natali et al., 2019; Schuur et al., 2015). In contrast, far less research has been devoted to VOC emissions in these areas.

VOCs play essential ecological roles: they can mediate the communication between living organisms and protect plants from biotic and abiotic stresses (Baldwin et al., 2006; Filella et al., 2013; Kessler and Baldwin, 2001; Peñuelas et al., 2005; Pichersky and Gershenzon, 2002; Seco et al., 2011b; Velikova et al., 2005)(Baldwin et al., 2006; Filella et al., 2013; Kessler and Baldwin, 2001; Peñuelas et al., 2005b; Pichersky and Gershenzon, 2002; Seco et al., 2011b; Velikova et al., 2005). In addition, biogenic VOCs engage in chemical reactions that substantially modify the oxidation capacity of the atmosphere. For example, VOCs enhance the lifetime of methane by competing for its atmospheric oxidants, promote the formation of tropospheric ozone, and ultimately contribute to aerosol formation in the atmosphere, which has climatic consequences (Atkinson, 2000; Liu et al., 2016; Seco et al., 2011a; Tunved et al., 2006). Meanwhile, climate change is affecting the fundamental functions of VOCs and altering their emission rates in northern ecosystems, directly via warming and indirectly by inducing changes in vegetation composition (Faubert et al., 2010a; Li et al., 2019; Lindwall et al., 2016a; Valolahti et al., 2015). Moreover, the atmospheric impact of VOCs emitted from natural sources may be comparatively more important in northern latitudes than in more populated territories due to the relatively low presence of anthropogenic VOC emissions (Paasonen et al., 2013).

VOC studies over the last few years have reported strong increases in arctic and subarctic vegetation emissions in response to moderate warming (Faubert et al., 2010a; Kramshøj et al., 2016; Lindwall et al., 2016a), highlighting the capacity of Arctic plants to respond to increasing temperature. However, these studies have been conducted using enclosure techniques with a range of unwanted side effects, such as temperature and humidity rise inside the enclosure and interactions with chamber materials (Ortega and Helmig, 2008). Micrometeorological techniques such as eddy covariance (EC) can overcome many of those undesirable side effects and, in addition, provide a more representative ecosystem-level VOC exchange quantification by minimizing potential sampling error when upscaling from a small number of enclosures to ecosystem fluxes. However, instrumental challenges have limited the number of ecosystem-level VOC studies using EC and only two such datasets over short time periods are available for high latitude ecosystems (Holst et al., 2010; Potosnak et al., 2013). Moreover, there are few or no air-water direct VOC flux measurements from northern lakes. Arctic latitudes possess one of the highest concentration and area of inland water bodies of our planet (Verpoorter et al., 2014). Despite being acknowledged as important regional and global sources of carbon dioxide and methane (Tranvik et al., 2009; Wik et al., 2016), the role of northern lakes in the VOC budget is largely unexplored. It is therefore vital to assess the lake and vegetation VOC fluxes in these high latitude areas exposed to large environmental changes to be able to estimate their impacts on the regional carbon cycle, atmospheric chemistry and climate.

We report here ecosystem-level VOC fluxes measured by EC from a subarctic shallow post glacial lake, a common lake form in the Arctic (Wik et al., 2016), and its adjacent fen dominated by tall graminoids. We aimed to identify which compounds were released at significant rates from the lake, which from the fen, during two contrasting periods: the peak of the growing season (mid July) and the senescent period post-growing season (September-October). Further, we assessed the deposition of compounds to the two ecosystems. In addition, we included here the EC fluxes of carbon dioxide and methane from both fen and lake, which have been discussed elsewhere (Jammet et al., 2015, 2017; Jansen et al., 2019), to provide a more thorough overview of the trace gas fluxes during our study.

## 2 Materials and methods

### 2.1 Site description and field campaign outline

Stordalen Mire is a subarctic palsa mire complex underlain by discontinuous permafrost (Johansson et al., 2006). It is located ca. 10 km east of Abisko in northern Sweden (68º20' N, 19º03' E). Local meteorology has been monitored at the Abisko Scientific Research Station (ANS) with records since 1913 (Callaghan et al., 2010). The average air temperature at ANS during the period 1981-2010 was 0.1 °C and average annual rainfall 332 mm; the mean annual air temperature and precipitation at Stordalen in 2018 were -0.04 °C and 340 mm, respectively. The Stordalen Mire was not affected by the drought that occurred in large parts of central and northern Europe during 2018 ~~(Buras et al., 2020)~~(Buras et al., 2020; Rinne et al., 2020).

Our measurements took place during the 2018 growing season from a 2.92 meter-tall eddy covariance mast located on the shore of a shallow post glacial lake, Villasjön. The geomorphological setting within the Torneträsk catchment determines a bimodal distribution to the surface wind flow of roughly ESE and WNW (Fig. 1). The lake edge mast is influenced by Villasjön to the east and by fen to the west. The fen is a permafrost-free, minerotrophic wetland with vegetation dominated by tall graminoids, mainly *Carex rostrata* and *Eriophorum angustifolium* (Palace et al., 2018). The lake is 0.17 $km^2$ in area, the largest of the 27 lakes that constitute the 15 $km^2$ Stordalen catchment (Lundin et al., 2013). It has a maximum depth of 1.5 m and it usually freezes close to the bottom in winter (Jansen et al., 2019). The bidirectional flow pattern throughout the year allows a clear distinction of the surface source or sink influences of the surface boundary layer. Thus, depending on the prevailing wind direction, the measured VOC flux data were assigned to either the lake or the fen (e.g. Jammet et al., 2015). Flux data originating outside of these wind directions, usually at very low wind speeds, contributed only a minor part of the total fluxes and were excluded from analysis. The average EC flux footprint used in our study (Fig. 1) was calculated with a two-dimensional model (Kljun et al., 2015), see the supplementary material for further details.

Several major instrumental issues precluded us from obtaining a season-long dataset of VOC fluxes. With the available data, when the instruments were operational, we present measurements from two distinct periods: the peak of vegetation activity (15-22 July) and the senescent period post-growing season (20 September-13 October). We determined the relative seasonal status of the vegetation at this site based on greenness data captured by an automatic camera installed on the EC mast (see Sect. 2.3 and Fig. S1). For the sake of simplicity, in this article we will refer to the season peak period as July and to the post growing season as September.

Considering the wind direction partitioning and the two periods for which we have data, the maximum number of half-hour EC fluxes in July were 64 and 246 for lake and fen, respectively. In September, we had a maximum of 429 EC fluxes for lake and 619 for fen. However, since some VOC fluxes were discarded according to strict quality assurance procedures recommended for EC measurements (see section 2.2), the actual number of valid half-hour VOC fluxes was smaller for individual chemical species (e.g., for isoprene in July, 22 and 161 valid data points for lake and fen, respectively). VOC fluxes from the lake for July were only available for some hours of the day (between 03:00 and 14:00 UTC+1).

**2.2 VOC measurements**

Mixing ratios of VOCs were measured with a Proton Transfer Reaction – Time of Flight – Mass Spectrometer (PTR-TOF-MS). This particular model (PTR-TOF 1000ultra, Ionicon Analytik, Innsbruck, Austria) was equipped with an ion funnel at the end of the drift tube that provided a higher sensitivity, and had a compound (diiodobenzene) added continuously to the air sample that provided a constant signal at high mass-to-charge ratio (m/z) for accurate TOF mass scale calibration. The drift tube was operated at 60 ºC, 550 V, and 2.3 mbar. Multipoint sensitivity calibration was performed at least once a month (including at the end of the July period and before, midway and at the end of the September period) by diluting a blend of several VOCs (e.g., methanol, acetaldehyde, acetone, isoprene, alpha-pinene, benzene, among others, in nitrogen at a VOC mixing ratio of $1 \times 10^{-6}$ mol mol$^{-1}$ each, manufactured by Ionicon Analytik) into clean nitrogen. The dilution (range 1-40 x $10^{-9}$ mol mol$^{-1}$) was achieved with a Liquid Calibration Unit (Ionicon Analytik). The background signal of the PTR-TOF-MS was checked for 1 hour every night by sampling VOC-scrubbed air produced by passing ambient air through a zero air generator (Parker Hannifin 75-83-220, Lancaster NY, USA). The PTR-TOF-MS instrument was sheltered inside a hut located approximately 15 meters from the eddy covariance mast. Air was sampled from the top of the mast, very close to an R3-50 ultrasonic anemometer (Gill Instruments, United Kingdom), at a flow rate of 20 liters per minute through a PFA (perfluoroalkoxy) ~~teflon~~ line (1/4’’ ID, 3/8’’ OD) inlet that was heated when ambient temperatures were below 20 ºC to minimize VOC and water condensation onto the inlet walls. The ~~teflon~~PFA line and its heating wire were inserted into a plastic pipe to shelter them from the environment.

Raw PTR-TOF-MS data were processed with the *PTRwid* software (Holzinger, 2015). PTRwid corrected the mass scale calibration, and then detected, fitted and quantified ion peaks present in the measured spectrum. In this study, we focus on several VOCs that were assigned to known protonated ionsIn this study, we focus on several VOCs that were assigned to known protonated ions (Yáñez-Serrano et al., in press) detected with the PTR-TOF-MS: methanol (m/z 33.03), acetaldehyde (m/z 45.03), acetone (m/z 59.05), dimethyl sulfide (DMS, m/z 63.03) isoprene (m/z 69.07), and monoterpenes (m/z 81.07 and 137.13).

Fluxes of VOCs were calculated with the eddy covariance technique using the *InnFLUX* software tool by Striednig et al. (2020), which was run in Matlab version R2018b (The Mathworks, Natick MA, USA). In short, InnFLUX first detrended the Reynolds averages of the raw data. Then, for each half hour EC flux calculation, it time-aligned the VOC mixing ratio time series for each m/z with the vertical wind data from the sonic anemometer by shifting one time series relative to the other until the absolute maximum covariance between the two time-series was determined. This time alignment also corrected for the variable time difference between the computer recording the PTR-TOF-MS data and the data logger recording the wind data. Previously, the wind data had been rotated according to the directional planar fit method, a correction dependent on wind direction that applies the planar fit method (Wilczak et al., 2001) to each wind direction (1 degree steps) using a rotational matrix computed with wind data of the ±15 degrees around that wind direction. Calculated fluxes were excluded from further analysis if turbulence was low ($u^* < 0.15$) or if results of the stationarity test (Foken et al., 2004) were higher than 30%. Of the total calculated half-hour EC fluxes, those excluded by these conditions represented 34% for isoprene, 40% for monoterpenes, 43% for acetone and DMS, 44% for methanol, and 62% for acetaldehyde.

Even though VOC measurements were made at 10 Hz, the damping of the turbulence inside the long inlet line and other possible losses of high frequency contributions to the VOC flux required the application of spectral corrections to the calculated fluxes. We chose the empirical method proposed by Aubinet et al. (2001), which derives a cospectral transfer function of the EC system based on the comparison of the covariance of the vertical wind speed with a non-attenuated signal (i.e. the temperature measured directly by the sonic anemometer) to that with an attenuated signal (i.e. the VOC; Fig. S2). Since the flux mast setup did not change during the measurement campaign, the spectral correction factor (i.e. number to be multiplied by the attenuated flux to obtain the corrected flux) was simply a function of the wind speed (Aubinet et al., 2001). The correction factor determined for isoprene was used for all reported compounds and ranged from 1 to 1.6, and on average was 1.2, which corresponded to a wind speed of 4 $m\ s^{-1}$. In addition, the EC system response time ($\tau_c$=0.21 s), including the PTR-TOF-MS and the inlet tubing, was calculated by fitting the same cospectral transfer function to the equation by Horst (1997; Eq 5 therein).

### 2.3 Ancillary measurements

Simultaneously with VOCs, and at the same mast, we measured EC fluxes of $CH_4$ and $CO_2$. The setup as well as the data processing procedures are detailed in Jammet et al. (2015, 2017) and Jansen et al. (2019). This EC system used the same Gill

R3-50 sonic anemometer as the PTR-TOF-MS. For the $CH_4$ fluxes, a tube inlet (8 mm ID Synflex), mounted just below the anemometer, was connected to a closed path cavity ring-down spectrometer (FGGA, Los Gatos Research, San Jose CA, USA). For $CO_2$ and $H_2O$ fluxes we used an open path sensor (LI7500a, LI-COR Biosciences, Lincoln NE, USA) mounted at 2.5m height. Digital data streams from the instruments were sampled at 10 Hz and stored on a CR3000 datalogger (Campbell Scientific Inc., Logan UT, USA). Raw data processing, flux calculations and spectral corrections were done in EddyPro version 6.2 (open source software hosted by LI-COR).

A second mast was set up ca. 10 m from the bank of the lake equipped with instrumentation for ancillary data. Air temperature and humidity (CS215 probe with passively-ventilated radiation shield, Campbell Scientific) were measured at 2 m above ground level (a.g.l~~.~~.). Incoming and reflected photosynthetic active radiation (PAR) were recorded at 1.5 m a.g.l. using two Li-190 probes (LI-COR Biosciences). All these data were recorded as 10 min-averages and stored using a CR1000 datalogger (Campbell Scientific).

The vegetation greenness was measured throughout the growing season (Fig. S1) for a general assessment of vegetation phenology and growing season dynamics. The greenness was derived as the green chromatic coordinate (GCC; Westergaard-Nielsen et al., 2017), based on images acquired every second hour with an automated Canon G7 X Mark II camera. We visually selected four regions in the images dominated by *Betula pubescens* var. *pumila* L., *Betula nana* L., *Salix* spp., and graminoids (*Carex* spp. and *Eriophorum* spp.), respectively, and averaged the GCC within each region, based on the average of four daily images from approx. 10:00 to 16:00.

~~We used the vegetation surface temperature, retrieved with an infrared radiometer (SI-111, Apogee Instruments, Logan UT, USA), from the nearby ICOS (Integrated Carbon Observation System) Sweden measurements within the same Stordalen Mire complex (Fig. 1).~~ Water temperature in Villasjön was measured with self-contained loggers (HOBO Water Temp Pro v2, Onset Computer) at 0.1, 0.3, 0.5 and 1.0m depth, at 5-minute intervals. The loggers were intercalibrated in a well-mixed water tank prior to deployment to achieve a measurement precision of $< 0.05$ °C.

We used the vegetation surface temperature, retrieved with an infrared radiometer (SI-111, Apogee Instruments, Logan UT, USA), from the nearby ICOS (Integrated Carbon Observation System) Sweden measurements within the same Stordalen Mire complex (Fig. 1). A technology used for decades (Fuchs and Tanner, 1966), the infrared radiometer measured non-invasively the vegetation surface temperature integrated over its field of view (4.8 $m^2$). Even though these radiation readings took place a couple of hundred meters away from our flux footprint, it was the best available proxy of the temperature experienced by the vegetation surface of the fen. Indeed, previous studies have shown that solar radiation can warm Arctic plants several degrees above their surrounding air temperature (Lindwall et al., 2016a; Wilson, 1957).

## 3 Results and discussion

### 3.1 Meteorological conditions

PAR and air temperature were much higher in July than in September (Fig. 2). Maximum hourly average PAR in September was one fifth of that in July (ca. 250 and 1200 µmol $m^{-2}$ $s^{-1}$, respectively). Average air temperature at 2 m height was higher when the wind was blowing from the east, especially in July, with hourly averages ranging from 14 to 28 ºC (11 to 19 ºC with wind from the west). In September, hourly average air temperatures ranged between 1 and 4 ºC, and at the end of this period (second week of October) the first snowfall and the first freezing nights of the season occurred. The water temperature at 10 cm depth did not vary as much in July as the temperature of the air blowing over the lake did, fluctuating between 19.5 and 22 ºC on average, whereas in September the water temperature closely resembled the air temperature and had minimal variations along the day, staying between 1.9 and 3 ºC (Fig. 2). In contrast, the vegetation surface temperature did oscillate much more than the air temperature, ranging between 10 ºC at midnight and 26 ºC at noontime in July. In September, the surface temperature showed a similar diurnal pattern but its hourly average range was limited between -1.2 and 3.3 ºC (Fig. 2).

### 3.2 Fen VOC fluxes

In July, the fen was a net source of methanol, acetaldehyde, acetone, DMS, isoprene, and monoterpenes (Table 1), with a clear dominance of isoprene (93 ± 22 µmol $m^{-2}$ $day^{-1}$ on average ± standard error of the mean). These VOCs showed a typical diurnal cycle with maximum emission around midday (Fig. 3). In September, fen emissions of methanol, isoprene and monoterpenes were drastically reduced, reaching mean net emissions of 1 µmol $m^{-2}$ $day^{-1}$ or less, and none of them followed a discernible diel pattern. Acetaldehyde, acetone, and DMS, in contrast, were deposited to the fen ecosystem with net average rates of -6.7 ± 2.8, -2.5 ± 0.3, and -0.2 ± 0.1 µmol $m^{-2}$ $day^{-1}$, respectively (Table 1). Thus, acetaldehyde and acetone deposition represented the bulk of VOC flux in the fen after the growing season.

Several biogenic VOC studies in recent years have revealed that isoprene is the major compound in VOC emissions of many arctic and subarctic ecosystems (Holst et al., 2010; Potosnak et al., 2013; Tiiva et al., 2007), including leaf-level measurements of two of the dominant sedge species of our fen: *C. rostrata* and *E. angustifolium* (Ekberg et al., 2009). Only two studies, though, measured the ecosystem-scale emissions with EC, one nearby in the Stordalen Mire fen and the other in an Alaskan moist acidic tundra (Holst et al., 2010; Potosnak et al., 2013). They published maximum hourly isoprene fluxes that were in the range of 1 to 5.5 nmol $m^{-2}$ $s^{-1}$ at the peak of the growing season, comparable in magnitude to our July fen measurements (Fig. 3). A third study that relied on micrometeorology (relaxed eddy accumulation, in this case) was carried out at a boreal fen in southern Finland dominated by *Sphagnum* spp. mosses. The summer isoprene emissions there were also comparable to our results, with daily average emissions in the range of 35-88 µmol $m^{-2}$ $day^{-1}$ (Haapanala et al., 2006).

Most of the other published studies derived ecosystem-scale isoprene fluxes with measurement chambers attached to the ground, enclosing the vegetation and the soil surface together. Pioneering VOC work started in boreal *Sphagnum* fens of

Sweden and Finland with static chambers, finding isoprene fluxes of up to 9 nmol $m^{-2}$ $s^{-1}$, which is in range with our measurements (Janson et al., 1999; Janson and De Serves, 1998). At a subarctic fen dominated by *Eriophorum* spp. and located close to our site in the same Stordalen mire complex, Bäckstrand et al. (2008) measured semi-continuously with automatic chambers and found average total non-methane volatile organic compound (NMVOC) fluxes of 18.5 mgC $m^{-2}$ $day^{-1}$. Assuming most of the NMVOCs were isoprene, this would equal 309 µmol $m^{-2}$ $day^{-1}$, which is approximately three times our result (Table 1). Several other push-pull chamber studies have published results from manipulative experiments and, in most cases, the non-manipulated control plots showed substantially lower isoprene emissions than the EC and chamber studies mentioned above. For instance, emissions in a Finnish subarctic peatland dominated by the moss *Warnstorfia exannulata* and the sedges *Eriophorum russeolum* and *Carex limosa* were in general at least one order of magnitude lower than ours but showed great year to year variation with some higher fluxes measured as well (Faubert et al., 2010b; Tiiva et al., 2007). At a fen in Greenland, dominated by the graminoids *Carex rariflora* and *E. angustifolium*, isoprene emissions were also at least one order of magnitude smaller than our results (Lindwall et al., 2016b). At an experimental site in a heath near Abisko, dominated by evergreen and deciduous dwarf shrubs, graminoids and forbs and with soil covered by *Sphagnum warnstorfii*, the average isoprene fluxes were one or two orders of magnitude lower than ours as well (Tiiva et al., 2008; Valolahti et al., 2015).

~~The~~Research on isoprene emissions from plant leaves has established that the instantaneous isoprene emission rate depends on the short-term (seconds to hours) light and temperature conditions (Monson et al., 2012). To assess the relative contribution of light and temperature in controlling the ~~fen~~ isoprene emissions measured at the fen, we used the light ($C_L$) and temperature ($C_T$) activity factors of the G93 empirical leaf-level isoprene emission model (Guenther et al., 1993) ~~and~~. We applied ~~it~~the G93 model to our ecosystem-level emissions~~,~~ assuming that the fen vegetation is a single big leaf (e.g. Geron et al., 1997; Seco et al., 2015, 2017). In addition, with the G93 model we could also estimate the standard isoprene emission potential of the fen (at standard conditions: 1000 µmol $m^{-2}$ $s^{-1}$ of PAR and surface temperature of 30 ºC), which was 5.8 ± 0.13 nmol $m^{-2}$ $s^{-1}$ (Supplement Fig. S5), almost double that calculated for a boreal *Sphagnum*-dominated fen in southern Finland (Haapanala et al., 2006). The evaluation of the relative contribution of light and temperature to the control of isoprene emissions revealed that, even though light is required for isoprene biosynthesis and subsequent emission, $C_L$ did not play a prominent role in driving the short-term variations of the isoprene fluxes and most of the actual emission regulation was in response to temperature (Fig. S5). However, our highest isoprene fluxes did not follow the expected $C_T$ temperature relationship and fell above the regression line (Fig. S5), suggesting a stronger response of our highest isoprene fluxes to temperature. The $C_T$ algorithm defines an exponential increase of isoprene emission with temperature until it reaches a maximum at an optimal temperature (35 to 40 ºC) and beyond that emission decays when denaturation of enzymes occurs (Guenther et al., 1993). At the relatively low temperatures of the Stordalen Mire, where vegetation surface temperatures exceed 35 ºC just on three half-hour periods during our campaign, only the increasing part of the response described by $C_T$ was observable. We thus fitted an exponential relationship between our measured isoprene flux and both the air and surface temperatures and calculated their respective $Q_{10}$ temperature coefficients (Fig. 5). In this case, the $Q_{10}$ coefficient represents the factor by which isoprene emission increases for every 10-degree rise in temperature. The $Q_{10}$ of the G93 $C_T$ activity factor is 3.3, comparable to similar biogenic VOC emission models with $Q_{10}$ values between 3 and 6 (Peñuelas and Staudt, 2010). These values over 3 are an indication of the synergy, as temperature rises, between the metabolic processes underlying isoprene emissions, namely isoprene synthase activity and availability of its substrate dimethylallyl diphosphate, that each have $Q_{10} \approx 2$ like biochemical reactions in general (Sharkey and Monson, 2014). For our calculation, we used only emission data points for which light was not a limiting factor (i.e. PAR ~~>~~≥ 1000 µmol m$^{-2}$ s$^{-1}$) to avoid interference from the correlation between light and temperature when fitting the temperature response. The $Q_{10}$ of isoprene emission in response to vegetation surface temperature was 14.5 and the $Q_{10}$ in response to air temperature was much higher, 131 (Fig. 5). Including in our calculation emission data points measured at PAR ≥ 800 µmol m$^{-2}$ s$^{-1}$ increased the number of data points involved (from 52 to 66 at PAR ≥ 1000 and ≥ 800 µmol m$^{-2}$ s$^{-1}$, respectively) at the expense of potential light-response interference, although according to the G93 model the light-response effect would be small ($C_L$ > 0.96 at PAR = 800 µmol m$^{-2}$ s$^{-1}$). The lower-PAR $Q_{10}$ for the surface temperature was 10.3, still above the range 3-6 of the G93 and other biogenic models. The $Q_{10}$ for the air temperature was 18.6, much lower than for the higher PAR, probably due to the less direct relationship of isoprene emissions with air temperature. Altogether, these calculations suggest a robust, strong response of isoprene fluxes to temperature.

Summarizing the results from an experimentally-warmed site, Tang et al. (2016) calculated the isoprene emission temperature response of a subarctic permafrost-free heath ecosystem in Abisko using an Arrhenius-type exponential algorithm, obtaining a $Q_{10}$ coefficient of 10. Kramshøj et al. (2016) performed similar warming experiments at a dry Arctic tundra heath in Greenland, obtaining a $Q_{10}$ of 22. These two $Q_{10}$ coefficients are higher than that of the $C_T$ algorithm ($Q_{10}$ =3.3) and closer to our result using the vegetation surface temperature ($Q_{10}$ =14.5; red squares in Fig. 5). Both studies used air temperature inside the chambers for their calculations, which is typically higher than the ambient air temperature, considering that the combined effect of solar radiation and limited air circulation normally heats up the inside of the chambers. Details about where the temperature is measured ~~–~~—temperature that later is used to derive temperature responses~~–~~— can be important because Arctic vegetation exhibits a large discrepancy between its surface temperature and that of the air. For example, the vegetation surface was on average 8 ºC, and up to 21 ºC, warmer than the air at a heath in Greenland (Lindwall et al., 2016a), which coincides with our ~~fen~~Stordalen temperature readings (Fig. 2, Fig. 5). Indeed, the response of our isoprene emissions to air temperature was even steeper ($Q_{10}$ = 131; blue triangles in Fig. ~~5) than to surface temperature, which could translate into increased modelled isoprene emissions if implemented in models that do not calculate the vegetation temperature but instead use air temperature to drive biogenic VOC emissions.~~5) than to surface temperature. At the same Stordalen wetland as our study, Holst et al. (2010) found a steep temperature response to air temperatures above 15 ºC, in agreement with our results (Fig. ~~5). Nevertheless~~5) and previous high-latitude studies (Kramshøj et al., 2016; Lindwall et al., 2016b, 2016a; Rinnan et al., 2014). Hence, our high $Q_{10}$ values corroborate that Arctic vegetation can have a stronger temperature sensitivity compared to plants from lower latitudes, which underpin~~ned~~ the most used biogenic emission models ~~(Guenther et al., 2006), as already suggested from previous high-latitude studies (Holst et al., 2010; Kramshøj et al., 2016; Lindwall et al., 2016b, 2016a; Rinnan et al., 2014)~~(Guenther et al., 2006).

There are few accounts of non-isoprene fluxes from subarctic wetland ecosystems. Monoterpene emissions from chamber experiments in an Abisko heath showed great variability: sometimes in the range of our fen measurements (we found average hourly maximum of 0.06 nmol $m^{-2}$ $s^{-1}$; Fig. 3) while sometimes one order of magnitude lower (Faubert et al., 2010a; Valolahti et al., 2015). Even lower (three orders of magnitude) were the monoterpene fluxes from a subarctic fen in Finland (Faubert et al., 2010b), while a boreal *Sphagnum* fen in Finland had comparable or higher fluxes (averages between 0.05 and 0.2 nmol $m^{-2}$ $s^{-1}$) than our subarctic fen (Janson et al., 1999).

Regarding methanol, EC fluxes investigated at the Stordalen Mire wetland by Holst et al. (2010) reached a noontime average hourly maximum of 1.3 nmol $m^{-2}$ $s^{-1}$ in early August, which is higher than our 0.2 nmol $m^{-2}$ $s^{-1}$ in July (Fig. 3). They measured net methanol deposition clearly at night, whereas we observed a net zero flux at the end of the day (Fig. 3). Deposition of methanol to vegetation during nighttime has been linked to dissolution into dew droplets because methanol is highly soluble in water (Seco et al., 2007). At our site, the wet surface of the fen could potentially play an important role, but our data do not show any significant methanol deposition. The net methanol fluxes observed at our subarctic fen in July are lower than most of the published methanol fluxes from a diverse array of ecosystem-scale studies, which also confirmed the widespread importance of methanol deposition (Seco et al., 2007; Wohlfahrt et al., 2015). Acetaldehyde and acetone net emissions in July were also smaller than other published fluxes from terrestrial vegetation (Seco et al., 2007), and in September they were mainly deposited. DMS showed the same behaviour as methanol, with mainly emission in July and deposition after the growing season (Fig. 3).

All these non-isoprenoid VOCs followed a diffuse relationship with temperature and/or light (Fig. S3), reflecting the complex nature of the controls over their fluxes at the ecosystem level (Seco et al., 2007). DMS can be emitted by plants (Fall et al., 1988; Geng and Mu, 2006; Jardine et al., 2010) and also, driven by temperature, from soils (Staubes et al., 1989; Yang et al., 1996). ~~Methanol is produced during plant~~Methanol can be emitted constitutively by plants throughout their growing season, with increased release linked to leaf expansion ~~(Hüve et al., 2007), while acetaldehyde is produced in flooded roots (Fall, 2003), which is potentially an important source in a waterlogged fen for species not adapted to this growth condition, like shrubs.~~(Aalto et al., 2014; Hüve et al., 2007) and emission bursts elicited by herbivore feeding (Peñuelas et al., 2005a). Methanol emissions have also been associated with soils. For example, methanol was one of the main compounds released from subalpine forest floor (Gray et al., 2014) and thawing permafrost (Kramshøj et al., 2018). Acetaldehyde is produced in flooded roots (Fall, 2003), which is potentially an important source in a waterlogged fen for species not adapted to this growth condition, like shrubs. The graminoids, in contrast, transport air down to their roots through a specialized tissue in their leaves and stems, and do not suffer from anoxia (Schütz et al., 1991). The exchange of acetone, acetaldehyde and methanol between plants and the atmosphere is controlled by the stomatal conductance due to their water solubility and, furthermore, their atmospheric mixing ratios can have influence on the fluxes to some extent (Filella et al., 2009; Jardine et al., 2008; Niinemets and Reichstein, 2003; Seco et al., 2007). In addition, the peat and its microbial communities are also a potential source and sink for many volatiles that can be exchanged between the soil and the atmosphere from many biogeochemical processes (Albers et al., 2018; Kramshøj et al., 2018; Woodcroft et al., 2018).

Lastly, our analytical system did not capture any sesquiterpene fluxes. We know from chamber measurements that vegetation present at the Stordalen Mire emits sesquiterpenes. For example, the mountain birch (*B. pubescens* var. *pumila*), which covers an area of almost 600 000 ha in the Scandinavian subarctic, can emit important amounts of sesquiterpenes (Haapanala et al., 2009). Other experiments in nearby Abisko heaths, mentioned above, documented sesquiterpene flux rates similar to those of monoterpenes measured in the same study (Faubert et al., 2010a; Valolahti et al., 2015). Most recently, sesquiterpenes have been detected as the main terpenoid emissions after isoprene at a subarctic wetland in Finland (Hellén et al., 2020). One obvious reason for our lack of sesquiterpene signal is that our flux footprint did not include a significant amount of high-emitting species since, for example, most of the nearby birch patches were outside of it. Equally important is the fact that, due to their high reactivity, sesquiterpenes are lost through fast chemical reactions and through interactions with our long inlet tubing wall, so presumably they never made it to our PTR-TOF-MS to be detected. Therefore, the measurement of ecosystem-wide fluxes of sesquiterpenes with EC remains a challenge for future field campaigns.

### 3.3 Lake VOC fluxes

The number of available lake half-hour fluxes in July was low (n≈20) due to technical issues, wind direction partitioning, and fluxes discarded by EC quality assurance criteria. These reasons and the consequent lack of data for half of the hours of the day (Fig. 3) justify that we consider these results exploratory. In particular, compounds such as DMS and monoterpenes had mean daily fluxes dominated by one or two hourly average data points that were not actually hourly averages, since they were based on only one measurement during that hour (i.e. data points without standard deviation shading in Fig. 3). However, there are so few observations of lake VOC fluxes that it is important that we document the sparse data we have.

VOC fluxes assigned to the lake wind direction could potentially have some influence from the vegetation of the island in the lake, because under certain conditions the edge of the EC tower footprint reached that far. A previous study at this site described $CO_2$ uptake during the day from the lake EC measurements in summertime (Jammet et al., 2017). Such uptake was later interpreted as a result of the photosynthetic activity on the island, since water sampling indicated the surface water of lake Villasjön was consistently supersaturated with respect to atmospheric $CO_2$ (Jansen et al., 2019). During our weeklong July measurements, we only observed lake $CO_2$ uptake in the early morning (Fig. 4) when VOC emissions were small (Fig. 3). Hence, we assume that the vegetation of the island did not substantially bias our lake VOC fluxes although some influence cannot be entirely ruled out.

The most striking feature of the lake ecosystem is that it was a sink for acetaldehyde and acetone in both studied periods (Fig. 3, Table 1). Similar to the fen, the deposition of these compounds accounted for most of the VOC flux in the lake in September. Acetone deposition peaked in July with an average of $-19 \pm 1.3$ µmol $m^{-2}$ $day^{-1}$, while that of acetaldehyde was highest in September with $-8.5 \pm 2.3$ µmol $m^{-2}$ $day^{-1}$ (Table 1). There was a correlation of the acetaldehyde and acetone deposition rates with their corresponding atmospheric mixing ratios (Fig. 6), with increasing deposition at higher mixing ratios, resulting in average deposition velocities of $-0.23 \pm 0.01$ and $-0.68 \pm 0.03$ cm $s^{-1}$ for acetone and acetaldehyde, respectively. The high water solubility of these short-chain oxygenated VOCs helps their deposition from the air to the water, and may partly explain the correlation of the deposition rate with their atmospheric mixing ratios (Fig.~~Air temperature also influenced the flux of these two carbonyl VOCs.~~ 6). The flux of these two carbonyl VOCs showed a relationship to air temperature as well, that might very well be coincidental and dependent on atmospheric mixing ratios. Acetone deposition was more intense at higher air temperatures, in July, when its mixing ratios were also higher (Fig. 6). In contrast to acetone, acetaldehyde did not present a clear relationship with air temperature but its strongest deposition rates occurred at air temperatures below 3 ºC ~~(Fig. 6).~~ , concurrent with higher mixing ratios (Fig.~~The high water solubility of these short-chain oxygenated VOCs helps their deposition from the air to the water, and may partly explain the correlation of the deposition rate with their atmospheric mixing ratios (Fig.~~ 6).

These carbonyl compounds have not only natural sources such as emission from vegetation and soil: they also originate from human activities and from atmospheric degradation of other precursor VOCs (Seco et al., 2007). The limited reactivity of acetone in the troposphere makes it relatively long-lived, typically up to 15 days (Singh et al., 2004), which means that the deposited acetone can be advected from far away (Patokoski et al., 2015). We have not found studies in the literature on air-water fluxes of acetaldehyde or acetone in freshwater environments, only a few in marine environments. Yet those marine studies have contradictory results on whether the ocean is a net sink or a source of acetone (Fischer et al., 2012), suggesting a location-dependent behaviour where tropical and productive areas are a net source while high latitude oligotrophic oceans are either in an air-water equilibrium (i.e. zero net flux) or act as net sinks of acetone (Beale et al., 2013, 2015; Lawson et al., 2020; Marandino, 2005; Schlundt et al., 2017; Taddei et al., 2009; Tanimoto et al., 2014). Villasjön, as an oligotrophic high latitude lake, would fit in that conceptual framework as a sink of acetone, in agreement with our observations. The direction of the acetaldehyde flux in seawater has been reported to vary along the year during an annual study in UK shelf waters (Beale et al., 2015) and also to be mostly emission during short-term measurements in a Norwegian fjord mesocosm experiment (Sinha et al., 2007). Further, the lake sink of acetaldehyde and acetone detected with our measurements in the snow-free season may be reversed to a source once the valley is covered in snow, as release of acetaldehyde, acetone and other carbonyl compounds from snow has been documented (Couch et al., 2000).

Interestingly, even though methanol is more soluble in water than acetone or acetaldehyde (Sander, 2015), its deposition to the lake did not reach the intensity displayed by the two carbonyl compounds (Fig. 3). Instead, average methanol fluxes showed ~~both net~~little to no flux, either deposition ~~and~~or emission, along the day during both seasons.~~ Furthermore, in July the overall methanol flux resulted in a net release from the lake (1.8 ± 2.1 µmol $m^{-2}$ $day^{-1}$; Table 1).~~ Again, given the dearth of published observations, we can only compare our methanol fluxes to marine studies. In contrast to acetone and acetaldehyde and their variable flux direction, methanol has been reported to be consistently deposited to the ocean surface, where it could represent a supply of energy and carbon for marine microbes (Beale et al., 2015; Sinha et al., 2007; Yang et al., 2013).

Like the fen, the lake also emitted isoprene in July, although without a visible diel pattern given the incomplete dataset (Fig. 3). Nevertheless, our available data showed maximum hourly average net emissions of 1 nmol $m^{-2}$ $s^{-1}$, ~~being the~~and a daily average net rate of 0.24 ± 0.12 nmol $m^{-2}$ $s^{-1}$ (equivalent to 20 ± 10 µmol $m^{-2}$ $day^{-1}$; Table 1). These numbers are two to three orders of magnitude higher than isoprene emissions calculated at the large temperate oligotrophic lake Constance (Germany) in the month of July, with maximum hourly average emission rates of 0.004 nmol $m^{-2}$ $s^{-1}$ (Steinke et al., 2018). Based on the data from lake Constance, Steinke et al. (2018) suggested that Arctic lakes could rival terrestrial vegetation emissions in these zones where lake areal coverage is high and terrestrial isoprene sources are small. Our numbers do not fully support that suggestion for the peak of the season at our site, since the fen net emission was roughly 4.5 times that of the lake (Table 1), albeit it may hold in zones with a ratio of lake to vegetation coverage over five. For instance, the Stordalen catchment has 4.5% of lake coverage and 3.9% of fen coverage (Lundin et al., 2016), so the lake to vegetation ratio is 1.2, and much lower if we include other types of vegetation. Still, their suggestion may be valid for other periods. For example, in our case during the senescent period in September, even though the flux magnitudes were much smaller than in July, the lake average isoprene emission was double that of the fen ($0.6 \pm 0.4$ and $0.3 \pm 0.3$ μmol $m^{-2}$ $day^{-1}$, respectively; Table 1). We found no other report of isoprene fluxes from lakes, despite the likely existence of many sources analogous to those known in seawater such as phytoplankton, seaweeds, bacteria, and cyanobacteria (Broadgate et al., 2004; Exton et al., 2013; Fall and Copley, 2000; Shaw et al., 2003, 2010). A number of available publications suggest that ocean waters are sources of isoprene to the atmosphere at rates comparable to those calculated for Lake Constance, i.e. two orders of magnitude lower than ours (Broadgate et al., 1997; Kameyama et al., 2014; Li et al., 2017; Sinha et al., 2007).

DMS is a commonly studied marine trace gas because of its role in aerosol and cloud nucleation chemistry (Carpenter et al., 2012) but there are far fewer observations in freshwater environments. As far as we know, no EC measurements of DMS from lakes exist, so the few published studies that report a DMS flux employed alternative techniques to calculate the fluxes, for example using the DMS concentration difference between water and air with an air-water transfer model to calculate the fluxes. DMS emissions calculated by Steinke et al. (2018) for the 252 meter-deep lake Constance were, as for isoprene, two orders of magnitude smaller (maximum hourly average emission rates of 0.003 nmol $m^{-2}$ $s^{-1}$) than our July fluxes. A study in Canadian boreal lakes estimated DMS emissions up to a few μmol $m^{-2}$ $day^{-1}$ for shallow lakes, which is on the lower range of the July fluxes in the shallow Villasjön. That study also noted that emissions from deeper lakes were smaller than from shallow or medium-depth lakes (Sharma et al., 1999), while a similar study in the same geographical area found average DMS fluxes of around 1 μmol $m^{-2}$ $day^{-1}$ from lakes ranging in depths from 1.5 to 20 m but with a 5 meter-deep lake showing much higher emissions of up to 4 μmol $m^{-2}$ $day^{-1}$ on average (Richards et al., 1991). Other authors measured DMS concentrations in a stratified lake in North America, at different depths down to 13 m, and concluded that DMS fluxes to the atmosphere must have been insignificant given that DMS was not present in surface and near surface water (Hu et al., 2007). Another study took a different approach and utilized the phytoplankton biomass and its content of DMS precursors in lake Kinneret (Israel) to estimate an average DMS emission of 3.3 μmol $m^{-2}$ $day^{-1}$ (Ginzburg et al., 1998), similar to our July average of $4.7 \pm 3.1$ μmol $m^{-2}$ $day^{-1}$ (Table 1). In contrast, DMS fluxes from the ocean have been directly measured by EC in different places around the globe, with reported emissions as high as 97 μmol $m^{-2}$ $day^{-1}$ (Bell et al., 2013; Marandino et al., 2007, 2009; Smith et al., 2018), even up to 300 μmol $m^{-2}$ $day^{-1}$ during an unicellullar phytoplankton bloom (Marandino et al., 2008), but in many cases with average emissions in the same range as our lake July average flux (Huebert et al., 2004; Tanimoto et al., 2014; Yang et al., 2011b, 2011a).

## 3.4 $CO_2$, $CH_4$, and $H_2O$ fluxes

The fluxes of $CO_2$ and $CH_4$ (as well as $H_2O$) were not the focus of this study and, moreover, their temporal patterns and environmental drivers over several years at the same site have been examined in detail elsewhere (Jammet et al., 2015, 2017; Jansen et al., 2019, 2020). Here, we mainly included them to contextualize the VOC fluxes and thus provide a broader overview of the trace gas exchange of our fen and Villasjön during our two measurement periods. Furthermore, as in the case of the July VOC fluxes, the limited data availability from the lake in July (36 and 51 half-hourly fluxes for $CO_2$ and $CH_4$, respectively) advises to consider the presented lake trace gas exchanges with prudence.

Net molar fluxes of $CO_2$, $CH_4$, and $H_2O$ were at least two, and up to seven, orders of magnitude higher than the VOC fluxes (Table 1). Water vapour and $CH_4$ showed net average daily emission in both lake and fen and during both periods, while $CO_2$ showed net uptake in July and net release in September, in both lake and fen (Table 1).

Uptake of $CO_2$ and evapotranspiration in the fen followed a well-defined diel cycle likely due to the physiological activity of the vegetated surface, with maxima around noontime, notably in July (Fig. 4). In September, a similar pattern was apparent in the fen's diel cycles (Fig. 4), but the magnitude of the daytime fluxes was much smaller. It was so much smaller that the weaker $CO_2$ uptake during daylight hours did not compensate for the $CO_2$ release during the rest of the day, resulting in a 24-hour aggregate mean flux that represented a net release of $CO_2$ to the atmosphere from the fen (Table 1). $CH_4$ emissions from the fen in July were on average 3.5 times higher than in September (Table 1), and their diel emission cycle showed an overall flat pattern in both periods (Fig. 4).

The lake was a net sink of $CO_2$ in July, especially due to stronger uptake during the early hours of the day, and a net source in September, during which there was no diel cycle (Table 1, Fig. 4). Evaporation from the lake was approximately 10-fold higher in July than in September on a 24-hour basis, and compared to the evapotranspiration from the fen, it was higher in July as well (Table 1, Fig. 4). Daily $CH_4$ emissions from the lake were smaller than from the fen during both periods (Table 1).

A comparison of the VOC carbon fluxes with the fluxes in the form of $CO_2$ and $CH_4$ (Table 1) reveals that the average net VOC emission of the fen in July, summing the six VOC species reported in this manuscript, represented 0.16 % of the fen net carbon uptake as $CO_2$ (of which isoprene alone was 0.15 %) and 4.2 % of the net carbon release as $CH_4$ (isoprene alone, 3.9 %). In September, the absolute VOC net carbon flux at the fen, i.e. the total net amount of carbon exchanged in the form of VOCs, including both the VOCs with net emission and those with net uptake, added up 0.06 % of the net $CO_2$ carbon and 0.76 % of the net $CH_4$ carbon emitted from the fen.

The same comparison for the lake (Table 1) shows that the aggregate absolute VOC net exchange amounts to 0.32 % of the $CO_2$ and 3.2 % of the $CH_4$ net carbon fluxes of the lake. In September, the absolute VOC net carbon flux in the lake was equivalent to 0.13 % of the net $CO_2$ carbon release flux and 3.8 % of the net $CH_4$ carbon emission flux.

## 4 Concluding remarks

Here we presented an eddy-covariance dataset measured from two distinct common subarctic landscape types: a permafrost-free fen and a shallow post-glacial lake. Isoprene dominated by far the VOC fluxes from the fen at the peak of the season, while after the growing season the fen was characterized by deposition of acetaldehyde and acetone (Fig. 3, Table 1). Furthermore, the isoprene emissions from the fen in July were strongly stimulated by temperature and, in agreement with previous arctic and subarctic VOC measurements (Holst et al., 2010; Tang et al., 2016), exhibited a higher temperature sensitivity ($Q_{10}$ = 14.5) than described by the temperature response curves typically used in biogenic emission models ($3 \leq Q_{10} \leq 6$), which are based on measurements made in lower latitudes (Guenther et al., 2006). Our measurements also displayed the disparity between the temperature of the air and that of the vegetation surface, the latter being several degrees warmer during daytime (Figs. 2 and 5). Consequently, it is advisable that future VOC studies measure accurately and precisely the vegetation temperatures that represent the thermal conditions controlling the VOC production and release processes. Furthermore, while we do not suggest taking these $Q_{10}$ values as true coefficients to be directly implemented into modelling, it is worth mentioning that care should be taken when applying $Q_{10}$ values in models. Otherwise, a mismatch could translate into erroneous results, for instance when using a $Q_{10}$ derived from the response to air temperature in models that drive VOC emissions with leaf temperature and vice versa.

Our lake VOC fluxes can be considered exploratory due to the low amount of data available. Despite this, they are valuable given the lack of observations of freshwater fluxes. We showed that the lake was a sink of acetone and acetaldehyde in both July and September with average deposition velocities of -0.23 ± 0.01 and -0.68 ± 0.03 cm $s^{-1}$ for acetone and acetaldehyde, respectively (Fig. 3, Fig. 6, Table 1).

The carbon exchanged as VOC net fluxes from both fen and lake constituted less than 0.5% and less than 5% of the $CO_2$ and $CH_4$ net carbon ecosystem exchange, respectively. These low proportions are probably one of the reasons, together with technical and logistical challenges (Rinne et al., 2016), of the limited amount of existing VOC studies in lakes or high latitude ecosystems. However, technological advances are gradually removing practical obstacles and, in addition, growing concern about climate change repercussions warrants more research in this rapidly warming area of the world, especially given the importance of VOCs as precursors for aerosols (Paasonen et al., 2013; Svenningsson et al., 2008). $CO_2$ and $CH_4$ fluxes are already under intense investigation to quantify the strength of their sinks and sources (e.g. Jeong et al., 2018; Oh et al., 2020). Recently, arctic VOCs have received increased attention (e.g. Kramshøj et al., 2016, 2018, 2019) and this study is another contribution towards the understanding of VOC budgets in northern wetlands and inland waters.

## Data availability

VOC flux data used in this article, together with PAR, air temperature, and vegetation surface temperature are available for download at https://doi.org/10.5281/zenodo.3886457 (Seco et al., 2020). $CO_2$, $H_2O$ and $CH_4$ fluxes, and wind direction and speed can be downloaded from http://www.icos-etc.eu/home/site-details?id=SE-St1. Villasjön water temperatures are available at https://bolin.su.se/data/crill-2019.

## Author contributions

RS, TH, MSM, AWN, TL, TS, and JJ performed measurements and contributed data. RR conceptualized and supervised the study and acquired funding to support this research. RS analysed the data and wrote the original draft. All authors contributed to manuscript writing and revision, and read and approved the submitted version.

## Competing interests

The authors declare that they have no conflict of interest.

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**Table 1: Average (± standard error of the mean) daily net exchange rates (µmol m$^{-2}$ day$^{-1}$) of VOCs, $CO_2$, $H_2O$ and $CH_4$. Negative values represent net deposition or uptake by the ecosystem, and positive values represent net emission. These daily averages were calculated from the hourly averages shown in Figs. 3 and 4.**

| | LAKE (µmol m$^{-2}$ day$^{-1}$) | | FEN (µmol m$^{-2}$ day$^{-1}$) | |
|---|---|---|---|---|
| Compound | July* | September | July | September |
| methanol | 1.8 (±2.1) | -0.2 (±0.3) | 7.7 (±1.1) | 1.1 (±0.3) |
| acetaldehyde | -3.8 (±2.4) | -8.5 (±2.3) | 2.6 (±0.9) | -6.7 (±2.8) |
| acetone | -19 (±1.3) | -4.4 (±0.2) | 1.9 (±1) | -2.5 (±0.3) |
| isoprene | 20 (±10) | 0.6 (±0.4) | 93 (±22) | 0.3 (±0.3) |
| monoterpenes | 2.8 (±2.2) | 0.3 (±0.1) | 2.2 (±0.3) | 0.3 (±0.04) |
| DMS | 4.7 (±3.1) | -0.2 (±0.1) | 1.1 (±0.4) | -0.2 (±0.1) |
| $CO_2$ | -6.3E+04 (±3.7E+04) | 2.7E+04 (±9.8E+03) | -3.1E+05 (±7.3E+04) | 4.6E+04 (±1.2E+04) |
| $H_2O$ | 3E+08 (±2.7E+07) | 3.2E+07 (±3.4E+06) | 1.2E+08 (±2E+07) | 4.6E+07 (±4.7E+06) |
| $CH_4$ | 6,400 (±1,400) | 950 (±110) | 1.2E+04 (±2.8E+02) | 3,500 (±90) |

*based on a limited dataset from 03:00 to 14:00 hours (UTC+1)

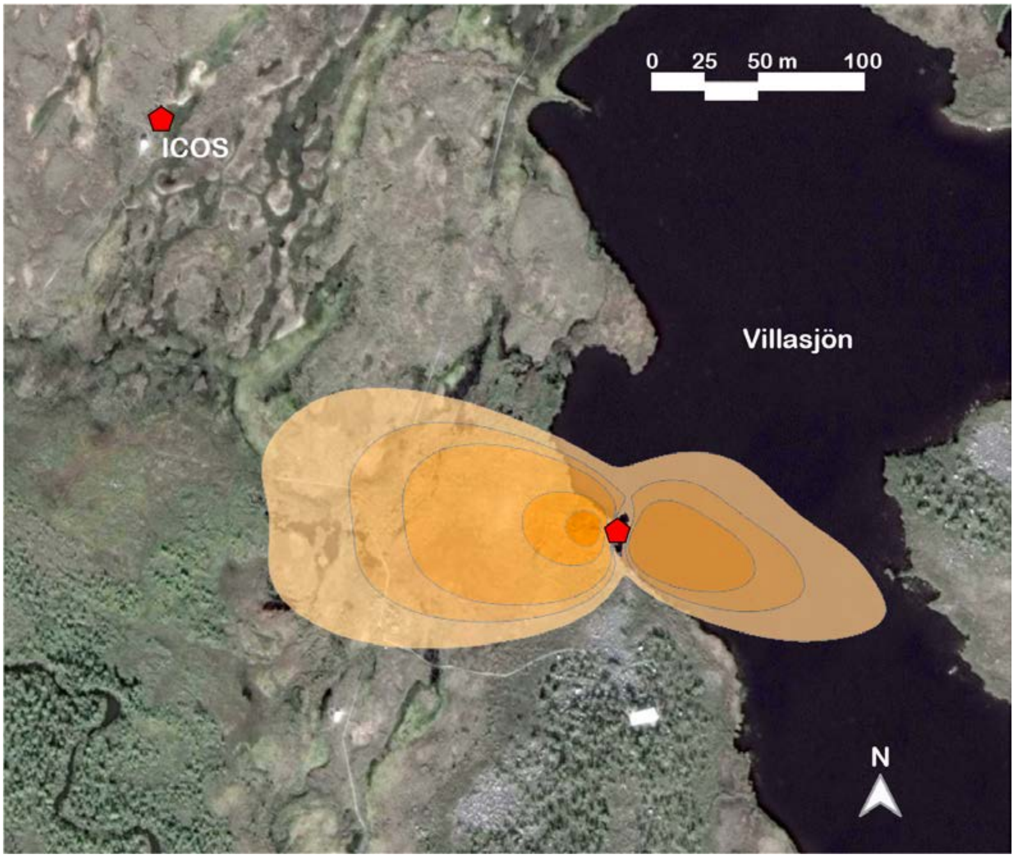


**Figure 1: Map of the Stordalen Mire study area, showing our EC tower by the shore of Villasjön, and the nearby ICOS station location that provided the vegetation surface temperature data. The shaded area represents the combined fen and lake footprint for the July EC measurements, at flux contribution intervals of 85%, 80%, 75%, 50% and 25%. The base map image is © Google Earth (image provided by DigitalGlobe).**

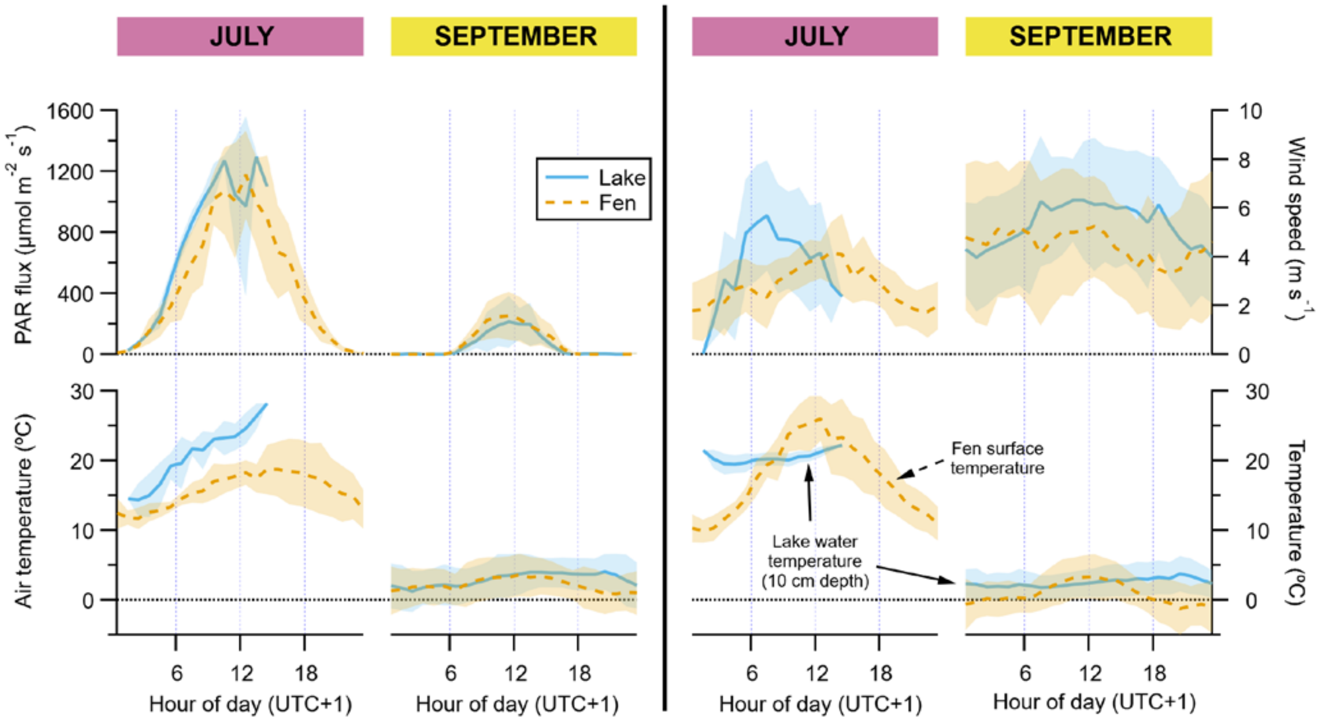


**Figure 2: Diel cycles of hourly averages of meteorological data, for July and September and for both lake (blue solid lines) and fen (dashed orange lines). Peak of growing season (July) is on the left panels of each graph pair, and the post growing season (September) is on the right panels, as indicated on top of the panels. Shaded areas represent ± 1 standard deviation. Each vertical axis has a different scaling, but all of them feature a horizontal dotted line showing where the value zero is located.**

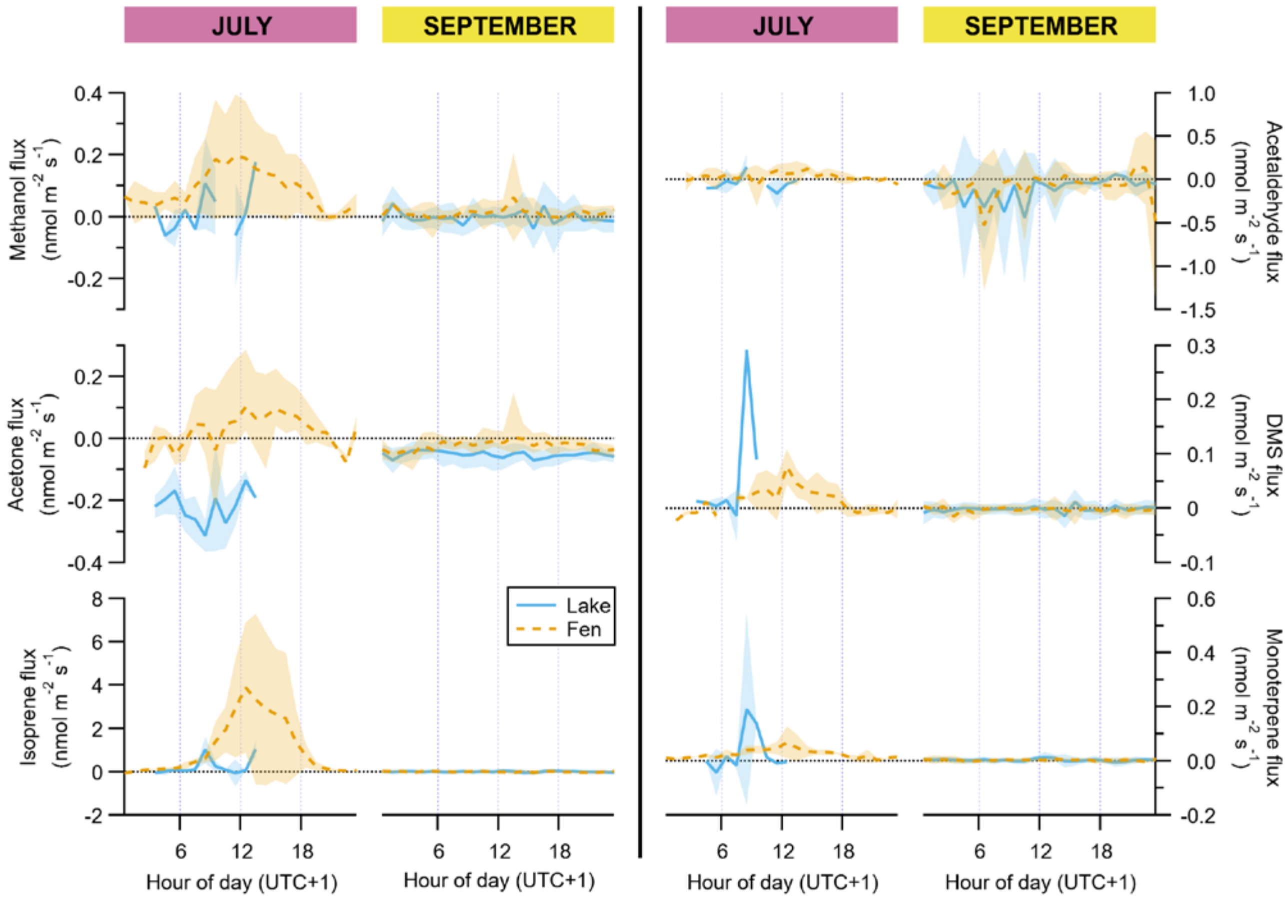


**Figure 3: Diel cycles of hourly averages of VOC fluxes, for July and September and for both lake (blue solid lines) and fen (dashed orange lines). Peak of growing season (July) is on the left panels of each graph pair, and the post growing season (September) is on the right panels, as indicated on top of the panels. Shaded areas represent ± 1 standard deviation. Each vertical axis has a different scaling, but all of them feature a horizontal dotted line showing where the value zero is located.**

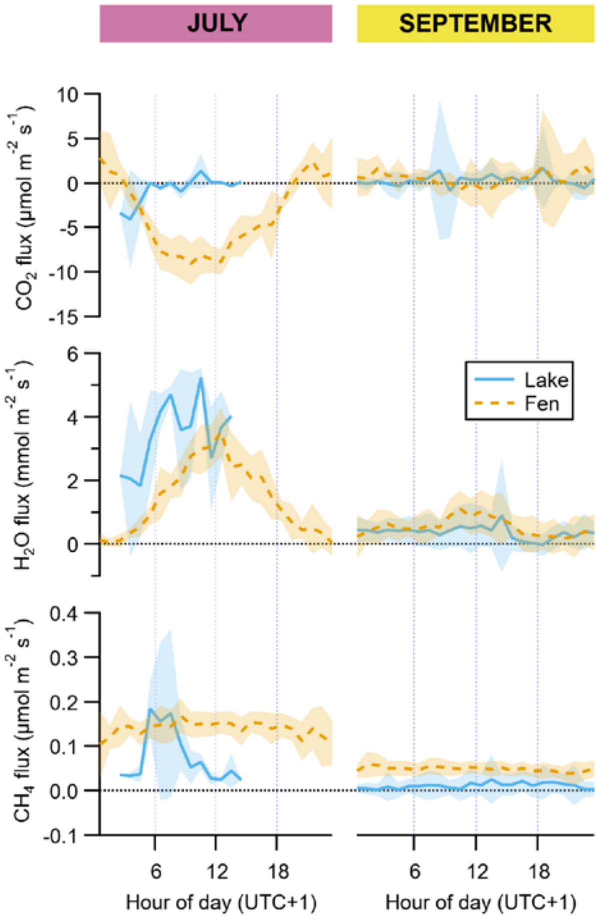


**Figure 4: Diel cycles of hourly averages of fluxes of $CO_2$, $H_2O$ and $CH_4$, for July and September and for both lake (blue solid lines) and fen (dashed orange lines). Peak of growing season (July) is on the left panels of each graph pair, and the post growing season (September) is on the right panels, as indicated on top of the panels. Shaded areas represent ± 1 standard deviation. Each vertical axis has a different scaling, but all of them feature a horizontal dotted line showing where the value zero is located.**

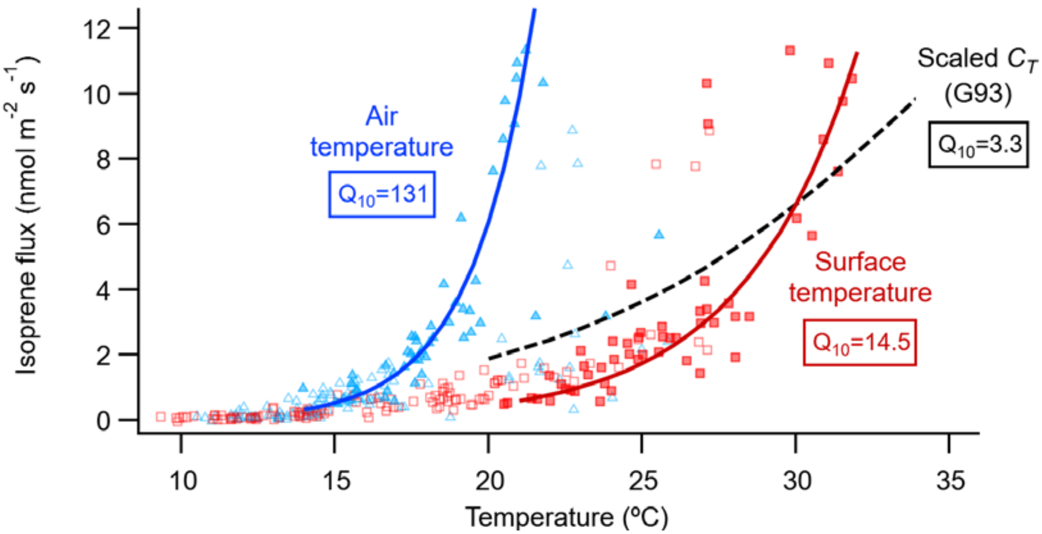


**Figure 5: Relationship of the isoprene flux from the fen with the air temperature (blue triangles) measured at 2 m height on the EC mast, and with the vegetation surface temperature (red squares) measured at the nearby ICOS station. The data points shown are all the July 30-minute fluxes that passed the EC quality criteria (n=161; open and closed symbols). Solid lines show the exponential equation $F = F_0 \cdot Q_{10}^{(T-T_0)/10}$, where $F_0$ is the isoprene flux rate at temperature $T_0$ (=0 ºC), $F$ is the flux rate at temperature $T$ (ºC), and $Q_{10}$ is the temperature coefficient. $F_0$ and $Q_{10}$ were calculated by fitting the data to the linear equation $\log(F) = T \cdot \log(Q_{10})/10 + a_0$, where $a_0$ is the intercept at T=0 ºC. For the fit, only fluxes not limited by light (when PAR was ~~above~~ 1000 µmol m$^{-2}$ s$^{-1}$ or more; n=52; closed symbols) were binned into 1-degree bins (not shown). Then the average fluxes of the bins, excluding bins containing a single flux value, were used to perform an orthogonal distance regression weighed by the standard deviation of each bin average. As a reference, the dashed black line shows the relationship with leaf temperature of the temperature activity factor ($C_T$) of the G93 model (Guenther et al., 1993), scaled to coincide with the surface temperature fit at 30 ºC.**

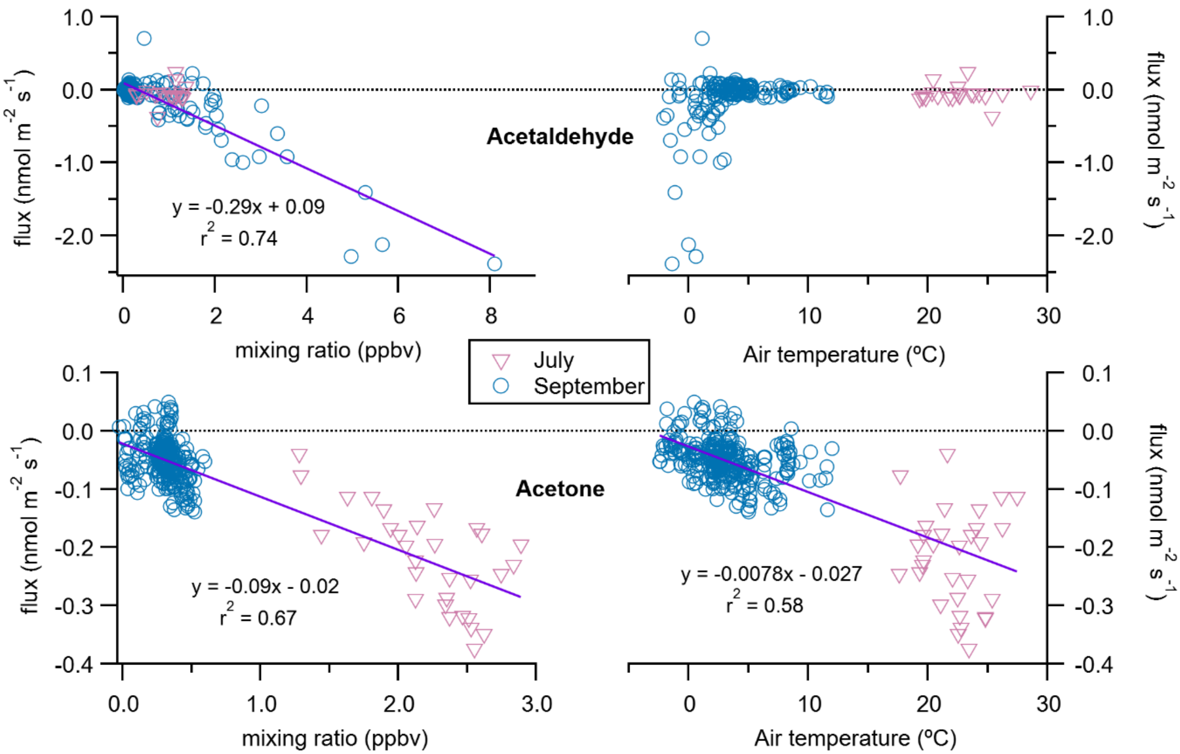


**Figure 6: Relationship of lake fluxes of acetaldehyde (top panels) and acetone (bottom panels) with their respective atmospheric mixing ratios (left panels) and the air temperature (right panels). Each solid line and corresponding equation represent an orthogonal distance regression to all 30-minute flux data points for both July and September (n=191 for acetaldehyde and n=338 for acetone).**