Transpiration directly regulates the emissions of water-soluble short-chained OVOCs

Authors: Rissanen, K., Hölttä, T & Bäck, J.

Institute: Institute for Atmospheric and Earth System Research / Forest Sciences, Faculty of Agriculture and Forestry, University of Helsinki

Author for correspondence:

Kaisa Rissanen

Address: Institute for Atmospheric and Earth System Research / Forest Sciences, Faculty of Agriculture and Forestry, University of Helsinki, P.O. Box 27, FIN-00014, Finland

Email: kaisa.rissanen@helsinki.fi

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Abstract

Most plant-based emissions of volatile organic compounds (VOCs) are considered to be mainly temperature dependent. However, certain oxygenated VOCs (OVOCs) have high water solubility and also regulation of their emission by stomatal conductance has been suggested. However, due to their water solubility and sources in stem and roots, transport in xylem sap has been suggested to play a role in their shoot emissions. Yet, further understanding on this role has been lacking until present.

We used shoot-scale long-term dynamic flux data from Scots pine (*Pinus sylvestris*) trees to analyse the effects of transpiration and transport in xylem sap flow on emissions of three water soluble OVOC: methanol, acetone and acetaldehyde. We found a direct effect of transpiration on the shoot emissions of the three OVOCs. The emissions were best explained by a regression model that combined linear transpiration and exponential temperature effects. In addition, a structural equation model indicated that stomatal conductance affects emissions mainly by regulating transpiration, and that a part of temperature's effect is also indirect.

The tight coupling of shoot emissions to transpiration clearly evidences that these OVOCs are transported in xylem sap from their sources in roots and stem to leaves and to ambient air.

Keyword index

Acetone, acetaldehyde, long-distance transport, methanol, OVOC emissions, temperature, transpiration, xylem sap

Introduction

Plant produced volatile organic compounds (VOCs) are an important factor in the troposphere. They contribute to ozone formation and destruction, as well as to the formation and growth of new atmospheric particles. The production and emissions of plant emitted VOCs have been extensively studied and modelled to explain and predict these atmospheric processes better. The emission models, for example for terpenoids, are mainly based on temperature and/or light (Guenther et al., 1993; Guenther 1995; Guenther 1995, Simpson et al., 1995). Other physiological controlling factors have been rarely used in the models. However, the emission dynamics of water-soluble compounds (Henry's law coefficient (H) under 100 Pa m^3 mol^{-1} at 25 °C), such as short-chained oxygenated VOCs (OVOCs), depend also on the dynamics of water phase inside the plant. This dependence could play a central role in regulating emissions and should not be ignored.

In contrast to the emissions of non-water-soluble compounds, the emissions of water-soluble OVOCs, such as, methanol (H= 0.461 Pa m^3 mol^{-1} at 25°C), acetone (H= 3.88 Pa m^3 mol^{-1} at 25°C) and acetaldehyde (H= 7.0 Pa m^3 mol^{-1} at 25°C) may be regulated by stomatal conductance (Niinemets et al., 2003, 2004; Harley et al., 2007). When stomatal conductance decreases, increase in the partial pressure in sub-stomatal cavity enhances the partitioning of the water-soluble compounds into water films. Thus, the partial pressure in the sub-stomatal cavity increases less than for non-water soluble compounds, and the partial pressure difference between sub-stomatal air and ambient air cannot necessarily overcome the stomatal limitation of flux (Niinemets et al., 2003). This regulation is apparent, for example, when the stomata open in the mornings. Low stomatal conductance in the nights enables the accumulation of water soluble compounds

that are then released as the stomata open, creating the sudden morning bursts that can be detected in several plant species (Mac Donald et al., 1993; Nemeck-Marshall et al., 1995; Harley et al., 2007; Folkers et al., 2008; Saunier et al., 2017).

In addition to stomatal conductance, transpiration has been detected to correlate with emissions of water soluble compounds. Kreuzwieser et al., (2001), Cojocariu et al., (2004) and Filella et al., (2007) have reported a correlation between transpiration and acetaldehyde emissions. Acetaldehyde is produced from ethanol (H= 0.507 Pa m^3 mol^{-1} at 25°C) that can be transported in the xylem (Kreuzwieser et al., 2000; Fall et al., 2003). Grabmer et al., (2008), Harley et al., (2007) and Folkers et al., (2008) have also reported links between methanol emissions and transpiration. This link has been explained by the fact that transpiration combines the impacts of temperature and stomatal conductance (Harley et al., 2007), or by possible methanol transport in xylem (Grabmer et al., 2006; Folkers et al., 2008). Cojocariu et al., (2004) observed a correlation between acetone emissions and transpiration, but had no further hypothesis on its origin. These findings suggest that also transpiration could play a role in regulating emissions of water-soluble compounds, for example, though the transport of the compound, or its precursor in case of acetaldehyde, in xylem sap. In addition, although less water soluble than, for example, methanol, acetone and acetaldehyde, also CO_2 (H= 2937 Pa m^3 mol^{-1} at 25°C) is known to travel long distances in the xylem sap (McGuire & Teskey, 2004; Bowman et al., 2005; Bloemen et al., 2013).

The transport of CO_2 in the xylem sap had been suggested as early as 1933 by Boysen-Jensen (Boysen-Jensen, 1933). Later in 2009, Hölttä and Kolari presented a detailed theoretical framework for CO_2 transport in the xylem sap (Hölttä & Kolari, 2009). Those authors found that a proportion of the CO_2 produced by stem respiration dissolves in the xylem sap and is transported upwards. The remainder of the CO_2 diffuses through the bark into the atmosphere, and it is measured as stem respiration. Xylem sap velocity should affect the stem CO_2 emissions negatively in the lower parts of stems, where a large proportion of the CO_2 is captured by dissolution in the xylem sap due to a combination of low CO_2

concentrations in the sap and the large diffusion resistances created by thick bark. Transported CO_2 affects the emissions positively in the top parts of stems, where bark is thinner and the water has become saturated with CO_2 due to stem tapering, and thus more CO_2 diffuses into the ambient air (Hölttä & Kolari 2009). The association between xylem sap velocity and CO_2 emissions in shoots is theoretically positive, but it cannot be directly measured, because photosynthesis consumes the CO_2 (Bloemen et al*.,* 2013). A negative correlation between CO_2 emissions from tree stem and xylem sap flux velocity has also been reported by McGuire and Teskey (2004), Bowman et al*.,* (2005), Gansert and Burgdorf (2005), McGuire et al*.,* (2007), among others. The difference between the dynamics in different stem parts is indicative of stem CO_2 fluxes that are higher in the upper compared to the lower stem (Hölttä & Kolari, 2009). A similar pattern could also be expected for OVOC emissions from stem (Fig. 1).

When analysing the role of transport in the emissions of water soluble compounds, it is important also to consider their sources in the plants. The site of production determines the proportion of a compound that can dissolve into the xylem sap and be transported to leaves in relation to the proportion that directly diffuses into the ambient air. Subsequently, it affects the role of transported compounds in total leaf emissions in relation to the compounds that are produced in leaves. Sources of methanol, acetone and acetaldehyde vary considerably in plants, but importantly, they are not confined to any single plant tissue (Seco et al*.,* 2007). The largest methanol source is the demethylation of pectin during cell wall formation (Galbally & Kristine, 2002; Hüve et al*.,* 2007). It is thus produced in all growing tissues from the leaves to the root tips. Smaller methanol sources in plants originate from processes that are related to protein repair (Fall & Benson, 1996; Seco et al*.,* 2007) and to plant stresses, such as, herbivory or mechanical wounding (Fall*,* 2003; Peñuelas et al*.,* 2005; Loreto et al*.,* 2006). As mentioned earlier, one source of acetaldehyde is ethanol that is produced in roots especially under anaerobic conditions (Kreuzwieser et al*.,* 1999, 2000; Fall et al*.,* 2003), or in vascular cambium (MacDonald and Kimmerer, 1991). Another acetaldehyde source is the pyruvate overflow mechanism in leaves (pyruvic acid decarboxylation) during light-dark transitions

(Karl et al., 2002; Fall, 2003; Hayward et al., 2004; Seco et al., 2007; Jardine et al., 2008). Acetone has many different and separate sources in plants, but these are currently not well known or quantified. One production pathway is possibly connected to the decarboxylation of the acetoacetates such as those that occur in micro-organisms and in animals (Fall, 2003).

Although the transport hypothesis has been suggested earlier and it is somewhat established for acetaldehyde, to the best of our knowledge this is the first attempt to address the roles of transpiration and long-distance xylem transport in the emissions of especially methanol and acetone. We studied this transport by using long-term field measurements that covered five annual growing seasons. Our approach was to analyse and separate the effects of temperature, transpiration and stomatal conductance on methanol, acetone and acetaldehyde emissions of Scots pine in uncontrolled field conditions. We hypothesised that 1) methanol, acetone and acetaldehyde can be transported to the shoots in xylem sap and 2) and that subsequently, the transpiration positively affects the emissions of methanol, acetone and acetaldehyde from the shoots.

Materials and methods

The data were collected in southern Finland, at the SMEAR II (station for measuring ecosystem-atmosphere interactions) site in Hyytiälä Forestry Field station. The site is an approximately 50-year-old Scots pine (*Pinus sylvestris* L.) dominated forest, with smaller numbers of silver birch (*Betula pendula* [Roth]), downy birch (*Betula pubescens* [Ehrh.], Norway spruce (*Picea abies* [L.] karst.) and European aspen (*Populus tremula*). The soil is mainly podzolic with a shallow humus layer. More details on the stand are found in the publications by Ilvesniemi et al., (2010) and Hari et al., (2013).

Exchange (fluxes) of OVOCs between the Scots pine (*Pinus sylvestris*) shoots and stems and atmosphere were measured continuously using a dynamic enclosure system that is described in detail by Kolari et al., (2012) and by Vanhatalo et al., (2015). The shoot scale emissions have been measured in a total of five

pines and 21 shoots of different age classes since 2009. The data used in this study were obtained from 3 different Scots pines on the site, and 5 different shoots measured from May to August 2010, 2011, 2013, 2014 and 2015. The 2012 data contained too many gaps due to instrument malfunctions, for example, to be comparable to the other years studied. All the shoots contained only 1-year-old needles, as the new buds had been removed before chamber installation. These buds were removed for two reasons: the first reason was because the growing shoot would have become too big to fit in the chamber in late summer and, the second reason was because our aim was to measure the emissions without the confounding large effect that shoot and needle growth in spring and early summer would have on emissions (Aalto et al., 2014). In addition, we used data from pine stem chambers that were attached to three heights above ground on one pine stem (Vanhatalo et al., 2015). The lowest chamber was positioned at 7 metres, well below the living canopy, where the stem diameter was 11.6 cm. The middle chamber was installed at 12 metres, in the lower part of the living canopy, where the stem diameter was 8.4 cm. The top chamber was placed at 16.5 metres, near the tree top, where the stem diameter was 3.5 cm. The three chambers were measured simultaneously throughout April 2013 and the middle chamber was measured through the entire 2013 growing season.

The dynamic enclosure system consists of shoot and stem chambers that close cyclically, for 3 minutes at a time. During the closure, sample air was drawn from the chamber into gas analysers. Small holes in the chamber enabled ambient air to replace sample air flow. Some of the sample air drawn from chambers was directed to a PTR-MS quadrupole (Photon transfer reaction – quadrupole mass spectrometer, Ionicon Analytik, Innsbruck, Austria), which was set to measure certain protonated masses, in this case, masses m/z 33 (methanol), m/z 45 (acetaldehyde) and m/z 59 (acetone). The shoot emissions were calculated for the OVOC concentration increase in the chamber air during enclosure time by using mass-balance equations as described by Hari et al., (1999) and by Kolari et al., (2012). Because ambient air was used as

replacement air, the concentration inside the chamber at the beginning of the closure equalled the concentration in the replacement air. In this case, we used the simplified equation (Eqn 1).

$$C(t) = C_0 + \frac{E}{F}\left(1 - e^{-\frac{Ft}{v}}\right) \qquad \text{(Eqn 1)}$$

In Equation 2, C(t) is the concentration in the chamber as a function of time, C_0 is the concentration in the chamber at the beginning of the measurement, ν is the chamber volume, F is the flow rate of air through the chamber, t is the time step, and E is the emission rate, which is solved by the equation using least-square fitting to the measured data. The shoot emissions were corrected for leaf dry mass of measured shoot and stem emissions for covered bark area at the end of growing season.

Some of the sample air was also directed to the infrared light absorption analysers (URAS 4, Hartmann & Braun, Frankfurt am Main, Germany), which determined the water vapour and CO_2 concentrations in the sample air. In addition, both the ambient temperature near the tree canopies and the internal temperature of the chambers, along with the relative humidity were monitored continuously. Stomatal conductance (G) was calculated as the division between measured transpiration (ET) and vapour pressure deficit (VPD).

We omitted any data taken when the relative humidity (RH) of the chamber was over 70% prior to data analysis. High humidity in chamber causes condensation of water and its absorption on water-soluble compounds, making the flux data unreliable.

We examined the effects of chamber temperature, ambient temperature, transpiration and stomatal conductance on shoot emissions of methanol, acetone and acetaldehyde by regression analysis for both

the entire growing season and monthly periods. The effect of temperature was calculated as described by Guenther et al*.,* (1995) (Eqn 2).

$$E_T = E_S * exp^{[\beta(T-T_S)]} \qquad \text{(Eqn 2)}$$

In Equation 2, E_T is the modelled emission rate at temperature T, E_S is the reference emission factor at 303 K, T is the temperature inside chamber (in K) and T_S is a reference temperature (303 K). β is an empirical parameter for the temperature sensitivity. We optimised β for each study period and compound for the best fit of temperature model. The effect of transpiration on emissions was best explained by a linear regression, whereas the effect of stomatal conductance was best explained by an exponential function. We first tested the goodness of each independent variable (T, ET and G) for explaining the emissions separately (Table 1, functions 1-3). Secondly, we tested the combinations of temperature and transpiration (T+ET), and temperature and stomatal conductance (T+G) (Table 1, functions 4-5). In the models (Table 1), *a* is an intercept and *b-d* are coefficients that were set freely to obtain the best fit for the models. The regression models explaining the OVOC emissions were evaluated based on their coefficient of determination (R2). We also analysed the effects of temperature and transpiration on stem emissions by testing the regressions at different time lags, and studied the similarity between the emission dynamics (shoot and stem) of the three compounds by Pearson's correlation. These analyses were made in Matlab (version R2017a, The MathWorks, Inc.).

TABLE 1

We used structural equation modelling (SEM) using the R lavaan package (R version 3.3.1, and the R Foundation for Statistical Computing) (Rosseel, 2012) to analyse further the interrelations between

temperature, transpiration and stomatal conductance in explaining the emissions of OVOCs. The SEM model is used for normal distribution and linear relations, thus we normalised the transpiration data and emission data of all compounds by using the square roots of their values. Temperature and stomatal conductance data did not need transformations as they were normally distributed. We built two models, the first one following the suggestion by Niinemets et al*.,* (2003) whereby temperature and stomatal conductance explain the emissions of water-soluble OVOCs. In the second model we included the effect of transpiration that describes transport in xylem sap. The goodness of fit of the two SEM models were evaluated by the R2 for emissions, and the comparative fit index (CFI) and the Tucker-Lewis index (TLI) needed to be close to 1. The interrelation between the variables in the SEM models and their importance in the models were evaluated by their estimated standardized parameter values in each regression and p-values attributed to the parameter values. P-values below 0.05 were regarded as statistically significant.

We picked data sets from periods that had sufficient numbers of data points to represent diurnal or seasonal dynamics, and that covered the different measurement years to illustrate the dynamics of OVOC emissions from shoots and stems (March–October 2013), emission correlations to temperature, transpiration and stomatal conductance (May–August 2010), the regression model fits (9^{th}–12^{th} of June and 16^{th}–19^{th} of August 2015.), and SEM model functioning (May–September 2014).

Results

Shoot emissions of methanol, acetone and acetaldehyde had both clear seasonal and diurnal patterns that were similar throughout all the five studied growing seasons. For example, the seasonal pattern was clearly manifested in 2013. The start of growing seasons in early May drastically increased the shoot emissions of methanol, acetaldehyde and acetone (Fig. 2, a, c, and e). The emissions further increased through June and then started to decrease in mid-July. Emissions steadily decreased starting from the later part of August, although a few peaks were still observed. The shoot emission dynamics of the three compounds

were very similar to each other throughout the five growing seasons and the acetone and acetaldehyde emissions correlated very closely, although the acetone emissions were larger (Fig. 2, a, c, and e, Table 2). The shoot emissions during the growing season were highest in the daytime, at night the emissions were low but usually still positive (Fig. 2, a, c, and e inserts). We observed shoot uptake only occasionally in early May and in late August (Fig. 2, a, c and e). We did not detect clear morning bursts of any of the three compounds.

TABLE 2

Stem emissions of methanol, acetone and acetaldehyde at 12 metres also had a clear seasonal and some diurnal variation during the growing season 2013 (Fig. 2, b, d, f). Emissions started to increase in mid-May. Acetaldehyde emissions peaked at the end of June and methanol emissions peaked in early July. The emissions of all the compounds increased slightly again at the end of July before decreasing towards the autumn. The stem emissions of the three compounds were not as similar as was the case for the shoot emissions (Table 2). From mid-May to August, emissions were usually highest in day-time and lowest at night, depending on the compound (Fig. 2, b, d, f and inserts). In April 2013, we found that stem emissions of all three compounds increased with increasing stem height, the biggest difference being between 12 and 16.5 metres (Fig. 3). The baseline stem emissions of acetone and acetaldehyde were nevertheless quite small at that time, and we observed clear diurnal patterns only at 16.5 metres. The methanol emissions were larger and had clear diurnal pattern at all heights.

Temperature and transpiration rate best explained the shoot emissions of methanol, acetone and acetaldehyde during all the studied periods (Tables 3-5). The effect of temperature was exponential, and on average, explained 70% of methanol, 51% of acetaldehyde and 62% of the acetone emission variation (Fig. 4, Tables 3-5, model T). Transpiration had a linear effect on the emissions, and on average, explained 59% of methanol, 63% of acetaldehyde and 67% of acetone emission variation (Fig. 4, Tables 3-5, model

ET). The effect of stomatal conductance on the mean emissions of the OVOCs was also exponential but smaller: stomatal conductance, on average, explained only 10% of methanol and 16% of acetaldehyde and acetone emission variation (Fig. 4, Tables 3-5, model G). These effects were well presented, for example, in 2010 (Fig. 4). In addition, the emissions seemed to be regulated by stomatal conductance only when stomatal conductance decreased to 0.25 $dm^3\ s^{-1}\ m^{-2}$ or below, at nigh time (Fig. 4, grey line). At higher conductance, the emissions were determined either by temperature or transpiration rate. During the exemplar growing season of 2010, we observed slight shifts in the temperature, transpiration and stomatal relations of methanol, acetone and acetaldehyde emissions (Fig. 4, Tables 3-5). In May and June, the temperature sensitivities of especially acetaldehyde and acetone emissions were higher than later in the summer. The sensitivity of methanol emissions to transpiration rate also increased in May and June. In addition, stomatal conductance seemed to affect all the compounds more in July and August than in early summer.

Of the all regression models (Table 1), the model that combined temperature and transpiration (model T+ET) best explained the emissions of all three compounds (Tables 3-5) and produced smallest root mean square error (Supporting information Tables S1-S3). For acetone and acetaldehyde emissions, model T+ET was usually considerably better than model T+G, but close to model ET (Tables 4-5, Supporting information Fig. S1). In contrast, for methanol, the differences between model T, model T+ET and model T+G were small in most periods (Table 3, Supporting information Fig. S1). The error degrees of freedom of all the models ranged from 278 to 2310 depending on the period analysed (Supporting information Table S4).

TABLES 3-5

Temperature and transpiration affected the stem emission less than they affected shoot emissions, and with certain time lags. The temperature explained 33% of variation in methanol emissions without a time lag and 32% of variation in acetaldehyde emissions at a time lag of approximately 3 hours (data not shown).

Acetone emissions did not correlate with temperature. Transpiration explained only 16% of variation in methanol emissions at a time lag of approximately 5 hours and 11% of variation in acetone emissions at a time lag of approximately 8 hours (data not shown). Acetaldehyde emissions did not correlate with transpiration. The correlation of methanol emissions with temperature was slightly stronger in the lower stem (0.70 at 7 metres) than in the upper stem (0.59 at 12 metres and 0.62 at 16.5 metres) in April 2013.

In addition to the regression models, we used structural equation modelling (SEM) to examine the effects and interrelations of transpiration, temperature and stomatal conductance in explaining OVOC emissions. The temperature and stomatal conductance were used in the first SEM to explain emissions (Fig. 5, a-c). These models show a major impact of temperature, and a minor impact of stomatal conductance on the emissions of methanol, acetaldehyde and acetone. Transpiration, affected by temperature and stomatal conductance, was added to the second SEM models (Fig. 5, d-f). Adding transpiration revealed that a proportion of temperature's effect on emissions was mediated through transpiration, especially for acetaldehyde and acetone emissions. Moreover, transpiration almost completely covered the effect of stomatal conductance so that the direct effect of stomatal conductance even became negative (Fig. 5, d, e and f).

Discussion

We found that during the growing seasons, the diurnal patterns of methanol, acetone and acetaldehyde emissions from shoots closely followed the dynamics of transpiration and temperature. Similar shoot emission patterns in field conditions have been reported for methanol by Folkers et al*.,* (2008) (*Quercus robur*), and for acetone and acetaldehyde by Cojocariu et al*.,* (2004) and Grabmer et al*.,* (2006) in *Picea abies*. Stem emissions from the top part of the stem (at 12 metres) also followed a temperature related diurnal pattern, but less clearly.

We did not observe clear morning bursts of any of the compounds from Scots pine shoots, or from shoots of deciduous species (*Populus tremuloides and Betula pendula*) measured at the same site (data not shown). Harley et al*.,* (2007) also reported unnoticeable or small bursts form *Pinus taeda* and *Pinus sabiniana*. The lack of morning bursts contrasts with results reported by Mac Donald et al*.,* (1993) (*Populus tremuloides*), Harley et al*.,* (2007), (*Populus deltoides, Sorghum bicolor, Magnifera indica)* and Folkers et al*.,* (2008) (*Quercus robur*, *Fagus sylvatica, Betula pendula*) in laboratory setting and Saunier et al*.,* (2017) (*Quercus pubescens*) in field conditions in Southern France, and questions the role of stomatal conductance in regulating emissions in boreal forest. In the moist boreal conditions, the stomata can remain partly open even at night. Thus, there are positive night-time emissions and compounds do not accumulate inside leaves, or any accumulation is released gradually together with the slow increase of irradiation in the morning.

An exponential temperature dependence is common for VOC emissions, and has been reported for methanol (Hayward et al*.,* 2004; Filella et al*.,* 2007; Harley et al*.,* 2007; Folkers et al*.,* 2008; Saunier et al*.,* 2017), acetone (Cojocariu et al*.,* 2004; Filella et al*.,* 2007; Saunier et al*.,* 2017) and acetaldehyde (Hayward et al*.,* 2004; Filella et al*.,* 2007; Saunier et al*.,* 2017). OVOC emissions have also been linked to photosynthetically active radiation (PAR) (Grabmer et al*.,* 2006; Saunier et al*.,* 2017). However, Oikawa et al*.,* (2011) and Folkers et al*.,* (2008) reported that over short timescales methanol emissions are not induced by light *per se*, but the light effect on emissions is indirect. We observed a linear association between PAR and especially acetaldehyde emissions, but its effect was smaller than that of transpiration, so it was not analysed further. We found only weak connections between stomatal conductance and emissions of methanol, acetone and acetaldehyde, contrary to the results reported earlier (Kreuzwieser et al*.,* 2000; Filella et al*.,* 2007, 2009; Harley et al*.,* 2007), but instead a clear linear effect of transpiration, as reported by Harley et al*.,* (2007), Folkers et al*.,* (2008) and Filella et al*.,* (2007) for methanol, Cojocariu

et al., (2004) for acetone and Kreuzwieser et al., (2001), Cojocariu et al., (2004) and Filella et al., (2007) for acetaldehyde.

In effect, in combination with temperature, transpiration seemed to directly regulate the shoot emissions of methanol, and especially acetaldehyde and acetone. This was apparent in the regression models where transpiration was the best parameter to explain the acetone and acetaldehyde emissions, and enhanced the emissions model based on temperature also for methanol. The SEM model further confirmed the role of transpiration: of the three tested variables: temperature, transpiration and stomatal conductance, transpiration had the largest effect on the emissions of acetone and acetaldehyde and, slightly after temperature, the second largest effect on the emissions of methanol. However, although temperature has an important direct effect on emissions by regulating tree metabolic rates, as well as the diffusion rates and vapour pressures of the compounds, we observed that a large part of its effect was mediated through transpiration. In addition, stomatal conductance affected emissions only by regulating transpiration.

The strong effect of transpiration on the emissions of methanol, acetone and acetaldehyde clearly indicates that these compounds or their precursors can be transported from their sources in the roots and stem to the leaves in the xylem sap. We also observed a small positive effect of transpiration on the stem emissions of methanol and acetone, although temperature explained the emissions usually better. The lags in both temperature and transpiration effects were due to the diffusion resistance though the wood and bark. The transpiration effect corresponded with what has been observed for CO_2 emissions in the topmost part of the stem of the same trees (Hölttä & Kolari, 2009) and it implies that increasing transpiration increases the transport of water soluble compounds to that area and subsequently their emissions. The transport hypothesis also fits well with the observed stem emission patterns: emissions increased towards the stem top.

335 The different production locations of methanol, acetaldehyde and acetone define their diffusion
336 resistances and probably create the small differences we observed in their emission dynamics from shoots
337 and stem. Methanol that is produced close to surface in growing tissue (Galbally & Kristine, 2002; Hüve et
338 al., 2007) has a short diffusion pathway and is thus less prone to partition to xylem water. Therefore, its
339 shoot emissions are less affected by transpiration despite its high water-solubility. This is somewhat in
340 accordance with Folkers et al., (2008), who suggested that transport in transpiration water is probably not
341 the main factor in regulating methanol emissions. Acetaldehyde's precursor ethanol originates mainly
342 from anaerobic conditions (Kreuzwieser et al., 1999, 2000); thus, its diffusion pathway is longer, and it is
343 more likely to partition into water phase. Consequently, its shoot emissions are dependent on
344 transpiration, which has been detected before (Kreuzvieser et al., 2000, 2001). The production of
345 methanol near stem surface also explains its large emissions form all stem heights compared to acetone
346 and acetaldehyde, although the shoot emissions of methanol and acetaldehyde are on the same scale,
347 acetone emissions being largest.

348 The most important limitations in this study arise from using the dynamic chamber and the PTR-MS
349 measurement modalities that contains a possible underestimation of 5-30% for the fluxes (Kolari et al.,
350 2012). However, the effect of these uncertainties diminishes due to the quantity of data over the five
351 growing seasons studied. Based on long-term field measurements, we conclude that along with
352 temperature, transpiration directly regulates the shoot emissions of the water-soluble compounds
353 methanol, acetaldehyde and acetone. Stomatal conductance under field conditions only has an indirect
354 effect through the regulation of transpiration especially during night time. The important role of
355 transpiration on the OVOC shoot emissions implies that a proportion of them originate from roots and
356 stem and are transported to the leaves in the xylem sap. The effect of transport on shoot scale emissions
357 and stem emissions depends on the production locations and water solubility of the compounds. More
358 specialized field and laboratory experiments should be performed to understand the process of transport

of water soluble compounds in detail, and to quantify the proportions of the transported compounds from the total shoot emissions.

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Tables

Table 1: Functions used in regression models to explain emissions (E) of methanol, acetone and acetaldehyde from Scots pine shoots by temperature, transpiration and stomatal conductance at the SMEAR II station in Hyytiälä, Southern Finland. E_{model}=estimated emissions, T=temperature, ET=evapotranspiration, G=stomatal conductance, *a*=changing empirical intercept, optimized for the best fit in each model, *b*-*d*=changing empirical coefficients, optimized for the best fit in each model, β=empirical coefficient for temperature sensitivity, optimized for best fit in model T (1))

1	$E_{model\ T} = a + b * exp^{[\beta(T-303)]}$
2	$E_{model\ ET} = a + b * ET$
3	$E_{model\ G} = a + b * exp^{[c * G]}$
4	$E_{model\ T+ET} = a + b * exp^{[\beta(T-303)]} + c * E$
5	$E_{model\ T+G} = a + b * exp^{[\beta(T-303)]} + c * exp^{[d * G]}$

Table 2. Pearson's correlation coefficients (r) between Scots pine shoot emissions of acetaldehyde, methanol and acetone during the years 2010–2011 and 2013–2015, and stem emissions in 2013, at the SMEAR II station, in Hyytiälä, Southern Finland. All correlations in the table are significant ($p<0.05$).

Year	Acetaldehyde-Methanol	Acetaldehyde-Acetone	Acetone-Methanol
2010	0.89	0.95	0.94
2011	0.88	0.94	0.82
2013	0.94	0.97	0.95
2014	0.62	0.62	0.86
2015	0.87	0.93	0.9
2013 (stem)	0.50	0.53	0.53

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536 Table 3. The coefficients of determination (R2) of regression models that explain methanol shoot
537 emissions from Scots pine with temperature (T), transpiration (ET) and stomatal conductance (G) and
538 combinations (T+ET and T+G) over five growing seasons at the SMEAR II station in Hyytiälä, Southern
539 Finland. The beta value for the temperature functions is shown in parenthesis after the temperature
540 model's coefficient. The R2 of model with the best fit is indicated in bold. The model functions are
541 presented in Table 1.

Year	Model T	Model ET	Model G	Model T+ET	Model T+G
2010	0.82 (0.06)	0.63	0.00	**0.87**	0.85
May	0.90 (0.08)	0.68	0.05	**0.93**	0.91
June	0.76 (0.07)	0.51	0.00	**0.82**	0.80
July	0.88 (0.05)	0.66	0.05	**0.91**	0.90
August	0.64 (0.02)	0.73	0.10	**0.83**	0.72
2011	0.39 (0.00)	0.55	0.26	**0.56**	0.54
2013	0.68 (0.09)	0.59	0.16	**0.76**	0.72
2014	0.84 (0.12)	0.60	0.02	**0.88**	0.86
2015	**0.78** (0.12)	0.56	0.05	**0.78**	0.76

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Table 4. The coefficients of determination (R2) of regression models that explain acetaldehyde shoot emissions from Scots pine with temperature (T), transpiration (ET) and stomatal conductance (G) and combinations (T+ET and T+G) over five growing seasons at the SMEAR II station in Hyytiälä, Southern Finland. The beta value for the temperature functions is shown in parenthesis after the temperature model's coefficient. The R2 of model with the best fit is indicated in bold. The model functions are presented in Table 1.

Year	Model T	Model ET	Model G	Model T+ET	Model T+G
2010	0.52 (0.04)	0.72	0.05	**0.75**	0.61
May	0.74 (0.10)	0.68	0.02	**0.82**	0.77
June	0.49 (0.02)	0.58	0.03	**0.68**	0.58
July	0.56 (0.05)	0.82	0.19	**0.83**	0.71
August	0.50 (0.03)	0.78	0.17	**0.81**	0.66
2011	0.45 (0.00)	0.79	0.35	**0.79**	0.65
2013	0.58 (0.12)	0.63	0.21	**0.73**	0.68
2014	0.31 (0.12)	0.31	0.03	**0.37**	0.33
2015	0.68 (0.12)	0.71	0.15	**0.76**	0.68

Table 5. The coefficients of determination (R2) of regression models that explain acetone shoot emissions from Scots pine with temperature (T), transpiration (ET) and stomatal conductance (G) and combinations (T+ET and T+G) over five growing seasons at the SMEAR II station in Hyytiälä, Southern Finland. The beta value for the temperature functions is shown in parenthesis after the temperature model's coefficient. The R2 of model with the best fit is indicated in bold. The model functions are presented in Table 1.

Year	Model T	Model ET	Model G	Model T+ET	Model T+G
2010	0.57 (0.05)	0.75	0.07	**0.79**	0.70
May	0.78 (0.08)	0.77	0.00	**0.89**	0.86
June	0.49 (0.04)	0.64	0.11	**0.72**	0.69
July	0.69 (0.04)	0.8	0.16	**0.86**	0.80
August	0.54 (0.02)	0.85	0.24	**0.88**	0.77
2011	0.67 (0.07)	0.76	0.22	**0.82**	0.76
2013	0.57 (0.11)	0.62	0.24	**0.72**	0.69
2014	0.44 (0.09)	0.41	0.05	**0.50**	0.47
2015	0.83 (0.11)	0.79	0.20	**0.91**	0.87

Transpiration directly regulates the emissions of water-soluble short-chained OVOCs

Authors: Rissanen, K., Hölttä, T & Bäck, J.

Figure legends

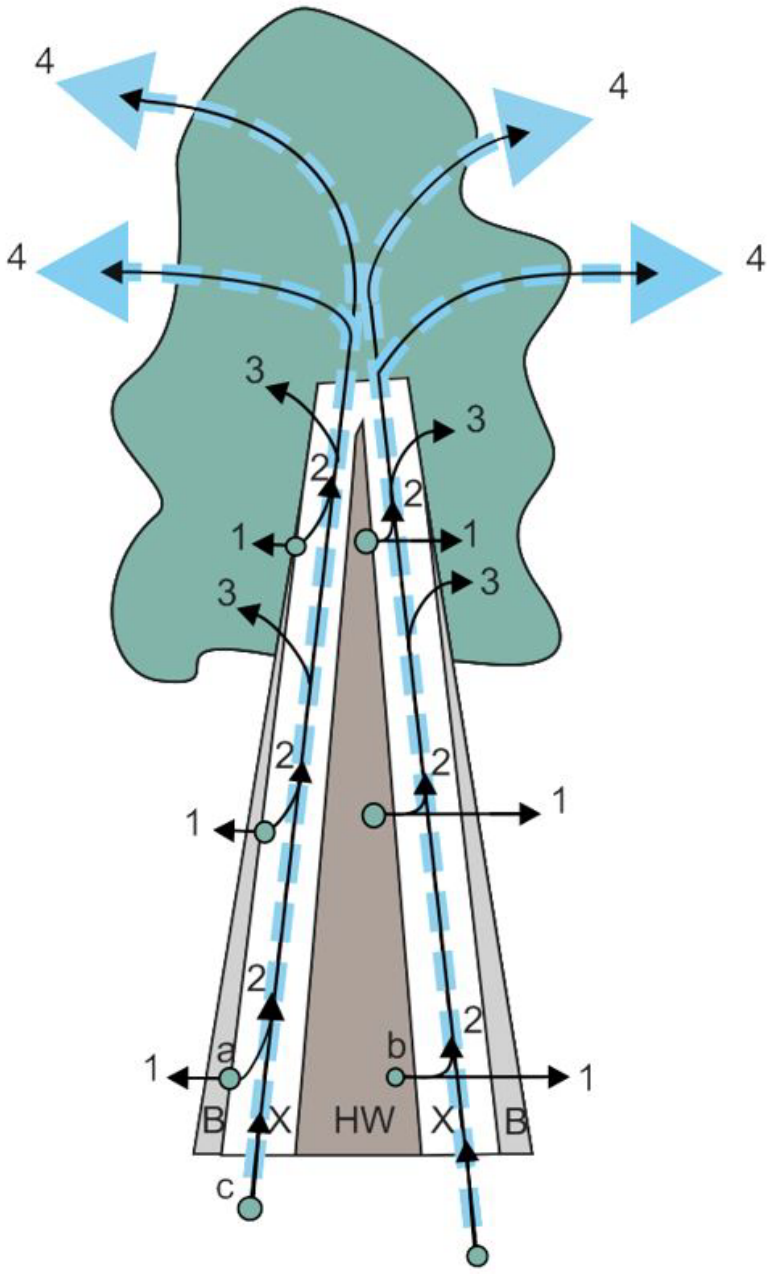
Figure 1. Schematic figure on how water-soluble compounds: carbon dioxide, methanol, acetone or acetaldehyde can diffuse into the ambient air or be partitioned into the xylem sap after being synthesized. After its synthesis at a certain production location such as the cambium (a), heartwood (b) or roots(c), the compound can either 1) diffuse through wood and bark (B) into the ambient air or 2) dissolve into the xylem sap (X) and be transported upwards in a transpiration stream. With the accumulation of water soluble compounds in the xylem sap, the compounds can also 3) escape the aqueous phase and diffuse through wood and bark into the ambient air. This pathway is more preferred in the upper parts of stems as the concentration in xylem water is higher and the bark is thinner. As the compounds reach the leaves, they can be either metabolized or diffuse out into the ambient air through the stomata (4).

Figure 2: Shoot (left, a, c, e) and stem (right, b, d ,f) emissions of methanol (top, a, b), acetaldehyde (middle, c, d) and acetone (bottom, e, f) from Scots pine at the SMEAR II station, in Hyytiälä, Southern Finland, in 2013. The smaller inset figures are examples of diurnal variations of emissions from 15th -17th July, 2013. DW = leaf dry weight, BA = bark area.

Figure 3. Stem emissions of methanol (a), acetaldehyde (b) and acetone (c) at 7 and 12 metres (left axis) and at 16.5 metres above the ground (right axis) of Scots pine and temperature (d, left axis) measured in three stem chambers, evapotranspiration (d, right axes) measured from the shoot of the same tree. BA = bark area, LA = leaf area. At SMEAR II station in Hyytiälä, Southern Finland, April 2^{ndt}-4th, 2013

Figure 4: Temperature (a, d, g), transpiration (b, e, h) and stomatal conductance (c, f, i) effects on Scots pine shoot emissions of methanol (a-c), acetaldehyde (d-f) and acetone (g-i) at SMEAR II station in Hyytiälä, Southern Finland, during May, June, July and August 2010. The vertical grey line in the right panel figures indicate the point, below which stomatal conductance regulates emissions. DW = leaf dry weight, LA = leaf area. R2 for these relations are presented in Tables 3-5.

Figure 5. Structural equation models (SEM) on the effects of temperature, stomatal conductance and transpiration on methanol (a, d), on acetaldehyde (b, e) and on acetone (c, f) shoot emissions from Scots pine, at SMEAR II station in Hyytiälä, Southern Finland during the 2014 growing season. Upper parts (a-c): Only temperature and stomatal conductance affected emissions. Lower parts (d-f): Transpiration was added to the path model. The arrow weights and parameters indicate the estimated standardized parameter values that are significant ($p<0.05$) unless in brackets. Standard error of the parameter value in parentheses. (sqrt) under a variable name indicates that square root transformation was made to obtain normal distribution. R2 in the left bottom corner is the whole model coefficient for the OVOC emissions' determination, df for the degrees of freedom.



a: production in the cambium

b: production in the heartwood

c: production in the roots

HW: heart wood

X: xylem, xylem sap

B: bark

1: diffusion from the production

2: partitioning into the xylem sap

3: diffusion from the xylem sap

4: emissions through leaf stomata

Fig. 1

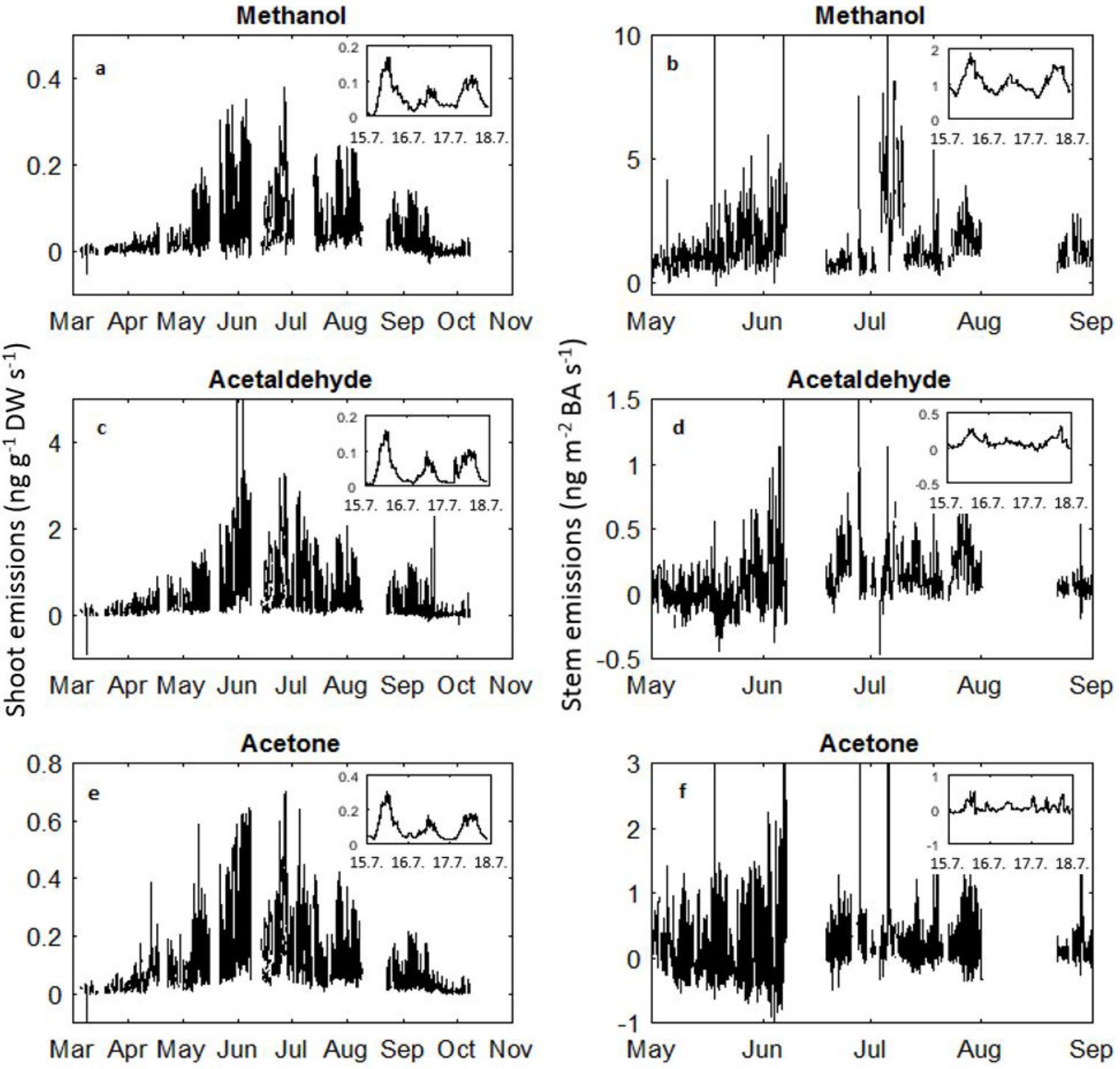

Methanol
a
b
Acetaldehyde
c
d
Acetone
e
f
Shoot emissions (ng g-1 DW s-1)
Stem emissions (ng m-2 BA s-1)
Mar Apr May Jun Jul Aug Sep Oct Nov
May Jun Jul Aug Sep
15.7. 16.7. 17.7. 18.7.

Fig. 2

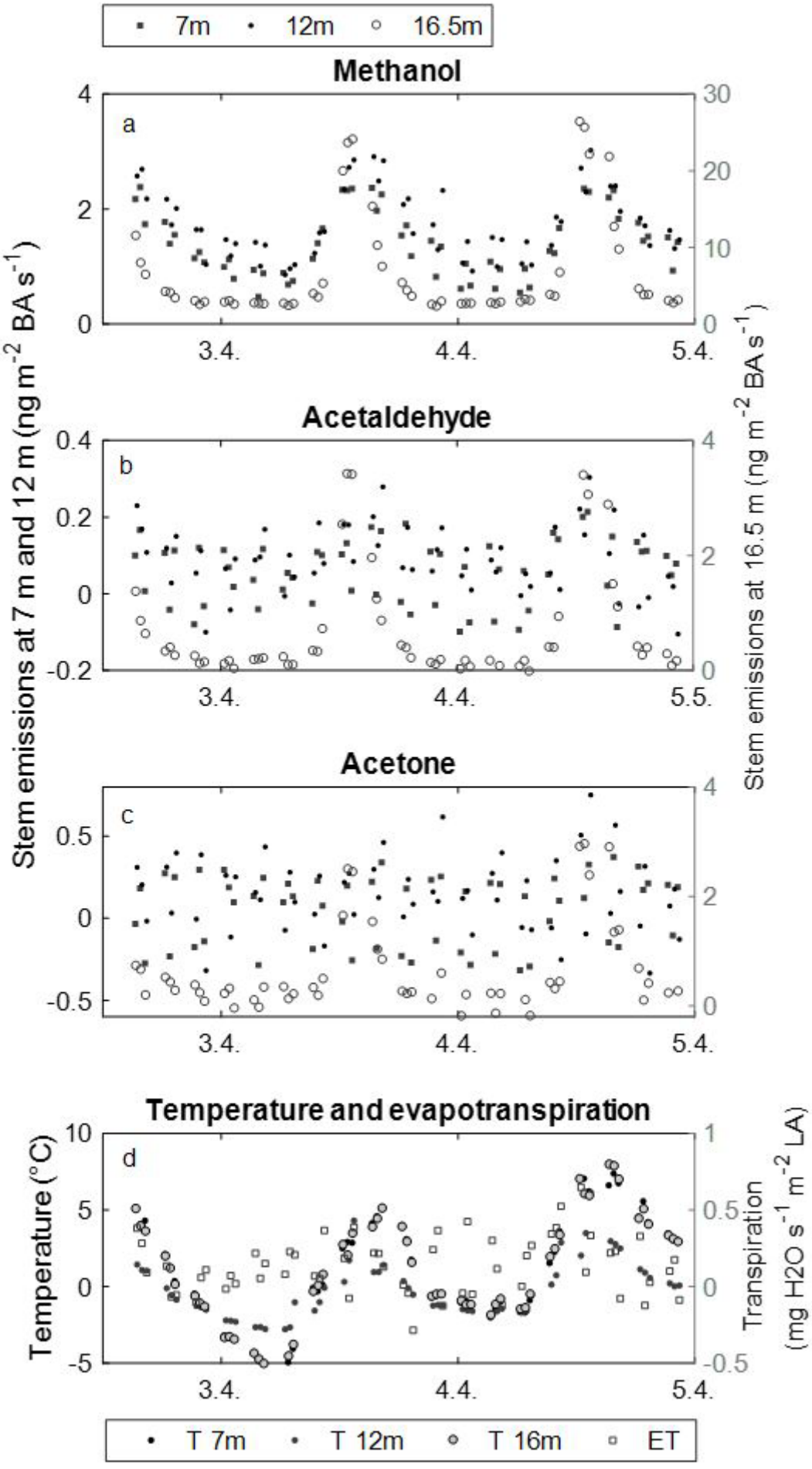

7m
12m
16.5m
Methanol
a
Acetaldehyde
b
Acetone
c
Temperature and evapotranspiration
d
Stem emissions at 7 m and 12 m (ng m-2 BA s-1)
Stem emissions at 16.5 m (ng m-2 BA s-1)
Temperature (°C)
Transpiration (mg H2O s-1 m-2 LA)
3.4.
4.4.
5.4.
5.5.
T 7m
T 12m
T 16m
ET

Fig. 3

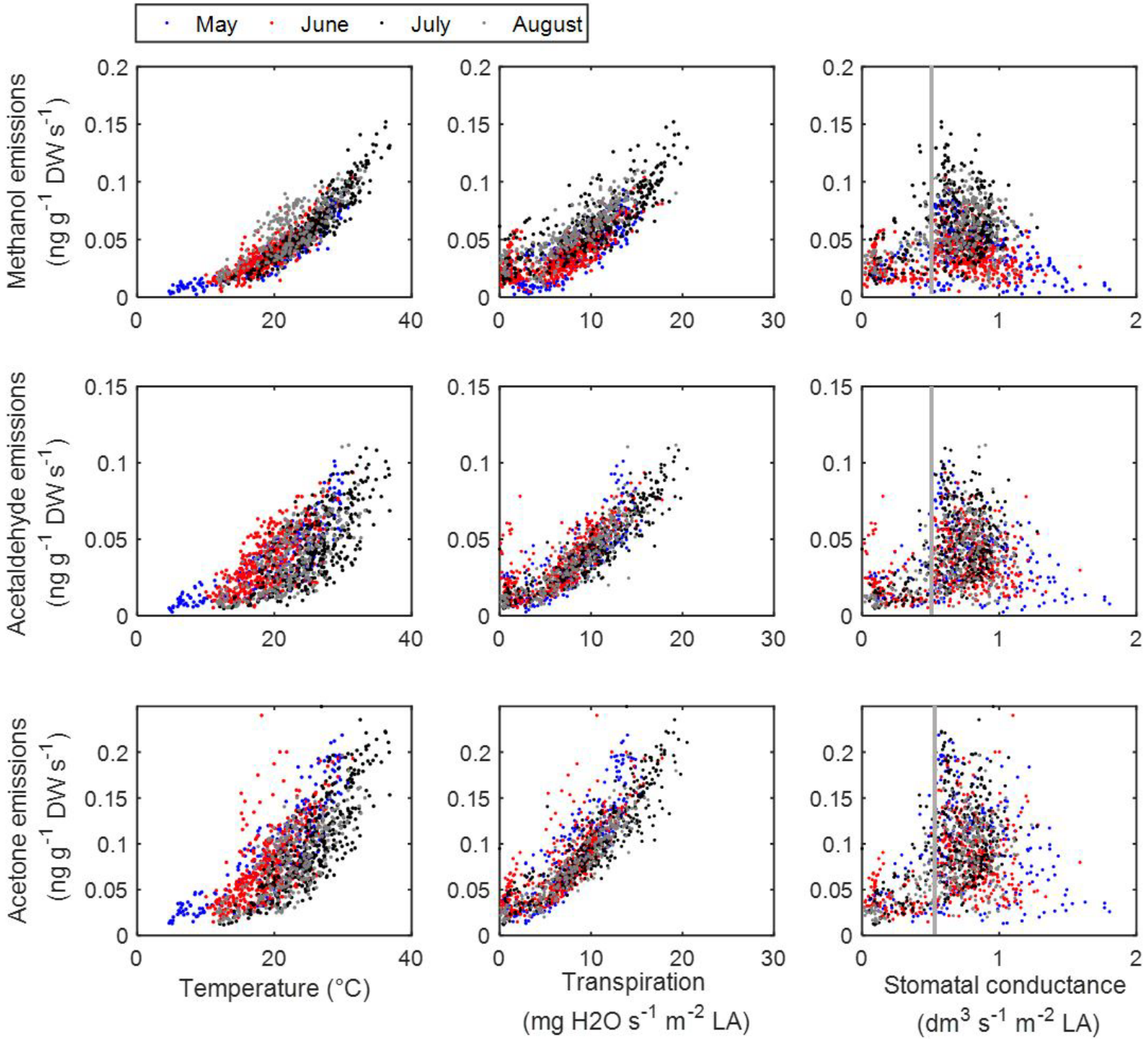

May
June
July
August
Methanol emissions
(ng g-1 DW s-1)
Acetaldehyde emissions
(ng g-1 DW s-1)
Acetone emissions
(ng g-1 DW s-1)
Temperature (°C)
Transpiration
(mg H2O s-1 m-2 LA)
Stomatal conductance
(dm3 s-1 m-2 LA)

Fig. 4

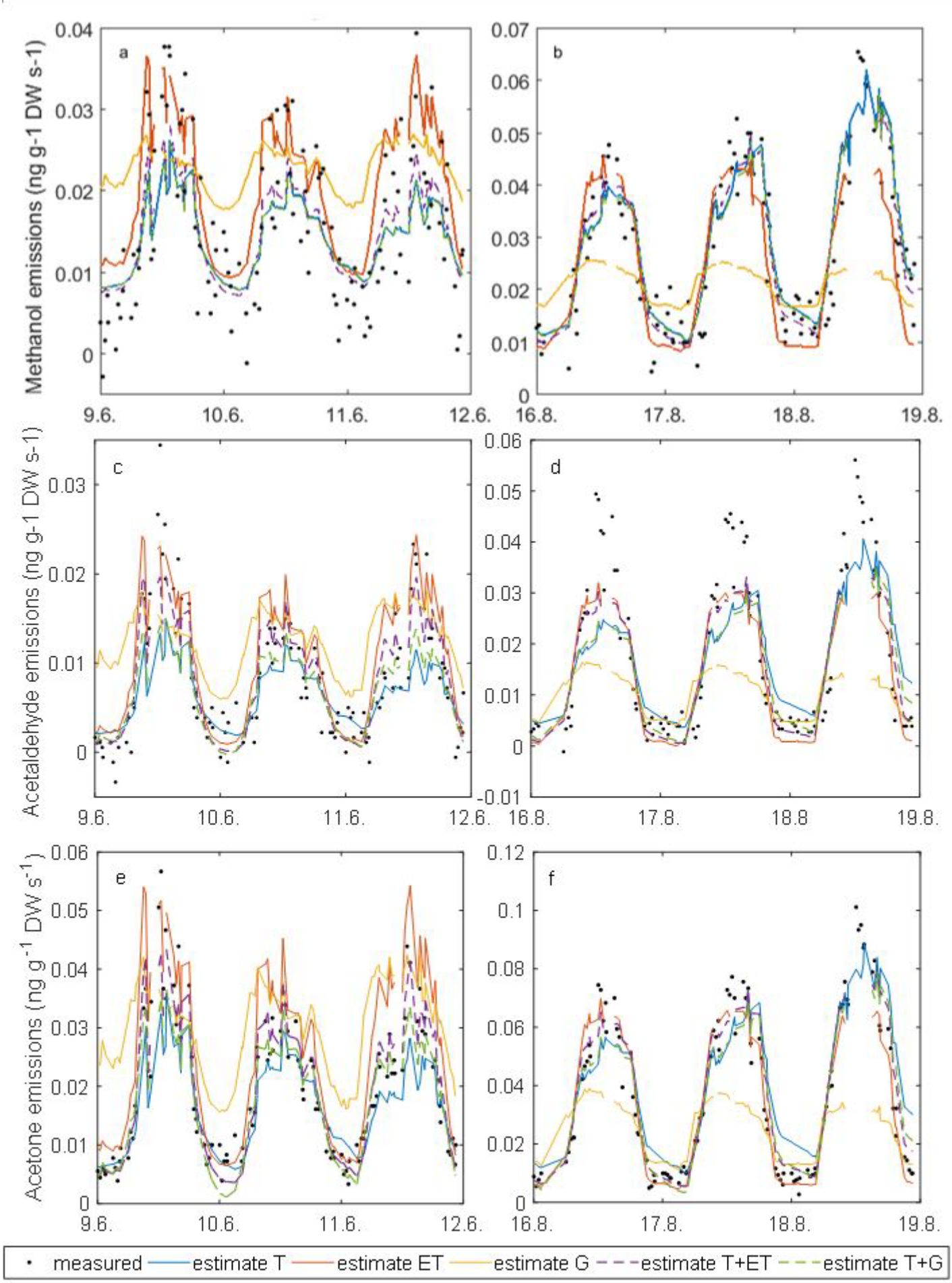

a
b
c
d
e
f
Methanol emissions (ng g-1 DW s-1)
Acetaldehyde emissions (ng g-1 DW s-1)
Acetone emissions (ng g-1 DW s-1)
9.6.
10.6.
11.6.
12.6.
16.8.
17.8.
18.8.
19.8.
measured
estimate T
estimate ET
estimate G
estimate T+ET
estimate T+G

Fig. 5

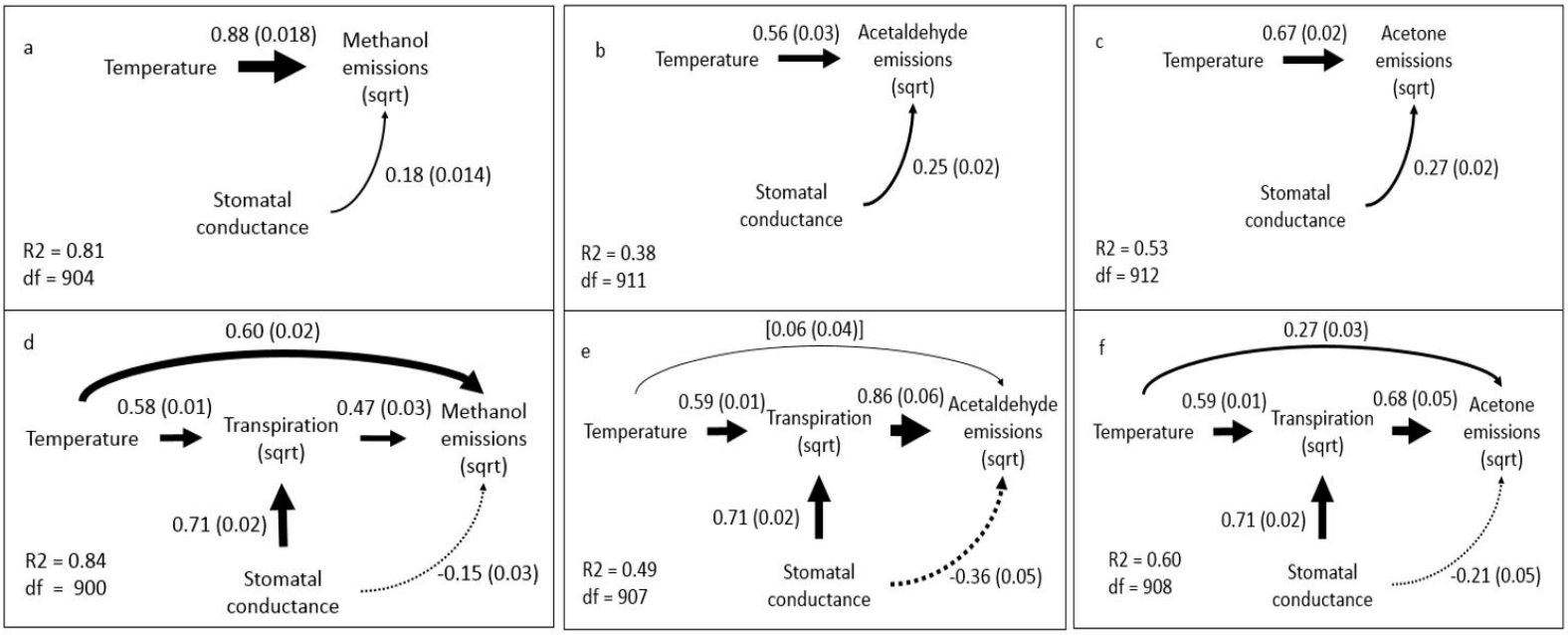

a
0.88 (0.018)
Temperature
Methanol emissions (sqrt)
0.18 (0.014)
Stomatal conductance
R2 = 0.81
df = 904
b
0.56 (0.03)
Temperature
Acetaldehyde emissions (sqrt)
0.25 (0.02)
Stomatal conductance
R2 = 0.38
df = 911
c
0.67 (0.02)
Temperature
Acetone emissions (sqrt)
0.27 (0.02)
Stomatal conductance
R2 = 0.53
df = 912
d
0.60 (0.02)
0.58 (0.01)
Temperature
Transpiration (sqrt)
0.47 (0.03)
Methanol emissions (sqrt)
0.71 (0.02)
Stomatal conductance
-0.15 (0.03)
R2 = 0.84
df = 900
e
[0.06 (0.04)]
0.59 (0.01)
Temperature
Transpiration (sqrt)
0.86 (0.06)
Acetaldehyde emissions (sqrt)
0.71 (0.02)
Stomatal conductance
-0.36 (0.05)
R2 = 0.49
df = 907
f
0.27 (0.03)
0.59 (0.01)
Temperature
Transpiration (sqrt)
0.68 (0.05)
Acetone emissions (sqrt)
0.71 (0.02)
Stomatal conductance
-0.21 (0.05)
R2 = 0.60
df = 908

Fig. 6