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From emissions to ambient mixing ratios: on-line seasonal field measurements of volatile organic compounds over a Norway spruce dominated forest in central Germany

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Abstract

Biogenic volatile organic compounds (BVOC) are substantial contributors to atmospheric chemistry and physics and demonstrate the close relationship between biosphere and atmosphere. Their emission rates are highly sensitive to meteorological and environmental changes with concomitant impacts on atmospheric chemistry. We have investigated seasonal isoprenoid and oxygenated VOC (oxVOC) fluxes from a Norway spruce (*Picea abies*) tree in Central Germany and explored the emission responses under various atmospheric conditions. Emission rates were quantified by using dynamic branch enclosure and Proton Transfer Reaction–Mass Spectrometry (PTR-MS) techniques. Additionally, ambient mixing ratios were derived through application of a new box model treatment on the dynamic chamber measurements. These are compared in terms of abundance and origin with the corresponding emissions. Isoprenoids govern the BVOC emissions from Norway spruce, with monoterpenes and sesquiterpenes accounting for 50.8 ± 7.2 % and 19.8 ± 8.1 % respectively of the total emissions. Normalizing the VOC emission rates, we have observed a trend of reduction of carbon containing emissions from April to November, with an enhancement of oxVOC. Highest emission rates were observed in June for all measured species, with the exception of sesquiterpenes that were emitted most strongly in April. We exploit the wide range of conditions experienced at the site to filter the dataset with a combination of temperature, ozone and absolute humidity values in order to derive the emission potential and temperature dependency development for the major chemical species investigated. A profound reduction of monoterpene emission potential (E30) and temperature dependency (β) was found under low temperature regimes, combined with low ozone levels ($E30_{\mathrm{MT,LTLO_3}} = 56 \pm 9.1$ ng g(dw)$^{-1}$ h^{-1}, $\beta_{\mathrm{MT,LTLO_3}} = 0.03 \pm 0.01$ K^{-1}) while a combination of both stresses was found to alter their emissions responses with respect to temperature substantially ($E30_{\mathrm{MT,HTHO_3}} = 1420.1 \pm 191.4$ ng g(dw)$^{-1}$ h^{-1}, $\beta_{\mathrm{MT,HTHO_3}} = 0.15 \pm 0.02$ K^{-1}). Moreover, we have explored compound relationships under different atmospheric condition sets, addressing

possible co-occurrence of emissions under specific conditions. Finally, we evaluate the temperature dependent algorithm that seems to describe the temperature dependent emissions. Highest emission deviations were observed for monoterpenes and these emission fluctuations were attributed to a fraction which is triggered by an additional
5 light dependency.

1 Introduction

While forest ecosystems are considered to be the largest CO_2 sink, global vegetation is redirecting back to the atmosphere a significant amount of the assimilated carbon in the form of volatile organic compounds (Guenther, 2002; Kesselmeier et al., 2002)
10 which is a substantial investment for the plant in terms of carbon and energy (Vickers et al., 2009). Emissions of BVOCs from vegetation are estimated to exceed by one order of magnitude the respective anthropogenic ones (Guenther et al., 1995) and they have vital role in biosphere-atmosphere interactions. From their impact on the oxidative capacity of the troposphere (Atckinson and Arey, 2003; Lelieveld et al., 2008),
15 to their contribution on secondary organic aerosol formation (Hoffmann et al., 1997; Bonn et al., 2008) and hence in the feedback on radiative properties (Pöschl et al.,2010; Paarsonen et al., 2013), BVOCs are the critical link between biology, chemistry and physics.

Tree responses to environmental and meteorological changes can create both posi-
20 tive and negative feedbacks (Arneth et al., 2010), depending on the summed effect of the various emission driving parameters that include physiological, physiochemical and environmental factors. BVOCs are associated with plant growth, development and defense (Kesselmeier and Staudt, 1999; Penuelas and Staudt, 2010). They are involved in plant communication (Baldwin et al., 2006) and reproduction by attracting pollina-
25 tors (Wright et al., 2005) while they are used by plants to deal with biotic and abiotic stresses (Vickers et al., 2009; Loreto and Schnitzler, 2010). Specifically, thermal and oxidative stress can be relieved in the presence of BVOC (Loreto and Schnitzler, 2010).

Penuelas and Lucia (2003) estimated that an increase of 2–3 °C in global average temperature will cause BVOC emissions to increase by 25–45 %. Average global temperature is increasing with a rate of 0.2 °C per decade, with predictions to estimate a rise of 1.1–6.4 °C by the end of the century (IPCC, 2007). At the same time background ozone concentrations have more than doubled since pre-industrial times and current models suggest future global annual mixing ratios to reach 42–84 ppb by 2100 (Vingarzan et al., 2004). Ozone is considered as the most critical pollutant for vegetation since it is phytotoxic and can significantly reduce agricultural crop yields (Matyssek et al., 2012 and references therein) and especially north hemisphere vegetation is regarded to be highly sensitive to ozone because of the humid climate (Matyssek et al., 2007). It is generally believed that isoprenoids can protect the plant against oxidative stress during photosynthesis (Loreto at al., 2001, 2004; Vickers et al., 2009; Jardine et al., 2012). Within this context Norway spruce has been found to regulate its sesquiterpene emissions rates according to ambient ozone concentrations (Bourtsoukidis et al., 2012) while Karlsson et al. (2006) provided statistical evidence on the negative effect of ozone in the stem diameter of mature trees. There is some evidence to suggest that ozone is causing even more damage to vegetation than drought induced limitation of photosynthesis (Karnosky et al., 2003; Matyssek et al., 2006).

Most biogenic emission studies are focused on isoprenoids, which comprise a large and diverse class of naturally emitted VOCs, derived from five-carbon isoprene units assembled and modified in thousands of different ways (Lichtenthaler et al., 1997). Because of their volatility, faster production and their role in atmospheric chemistry, isoprene (C_5H_8), monoterpenes (MT; $C_{10}H_{16}$) and recently sesquiterpenes (SQT; $C_{15}H_{24}$) dominate BVOC emission studies. Nevertheless, plants also emit a large amount of oxygenated VOCs (oxVOC) such as methanol (CH_4O), acetaldehyde (C_2H_4O), ethanol (C_2H_6O) and acetone (C_3H_6O) (Kesselmeier and Staudt, 1999), the importance of which should be better addressed in future studies (Oderbolz et al., 2013). Short term laboratory experiments provide valuable information under controlled conditions, but their results are not comparable with longer term field experiments (Kivimanpaa et al.,

2013) due to the controlled unnatural environments they grow at. Therefore, seasonal field campaigns that cover a wide spectrum of environmental and meteorological conditions are the key to understanding emission responses and trends, along with the impact on ambient mixing ratios and atmospheric chemistry.

More realistic emission rates are obtained from a well-ventilated dynamic branch enclosure where environmental parameters are close to ambient levels (e.g. Ortega and Helmig, 2008). Assuming homogenous mixing inside the chamber, when the enclosure is open the measurements should reflect ambient mixing ratios, albeit at a point closely positioned to the emitting branch. Here, we provide a box model method that calculates ambient mixing ratios, of which the seasonality is investigated and compared with the contribution of the Norway spruce emission rates for the site of interest. The main goal of this study is to address the dominant factors determining the driving forces of VOC emissions from Norway spruce, over a seasonal snow free period by using dynamic enclosure and on-line Proton Transfer Reaction-Mass Spectrometry (PTR-MS) techniques. Since oxVOCs contribute dominantly in the total annual BVOC emissions in Europe (Oderbolz et al., 2013) but are absent in more detailed models (McKinney et al., 2011), their emission rates have been investigated in parallel to isoprenoids and compared in terms of correlation, emission potential and temperature dependencies for different environmental condition sets. Monthly diel emission patterns were investigated for both VOC class compounds and a parameterisation evaluation was performed for oxVOC along with monoterpenes. Overall, we try to approach seasonal emission rates from Norway spruce in terms of environmental responses at a site that provides a high variability of atmospheric conditions.

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2 Material and methods

2.1 Site description

The measurements were conducted at Taunus Observatory (50°13′ N, 8°26′ E) which is located at the top of Mt. Kleiner Feldberg (825 m a.s.l) in central Germany. The mountaintop ecosystem experiences a variety of meteorological and chemical conditions throughout the year due to its altitude, and occasional impacts from transported pollution from the heavily industrialized Rhine–Main area. Norway spruce is the dominant species in the surrounding coniferous forest, which also includes some Pine trees. A few willows, mountain ash and birch trees along with shrubs and blue berry plants make up the vegetation, surrounding the measuring station.

2.2 Basic atmospheric measurements

The summit of Kl. Feldberg has been cleared of trees in about a 100 m radius of the summit half a century ago, giving space for continuous meteorological and environmental measurements, that are conducted by the German weather service (DWD; Deutsche Wetterdienst) and the county's environmental agency (HLUG; Hessian Agency for the Environment and Geology). For the purposes of this study, a comprehensive set of meteorological and environmental data was retrieved from the aforementioned stations, with the aim to characterize the atmospheric conditions while investigating BVOC emission responses. Temperature, global radiation, relative humidity (RH), atmospheric pressure, wind speed and direction, sunshine duration and precipitation were the basic meteorological parameters used, while ozone (O_3), nitrous oxide (NO), nitric oxide (NO_2) and atmospheric particulate matter (PM_{10}), in parallel with the benzene mixing ratios measured by the PTR-MS, were the main environmental parameters investigated. Additionally, a temperature-humidity sensor (Hygrosens Instruments) and an ozone analyzer (model APOA-350E, Horiba) were continuously

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monitoring the temperature, relative humidity and ozone mixing ratios inside the dynamic chamber, that was used for emission rate quantification.

2.3 Dynamic branch enclosure

In order to obtain VOC emission rates, a dynamic branch enclosure was applied in a healthy (13 ± 1 m tall and ca. 80 yr old) Norway spruce tree from the 8 April to the 11 November 2011 as described in Bourtsoukidis et al. (2012). Briefly, the 15 L cylindrical shaped glass cuvette remained open for most of the time in order in order to keep the environmental parameters close to ambient levels (Ortega and Helmig, 2008). Furthermore, the chamber was leak tight in order to avoid pressure differences (Ruuskanen et al., 2005) while an inbuilt fan ensured homogenous mixing. The chamber was mounted in a selected branch 5 m above ground at the edge of the forest and was programmed to close for 3 min every 20 min, as a compromise between changing conditions inside the chamber and the achievement of steady state in the VOC mixing ratios.

During May, a two week intercomparison of temperature and relative humidity measurements indicated small discrepancies with the ambient environment. Enclosure temperature was slightly higher than the ambient (on average $0.7\,°C$, $R^2 = 0.97$), while relative humidity was marginally lower (on average $3.1\,\%$, $R^2 = 0.97$). Stronger differences were observed in a similar intercomparison with photosynthetic active radiation (PAR) during September. Two PAR sensors (LI-190SZ, LI-190SL/Li-Cor Inc., Lincoln, NB, USA) have been mounted inside and outside of the chamber and revealed differences from 25 up to 45 %, depending on the solar zenith angle (Bourtsoukidis et al., 2012). For the duration of the closing period, during the complete measuring period, temperature rose on average by $0.91 \pm 0.82\,°C$ while relative humidity and ozone dropped by $3.5 \pm 3.5\,\%$ and $2.9 \pm 2.5\,ppb_v$ respectively. In general, the aforementioned parameters did not differ more that 20 % from open chamber conditions, apart for some rare extreme cases ($\Delta T_{max} = 4.3\,°C$, $\Delta RH_{max} = 39.8\,\%$, $\Delta O_3 = 21.2\,ppb_v$).

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2.4 PTR-MS measurements

On-line VOC measurements were conducted by using a commercial high sensitivity PTR-MS (Ionicon GmbH, Austria). General information about the analytical technique can be found in literature (Lindinger et al., 1998; Blacke et al., 2009 and references therein), while more specific information about the settings of this study can be found in Bourtsoukidis et al. (2012). Briefly, the PTR-MS was operated under standard conditions with a drift tube voltage of 600 V and drift tube pressure of 2.3 mbar. Optimization of the instrument resulted in high and sustained primary ion signal ($[H_3O^+]$ = 4–7×10^7 cps). Frequent calibrations for the PTR-MS were performed with a gas standard containing about 1 ppm of formaldehyde, methanol, acetaldehyde, ethanol, acetone, isoprene and α-pinene (L4763, Ionimed analytic GmbH, Austria), while SQTs were calibrated using a permeation oven technique and a β-caryophyllene standard (W225207, Sigma-Aldrich, Inc.). Analytical fragmentation patterns were either derived experimentally or calculated according to the literature (Dhooghe et al., 2008; Kim et al., 2009; Demarcke et al., 2009). The tuning of the mass spectrometer and the transmission curve were frequently checked for achieving the best optimized conditions. The transmission curve had minor discrepancies during the complete period and varied by less than 15 %, mainly in the higher masses. Since the selected branch was 5 m above ground and the instrumentation was kept inside a van just below the investigated tree, the sample line was very short (4.1 m) with respectively short residence time (2.2 s). By choosing a chemically inert material, namely glass (inner diameter = 3 mm), and by heating the inlet line up to 70 °C, the losses were minimized and quantified prior to the measuring period in the laboratory (Bourtsoukidis et al., 2012).

The compounds continuously monitored during a PTR-MS cycle (36 s) along with their protonated masses were: methanol (m/z = 33), acetaldehyde (m/z = 45), acetone (m/z = 59), isoprene (m/z = 69), benzene (m/z = 79), main MT fragment (m/z = 81), total MT (m/z = 137), nopinone (m/z = 139), main SQT fragment (m/z = 149), linalool (m/z = 155), pinonaldehyde (m/z = 169) and total SQT (m/z = 205). While

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methanol exhibits little fragmentation and the parent ion mass is considered to represent only this compound (Warneke et al., 2003) acetone may have interferences from propanal (m/z = 59) or from thedehydrated Methyl-butenol fragment (m/z = 69). Similarly, we assume that mass 69 corresponded only to isoprene. Nonetheless, other aldehydes and ketones that are detected at the same mass (Fall et al., 2001; Warneke et al., 2003) add some uncertainty to the monitored mixing ratios. The masses m/z = 81 and m/z = 137 showed and consistent relationship throughout the year (R^2 = 0.90). Hence the sum of the two signals was used to determine the total abundance that was representing the 90 % of the total MT signal. The major SQT fragment (m/z = 149) also corresponds to methyl chavicol (Bouvier-Brown et al., 2009a) and therefore, because of the interferences at this mass, only the parent ion signal was used, with a quantified contribution of 32 ± 2 %, that is in agreement with previous studies (Kim et al., 2009).

2.5 From emissions to ambient mixing ratios

Emission rates of the measured VOCs were calculated by using the mass balance equation:

$$E = F \frac{C_2 \cdot \exp\left(k_{dil} + k_{chem} + k_{dep}\right) \cdot t - C_1}{m} \tag{1}$$

Here, F is the total flow rate through the chamber, C_1 is the concentration at the last measurement interval before the cuvette closes and C_2 is the last measurement conducted with closed cuvette. The final value is corrected for dilution (k_{dil}), ozone reaction losses ($k_{VOC} \cdot [O_3]$) and dry deposition on the cuvette walls (k_{dep}). Time t is the closing period (t = 3 s), while m is the total dry needle biomass of the enclosed branch. Hereafter, biogenic emissions were quantified in $\mathrm{ng\,g(dw)^{-1}\,h^{-1}}$. More details on the correction terms applied can be found in Bourtsoukidis et al. (2012).

When the enclosure is open, it can be assumed that ambient mixing ratios (C_a) are identical to the mixing ratios measured by the PTR-MS when the cuvette is open (C_1) since the fan ensures well mixed conditions. However the measurements are taken

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very close to a branch and our inlet was located at the inner side of the chamber. By using a box model when the chamber is closed and by assuming steady state of the measured monoterpene signal, we can derive an equation that calculates ambient mixing ratios without the nearby tree emissions:

$$C_a = C_2 - F \frac{C_2 - C_1}{m} - C_a \frac{F \cdot t}{V} \tag{2}$$

where V is the volume of the chamber. Solving the above equation for C_a we derive the ambient mixing ratios:

$$C_a = \frac{C_2 - F \frac{C_2 - C_1}{m}}{1 + \frac{F \cdot t}{V}} \tag{3}$$

The latest equation has been evaluated by comparing the derived results with the sum of ambient monoterpene mixing ratios, as they were measured by Gas Chromatography–Mass Spectrometry (GC-MS) techniques (Nölscher et al., 2012) during the PARADE campaign (Fig. 1). Despite some minor discrepancies, averaged values for the reported period indicate a minor difference between the model and ambient mixing ratios (15.3 ± 5.5 ppt$_v$). On the contrary, raw data with open chamber are more than double compared with ambient mixing ratios measured 100 m from the tree at the mountain summit. Therefore, the above equation derives representative ambient mixing ratios without the influence of the tree in the immediate vicinity, as it is supported by the comparison of these measurements. Under flow-through enclosures, a second empty chamber is used as reference and ambient mixing ratios can be directly monitored. Since we have used a dynamic method and our inlet was in the inner side of the chamber and hence always affect the monitored mixing ratios, we used Eq. (3) to derive all the ambient mixing ratios presented.

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2.6 Absolute humidity

Absolute humidity (Ah) is the amount of water vapor present, expressed in $g\,m^{-3}$. Absolute humidity was calculated by:

$$Ah = \frac{Rh \cdot 6.1078 \cdot \exp\left(\frac{17.08085 \cdot T}{234.175 + T}\right) \cdot Mw}{R(273.175 + T)} \tag{4}$$

here, T is the ambient temperature in $^{\circ}C$, Rh the relative humidity expressed in %, $Mw = 18.016\,kg\,kmol^{-1}$ is the molecular weight of water and $R = 8314\,J\,k^{-1}\,kmol^{-1}$ is the molar gas constant. Absolute humidity data support to indicate the leaf to air vapor pressure deficit (VPD) which is the driving force for transpiration and stomatal behavior (Buck, 1981; Jones, 1992; Larcher, 1994; Franks and Farquhar, 1999).

3 Results

3.1 Atmospheric conditions

From climatological point of view, the year of 2011 can be characterised as peculiar. Spring was exceptionally as warm and dry (precipitation anomaly < 25 %; DWD – comparison with 1961–1990 averages) with the highest sunshine duration since 1950 (DWD). Ozone mixing ratios were almost 20 % higher, reaching an average of $55.4 \pm 14.4\,ppb_v$, with a maximum observed value of $96.2 \pm 0.3\,ppb_v$. In contrast, summer was relative wet (precipitation anomaly = 126–150 %; DWD) with averaged July temperatures to be about $2\,^{\circ}C$ lower, in comparison with the previous 14 yr average. The wet summer was followed by a dry (precipitation anomaly < 50 %; DWD) and relatively hot autumn. Figure 2 presents a comparison of the main BVOC emission drivers between the seasonal averages since 1997, in comparison with the daily and monthly averages for the period of interest. The means of the major driving forces (tempera-

ture, radiation, ozone) were higher during spring, and slightly lower during summer but within the extremes of observations of the past years.

North-westerly winds prevailed during most of the measuring period of spring and summer. This direction is associated with no heavily populated areas within 100 km and indicates minor anthropogenic impact on the local to regional scale. In general, wind speeds were lower compared to the previous years for the period of interest ($WS_{1997-2010} = 3.83 \pm 0.5\,ms^{-1}$, $WS_{2011} = 2.96 \pm 1.4\,ms^{-1}$), with no major differences among the seasons ($WS_{spring} = 3.11 \pm 1.37\,ms^{-1}$, $WS_{summer} = 2.78 \pm 1.31\,ms^{-1}$, $WS_{autumn} = 3.32 \pm 1.57\,ms^{-1}$). During autumn, the wind direction changed to south-west, originating from the heavily industrialized Rhein–Main area. This resulted in elevated NO_x ($NO_x = NO + NO_2$) mixing ratios ($NO_{x,spring} = 3.94 \pm 2.41\,ppb$, $NO_{x,summer} = 3.52 \pm 2.32\,ppb$, $NO_{x,autumn} = 5.21 \pm 4.01\,ppb$) which were about 40 % higher in comparison with both previous seasons.

3.2 Emission rates

Emissions rates are defined as the positive fluxes calculated from Eq. (3), i.e. when the corrected maximum concentration of VOCs with closed cuvette is higher than the minimum one (C_1), measured with open cuvette. Table 3 presents the median fluxes of all compounds measured, along with their minimum and maximum values obtained for each season. The highest emission rates were observed for monoterpenes that were occasionally two orders of magnitude stronger than the median values, probably as a result of mechanical stress under strong winds. Such events had, however, short duration and emissions returned to normal values after several hours. Persistent and exceptionally strong emissions of methanol were observed during the growing period (May–June) but also some days before the new twigs start to grow. The strongest emission rates for the majority of oxVOC and isoprenoids occurred after a storm event when strong winds damaged the bark of the enclosed branch (DOY = 167). Interestingly, the maximum emission rates for methanol and sesquiterpenes during these wind damage

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events were still lower than those observed during the growing period. In order to obtain realistic emission rates representing an undamaged tree, a new branch was selected and the aforementioned data were excluded from any further analysis presented in this study.

Occasionally, negative fluxes have been quantified for all compounds but mainly for the oxygenated species. This observation can be attributed to the enhanced water solubility of oxVOCs but also due to chemical reactions. Isoprene is highly hydrophobic and does not dissolve significantly in water. Therefore, the negative isoprene fluxes can be explained only by reactions or by hypothesising that the corresponding mass was not assigned only to isoprene, but also to other aldehydes and ketones that can be detected in this mass. Negative acetaldehyde and acetone fluxes were mainly observed under during rain events but their values were always small compared to the average emissions. In general, negative fluxes occurred sporadically and were small comparing to the average for all species ($< 8.9\%$) apart from nopinone, linalool and pinonaldehyde that display positive and negative fluxes of the same magnitude.

In Fig. 3 we illustrate the monthly fluxes observed for the major oxVOC and isoprenoids. All compounds (apart from sesquiterpenes) peaked during June, decline during July and peak again in the late summer, to gradually decline towards the end of the year. July was relatively cold and wet and therefore reduced emissions were expected. Methanol, acetone and isoprene median emission rates in July were less than half of the respective June ones, while acetaldehyde and monoterpenes were profoundly reduced by more than 70%. In contrast, sesquiterpene median emission rates were almost identical for these two months, although the emissions did rise during August, similar to the rest of the VOCs.

By investigating the individual contribution of each measured compound to the sum of VOC emissions, we found that monoterpenes dominate Norway spruce emissions through the entire measuring period (Fig. 4). With contributions varying between 43.4–63.4%, monoterpenes accounted for $50.8 \pm 7.2\%$ of the total seasonal emissions by mass of carbon. The second most important emissions were the sesquiterpenes,

with larger variations in their contribution (9.3–33.4 %) and an average contribution of 19.8 ± 8.1 %. Methanol and acetone were one fifth of the emissions with similar average fractions throughout the year (methanol: 11.7 ± 2.4 %, acetone: 10.7 ± 2.8 %). Total emission rates of acetaldehyde were 4 ± 1.3 %, while the remaining compounds had minor role in total emissions. Isoprene constituted the 1 ± 0.16 %, linalool the 0.8 ± 0.4 %, pinonaldehyde the 0.8 ± 0.5 % and nopinone the 0.4 ± 0.2 %.

The oxygenated compounds enlarge their share in the total emission rates towards the end of the year and their maximum contribution (35.9 ± 5.4 %) observed in November (Fig. 4). The average amount of carbon emitted as VOCs was calculated by season ($E_{c, \text{spring}}$ = 326.7 ± 103.6 ng (C) g(dw)$^{-1}$ h^{-1}, $E_{c, \text{summer}}$ = 307.4 ± 98.8 ng (C) g(dw)$^{-1}$ h^{-1}, $E_{c, \text{autumn}}$ = 112.2 ± 35.9 ng (C) g(dw)$^{-1}$ h^{-1}) and quantified the amount of carbon in the total (monitored) VOC emissions. Along with their relative contribution, in Fig. 4 we illustrate the percentage of carbon on the sum of normalized monthly emission rates. From both perspectives we can observe a tendency of reduced carbon containing emissions and increased contribution of other species such as oxygen towards the end of the year. In general, the percentage of carbon the total VOC emissions was reduced about 10 % from April to November.

Diel emissions usually peaked in the evening (1–4 p.m.) when maximum temperature and ozone occurred. However, this was not the case for all compounds and all months (Fig. 5). Methanol emissions were stronger during the growing period of May and June, with their nighttime emission rates being larger than most of the daily maxima of the other months. A clear diurnal cycle was observed in methanol during April, May and June with but differing temporal patterns. During May emissions peak after sunrise but during June a second emission burst was observed around midday. Similar diurnal patters were observed for acetaldehyde, with the difference that a clear diel cycle could be observed for almost all months. Acetone emissions were characterised by a distinct diel cycle for all months and steep decline after sunset. Similar to the other oxVOC we observe an emission burst following sunshine during May, when new twigs were growing. The diel cycle of isoprene was in line with global radiation observations, and

the maximum emissions occurred at local noon. Constitutive emissions during night were within the uncertainty range of zero but their strength during the day is closely correlated with global radiation. Monoterpenes and sesquiterpenes displayed a clear and distinct maximum at the afternoon of April. However, for both compounds May was different with emission bursts during early (for monoterpenes) or late (for sesquiterpenes) morning, followed by a plateau until evening. For the rest months a diel cycle was always visible. Constitutive sesquiterpene emissions were measured also during October and November with a small rise during daytime. In general, monoterpenes and sesquiterpenes peaked with the local maxima of temperature and ozone while isoprene peak at the same time with global radiation.

3.3 Emission responses to meteorological and environmental parameters

All measured VOC compounds clearly responded to temperature changes, with varying sensitivity among the species and the seasons. Considering the complete dataset, the highest correlation coefficients between temperature and emission rates, were observed for acetone ($CC_{T,\text{acetone}} = 0.71 \pm 0.02$) and monoterpenes ($CC_{T,\text{MT}} = 0.63 \pm 0.03$). Isoprene displayed high correlation with global radiation ($CC_{T,\text{isop}} = 0.58 \pm 0.02$), while an even stronger correlation was observed between sesquiterpenes and ambient ozone mixing ratios ($CC_{O_3,\text{SQT}} = 0.63 \pm 0.01$) with a time shift of 2–4 h before the emissions occur. Negative correlations have been observed between all VOCs and relative humidity.

Emissions of monoterpenes and, in the absence of more detailed models, of all oxVOCs are modeled by a temperature dependent algorithm, with an exponential relationship between temperature and the induced emissions (Guenther et al., 1995):

$$E = E_{s,T} \cdot \exp(\beta \cdot (T - T_s)) \tag{5}$$

In the above equation, E is the emission rate observed at temperature T. Emission rates are usually expressed in $\text{ng} \, \text{g(dw)}^{-1} \, \text{h}^{-1}$, where g(dw) represents the dry weight of biomass. $E_{s,T}$ is the standard emission potential at $T_s = 30\,°C$ and β (in K^{-1}) is an

empirical factor that describes the temperature dependency from the slope of the best fit curve between the temperature and emission rates.

Emissions of sesquiterpenes are parameterised similar to monoterpenes, but with an additional term that includes the ozone impact on induced emissions (Bourtsoukidis et al., 2012):

$$E_{SQT} = E_{s,T} \cdot \exp(\beta \cdot (T - T_s)) + E_{s,O_3} \cdot \exp(\sigma \cdot ([O_3] - [O_{3,s}])) \tag{6}$$

In the additional term, E_{s,O_3} is the standard emission potential at $[O_3] = 40\,\text{ppb}_v$ and σ (in ppb_v^{-1}) is the respective ozone dependency.

In Table 2 we present the results of regression analysis performed between the enclosure temperature and the emission rates, separated for different seasons and light abundance. In all cases monoterpene emission potential was the highest calculated, while stronger temperature dependency was for acetone. From seasonal point of view, E_{30} declined from spring to autumn for the majority of VOCs investigated, with the exception of acetaldehyde that displayed the same values during spring and summer, and acetone that had the highest emission potentials during summer. $E_{30,\text{methanol}}$ was halving for each seasonal change step, but the respective one for monoterpenes was even more profound ($E_{30,\text{MT (spring)}} \approx 1/3 E_{30,\text{MT (summer)}} \approx 1/3 E_{30,\text{MT (autumn)}}$). The temperature dependency was relatively constant and inside the error bars for each VOC. Highest β-factor was observed for acetone and lower for methanol. The remaining compounds had similar annual temperature dependencies of $\beta = 0.11 \pm 0.02\,\text{K}^{-1}$. The best fitting obtained, was calculated by the regression analysis performed for sesquiterpenes during autumn. This observation demonstrates that under low ambient O_3 mixing ratios (Fig. 1) temperature is the main driving force of sesquiterpene emissions.

Methanol, acetaldehyde and sesquiterpene E_{30} and β-factor were unaffected by changes in light availability, as was observed by separating the dataset between day and night. In contrast, monoterpenes were the most affected by decreasing their emission potential by almost six times compared to the daytime values. In the same line, temperature dependency was found to be weaker during night ($\beta_{\text{MT, night}} =$

0.06 ± 0.01 K^{-1}), with the lowest observed β derived from the above-mentioned regression analysis. The reduced emission responses during nighttime indicate that monoterpenes are also light dependent, as has been noted previously in spruce emission studies (e.g. Yassaa et al., 2012).

Temperature, radiation, ambient ozone mixing ratios and humidity are the parameters that thought to most influence VOC emission rates. Nevertheless, most of these parameters are highly connected with each other. Given the fact that throughout the measuring period we could observe a variety of atmospheric conditions at the site of interest, depending on the wind direction, we have classified the data in 12 different atmospheric conditions and examined their emission responses (Fig. 6). As low ($T < 9.5\,°C$) and high ($T > 17.1\,°C$) temperature we define the respectively lowest and highest 25 % of a Gaussian type temperature distribution. In a similar way, we used the lower and uppermost 25 % of absolute humidity data (LAh < 6.1 $g\,m^{-3}$; Hah > 13.2 $g\,m^{-3}$). Ozone classification was performed according to the threshold on sesquiterpene emission driver defined by Bourtsoukidis et al. (2012) ($LO_3 < 32.7\,ppb_v$, $HO_3 > 40.5\,ppb_v$).

In general, oxVOC emission potential was inside the uncertainty range for the most of the cases apart from the filtered data that included high absolute humidity. High Ah resulted in reduced emissions but also in reduced temperature dependencies as seen in Fig. 6d. The highest Es for methanol was observed under low temperatures but high ozone, while the lowest was observed under low temperatures and low ozone. This might indicate that ozone itself trigger stronger methanol emissions. Correlation coefficient analysis showed only a moderate correlation of methanol with ozone of 0.48 ± 0.4. On the other hand, the majority of the data in this regime were during the growing period, where maximum methanol emissions were observed as a result of the growing process and therefore the ozone effect cannot be conclusive as it may be coincidental that the spring time peak in ozone is synchronous with springtime growth spurts.

For isoprenoids, monoterpenes showed enhanced sensitivity along different temperature regimes, while sesquiterpenes were more sensitive in terms of ambient ozone

mixing ratios. Low temperatures and especially in combination with low ozone reduced $E_{s, MT}$ and β_{MT}. It is therefore reasonable to assume that elevated temperatures will highly influence the temperature sensitivity of monoterpene emissions from Norway spruce. Similar to oxVOCs, we recognize a tendency of lower $E_{s, MT}$ under elevated absolute humidity, but this effect was more profound on sesquiterpenes that also present very low β-factors. β_{SQT} was profoundly reduced under elevated ozone, since in that case ambient ozone mixing ratios is the major driving force (Bourtsoukidis et al., 2012).

3.4 Emission relationship between compounds

Metabolic pathways of BVOC biosynthesis in plants are now known (Laothawornkitkul et al., 2009). Isoprenoids are synthesized via two different metabolic pathways: isoprene and MT are synthesized via the plastidic 2-Cmethyl-D-erythritol 4-phosphate (MEP) pathway while SQT via the mevalonic acid (MEP) pathway. For the investigated oxVOC, acetaldehyde is produced at root cells but also at leaves, while acetone and methanol originate from the b-glucosidase (GLU) and wall-localized pectin methylesterases (PME) pathway accordingly. In order to distinguish co-occurrence of VOC emissions for Norway spruce, we have examined the correlation coefficients among all compounds, under seasonal and extreme condition cases (Fig. 7).

The common biosynthetic origin of isoprene and MT has been observed by the high CC calculated for the majority of the 16 cases. Nevertheless, this relationship breaks under low ozone regimes and during nighttime. Despite the radiation effect observed for monoterpenes, their emissions originate from pools and constitutive emissions occur also during nighttime as a function of temperature. On the contrary, isoprene is emitted just after synthesis and nullified emission rates were observed after sunset. SQT were found to be correlated with the MEP produced isoprenoids mainly under low atmospheric humidity and co-occurrence of stresses, such as LAh and high ozone or high temperature coupled with high ozone. An interesting observation is the observed relationship between SQT and oxVOC, with emphatic correlation between SQT and acetaldehyde, especially under low ozone conditions and independent of the ambient

temperature. Note that in this context the composition of acetaldehyde at root levels and its subsequent transport to the investigated branch may indicate similar transport of the SQT. On the other hand, when filtering the data with the amount of absolute atmospheric humidity, we observe stronger correlations of all oxVOCs and SQT under high ozone conditions. Oxygenated VOCs were in general correlated with each other but more profound relationship was observed between acetaldehyde and acetone. Methanol was poorly correlated with acetaldehyde and acetone under low ozone with the exception of the case with low ozone but high temperatures.

It should also be noted here that we cannot exclude any combination of abiotic and biotic stresses which may significantly alter VOC emissions (Holopainen and Gershenzon, 2010). Furthermore, intra- and interspecific plant competition is reported to economize VOC emissions in view of defense strategies (Kigathi et al., 2013) demonstrating the complexity of plant reactions to environmental triggers.

3.5 Ambient mixing ratios

While isoprenoids dominate the emissions from Norway spruce, oxVOCs prevailed in terms of mixing ratio in the ambient atmosphere. As previously reported, monoterpenes covered the $50.8 \pm 7.2\%$ and isoprene the $1 \pm 0.16\%$ of the total seasonal emissions. Nevertheless, both species had similar abundance in the ambient mixing ratios, with monoterpenes constituting $4.7 \pm 0.8\%$ and isoprene $3.4 \pm 0.9\%$ of the total measured mixing ratios. This change is caused by different atmospheric lifetimes and by atmospheric mixing. Over the measuring period methanol volume mixing ratios were dominating, by comprising $48.4 \pm 4.1\%$ of the detected total ambient BVOC mixing ratios. Second most abundant compound was acetone ($20.8 \pm 1.6\%$) that was comparable with acetaldehyde ($19.4 \pm 1.1\%$). Despite the fact that sesquiterpene emissions were almost the one fifth of the emitted VOCs, their atmospheric contribution in terms of mixing ratio was minor ($1.1 \pm 0.5\%$). The dominance of oxVOC in the ambient atmosphere is due to their reduced chemical reactivity that enables them to persist over longer spatial and temporal scales, due to their longer atmospheric lifetimes ($\tau > 1$ day). In

contrast, isoprenoids are highly reactive and get destroyed in few hours or even minutes as is the case of sesquiterpenes (Kesselmeier and Staudt, 1999). In Table 3 we present the monthly averaged mixing ratios of the VOCs measured. Highest values were measured during June, when also a maximum in the Norway spruce emissions was quantified. Highest mixing ratios for the most of the species were observed during August, with the exception of the above-mentioned methanol and sesquiterpene mixing ratios that followed similar pattern with the emission rates.

Because of its extremely high reactivity that leads to short atmospheric lifetimes, sesquiterpenes cannot be transported over large distances. Additionally, there are no known anthropogenic sources of sesquiterpenes and therefore their presence in Taunus observatory can be attributed only to Norway spruce. This becomes clear when we plot the monthly emission rates against the ambient mixing ratios (Fig. 8). The best fitting was observed for sesquiterpenes ($R^2 = 0.95$) and methanol ($R^2 = 0.80$), indicating biogenic origin. Acetone and acetaldehyde display moderate relationship between emissions and ambient mixing ratios ($R^2_{acetone} = 0.63$, $R^2_{acetald} = 0.71$) especially when we consider the complete dataset. Since Norway spruce is a weak isoprene emitter, the poor correlations observed can be attributed to deciduous trees in the vicinity. Interestingly, and despite their high emission rates, monoterpene emissions were poorly correlated with the respective mixing ratios. This may be also a result of the chemical reactions with OH, O_3 and NO_3 that relatively fast, "consume" the emitted monoterpenes.

4 Discussion

In terms of climate impact, BVOC mediate the relationship between atmosphere and biosphere (Laothawornkitkul et al., 2009) with the ability to moderate the induced warming by creating particles, which in later stages act as cloud condensation nuclei and affect cloud radiative properties (Pöschl et al.,2010; Siostedt et al., 2011; Paasonen et al., 2013). Isoprenoids have been a main focus due to their highly reactive nature

but some oxVOC may also play a substantial role (Guenther et al., 1995; Kesselmeier and Staudt, 1999; Fuentes et al., 2000) and their importance of oxVOC should be more deeply investigated (Oderbolz et al., 2013) Emission measurements from vegetation may be the compass for the biogenic source of these compounds with respect to future mixing ratios. Here, we have checked thoroughly into the emission rates of both class compounds by quantifying their emission rates along with the atmospheric abundance.

4.1 Diel cycles

Hewitt et al. (2011) emphasized that despite the importance of circadian rhythms in controlling ground level ozone concentrations there are gaps in evaluating their importance in biosphere-atmosphere interactions. Clear diurnal patters were observed for the main oxVOC and all isoprenoids for almost all months. However, the intensity and time maximum differed for different months and compounds (Fig. 5). High methanol emissions were observed mainly during the growing period, with also high nighttime values. Constitutive emissions are more often observed under developmental stages and especially methanol is predominantly emitted during cell expansion (Loreto and Schnitzler, 2010). Parallel with methanol, we observed high emissions of acetone and acetaldehyde for the same period of May–June. Acetaldehyde and acetone were also measured in high concentrations under the flowering period in a citrus orchard (Fares et al., 2012). We have observed high CC between these compounds under most environmental conditions and therefore it is reasonable to hypothesise co-occurrence of the aforementioned emissions. This might be linked to their identical destruction pathway (OH reaction), too that controls their appearance. Acetone emissions were stronger at afternoon and late evening and steeply decline after sunset for Norway spruce (Cojocariu et al., 2004), but also in tropical rainforest (Karl et al., 2004). We found a similar steep decline under light-dark transitions probably as a result of the "pyruvate overflow mechanism" (Karl et al., 2002).

Several studies (Calfapietra et al., 2009; Vickers et al., 2009) suggest that plants with constitutive isoprenoid emissions are less damaged for ozone and therefore they have a competitive advantage over non-emitting plants (Lerdau, 2007). Since constitutive emissions of sesquiterpenes were observed along the complete measuring period, we can assume that Norway spruce might have a competitive advantage at the site of interest, which is characterised by high ozone concentrations (compared to the national average) during the past two decades. On the other hand, isoprene emissions remained low during the measuring period. Norway spruce is considered to be a weak isoprene emitter (Kesselmeier and Staudt, 1999; Grabmer et al., 2006; Filella et al., 2007) and the emissions are known to be driven from a combination of temperature and light abundances (Guenther et al., 1993, 1995). As seen in Fig. 5, isoprene emission intensity and diel cycle followed the respective global radiation. On the contrary, monoterpenes and sesquiterpenes peaked during the evening, reflecting the temperature maximum. Interestingly, during the extremely hot and bright May, both compounds had a plateu, similar to oxVOCs.

4.2 Emission rate parameterization

Niinemets et al. (2010) have discussed the problems on current isoprenoid emission algorithms, emphasizing the need to include missing environmental and physico-chemical controls in the parameterizations. Steps towards this direction have been made by the Model of Emissions of Gases and Aerosols from Nature (MEGAN), which includes biological, physical and chemical driving variables in the isoprene emission modeling (Guenther et al., 2006) but still remains empirical. Additionally, Bourtsoukidis et al. (2012) suggested an algorithm that includes the impact of ambient ozone concentrations in the induced sesquiterpene emissions. Different parameters can be tested under controlled, laboratory conditions but anyhow these plants grow under an unnatural environment, which does not include the biotic relationships and atmospheric variability we meet in ecosystems. Under natural environments plants can experience multiple stress factors simultaneously. These factors can act through a common bio-

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chemical mechanism elicited by temperature, light, ozone or competition complicating their emission investigation (Holopainen and Gershenzon, 2010; Kighati et al., 2013). Additionally, we have observed a tendency of reduced carbon containing emissions towards the end of the year (Fig. 4) which might imply additional parameters that drive the emissions. It is tempting to assume that while storage pools are getting empty, the investment of carbon in the form of isoprenoids is more carefully used. An example towards this direction is the first half of October, which was characterised by lack of rain for more than two weeks. During this period, monoterpene emissions were stronger and begin to predominate the total VOC emissions, while possibly affected stomatal conductances reduced oxVOC emissions.

Here, we took advantage of continuous measurements on a peculiar site and explored emission relationships under different conditions. We found that humidity can be emission driver but also can protect the needles from other abiotic stresses, when it is high enough to create a water film on them. However, the effect of humidity is not yet included in emission models. Additionally, oxVOCs were modeled with the same temperature dependent algorithm described by Eq. (5) (e.g. Shade and Goldstein, 2001). In Fig. 9 we evaluate this parameterisation for the main oxVOC measured along with monoterpenes. Sesquiterpenes have been previously studied in detail for the site of interest (Bourtsoukidis et al., 2012) while the lack of continuous PAR measurements does not allow similar comparison between measurements and the temperature and light dependent algorithm that describes isoprene emissions (Guenther et al., 1995). For minimizing the impermanent effect of emission bursts, we calculated the median values under 10 temperature regimes with the same probability between the limits. The results indicate that Eq. (5) can indeed describe the measured emission rates, but it is critical to include the seasonal emission potentials and temperature dependencies. Acetone emissions had the best correlation with the respective modeled ones, while monoterpenes had the worst. This observation is explained by the highly reduced $E_{s, MT}$ and β_{MT} during nighttime that indicate also light dependent monoterpene emission. Generally, monoterpenes have been found to be light dependent in many

European species (Staudt and Seufert, 1995; Kesselmeier et al., 1996, 1997; Ciccioli et al., 1997; Kesselmeier and Staudt, 1999; Dindorf et al., 2006) but also in tropical forests (Rinne et al., 2002; Kuhn et al., 2002; Kuhn et al., 2004; Karl et al., 2004). On the contrary, relative few light dependent monoterpene emissions have been observed in North America, with most of the studies to indicate only temperature depended emissions (Schade and Goldstein, 2001; Lee et al., 2005; Helmig et al., 2006; Kim et al., 2010). The large biodiversity observed in the composition of monoterpenes even among individuals of the same species (Bäck et al., 2011) may be an explanation for this diverse observation between the two continents.

4.3 Ambient mixing ratios

Once emitted, BVOCs enter the atmosphere with significant implications for atmospheric chemistry. A combination of boundary layer conditions with enhanced reactivity during the day, results in lower atmospheric mixing ratios during the day and higher during the night (e.g. Bouvier-Brown, 2009b; Hakola et al., 2012) despite the opposite pattern of emission rates. In our study, the selected tree was at the edge of the forest and the homogenous mixing that was constantly taking place (Bonn et al., in preparation) resulted in maximum ambient mixing ratios during the day (Fig. 1). Independent of time, oxVOC dominated the ambient mixing ratios, as expected for Europe conditions (Oderbolz et al., 2013). Their impact in atmospheric reactivity is less profound than isoprenoids, but they still share an important portion of the total OH reactivity emission rates (Nöelsche et al., 2012). Additionally their share in wintertime OH reactivity is enhanced as result of reduced isoprenoid emissions (Hakola et al., 2012) and therefore their ambient mixing ratios play important role in OH oxidation. Isoprenoids were less abundant in the ambient atmosphere but despite their lower fractions sesquiterpenes, monoterpenes and linalool dominated the organic O_3 and NO_3 reactivity.

5   Conclusions

We have obtained seasonal emission rates of the most important oxygenated VOC and isoprenoids at a site that covers a wide range of atmospheric conditions. Monoterpenes were the dominant species emitted by Norway spruce throughout the complete measuring period, covering almost the half of the induced emissions. Especially under mechanical stress, monoterpene emission rates can rise up to two orders of magnitude. Methanol and sesquiterpenes were also significantly enhanced under mechanical stress but their emission rates were still low compared to the values observed during the growing period. All emission rates peaked during June and were profoundly reduced during the wet and relatively cold July. Monoterpenes and acetaldehyde were the most affected by this meteorological change and the observed decrease in their emission rates was more than 70 %. Similarly, isoprene, methanol and acetone median emissions have been halved during this weather transition but sesquiterpenes did not, implying different response mechanisms. In normalized emission rates we have observed a tendency of reduced carbon containing emissions from April to November. During this period, the oxygenated species enlarged their portion in total VOC emissions, but isoprenoids were always prevailing.

By taking advantage of the large dataset obtained and the variability in atmospheric conditions, we have separated our measurements in 12 different atmospheric conditions and investigated the emission potentials and temperature dependencies. We found that the aforementioned model parameters are highly diverse under different outbound conditions. Especially monoterpenes can alter their temperature dependence under warm conditions, while the opposite was observed for sesquiterpenes. High temperatures are frequently coincident with high ozone mixing ratios and as Bourtsoukidis et al. (2012) have shown, under elevated ozone β_{SQT} is reaching its lowest value. Despite the fluctuation in the model parameters under different conditions, we have evaluated the temperature dependent algorithm by separating emission rates and modeled results in 10 different temperature regimes and found that the model can suf-

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ficiently describe the induced emissions. The worst correlation however, was observed for monoterpenes due to their observed light dependence.

In order to investigate VOC abundance in the atmosphere, we have developed a box model that derives the respective ambient mixing ratios from dynamic enclosures. In contrast with the emission rates from the dominant species, oxVOC dominated the ambient mixing ratio due to their reduced reactivity and longer lifetimes. Sesquiterpenes and most possible methanol and acetone have biogenic origin at Taunus Observatory. Isoprene may originate from other species since it was emitted in negligible amounts from Norway spruce.

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Table 1. Median, minimum and maximum fluxes calculated for all the compounds measured in $ng\,g(dw)^{-1}\,h^{-1}$. The maximum fluxes observed during summer occurred simultaneously after a storm event as a result of mechanical stress.

	spring			summer			autumn		
	median	min	max	median	min	max	median	min	max
Methanol	33.7	−5.2	4425.8	35.1	−7.2	2786.2	20.7	−21.8	152.9
Acetaldehyde	10.1	−23.9	413.7	14.6	−14.1	1422.2	5.3	−19.8	126.4
Acetone	27.5	−4.3	466.7	38.5	−18.1	7482.2	16.7	−29.3	322.7
Isoprene	3.7	−11.2	95.5	3.2	−5.8	128.2	1.6	−5.5	29.3
Nopinone	0.9	−6.4	98.9	1.2	−8.5	20.3	0.9	−4.7	6.7
Linalool	1.6	−9.7	61.2	2.2	−20.7	20.8	1.7	−10.5	12.4
Pinonaldehyde	1.4	−13.6	15.9	1.8	−27.9	18.5	1.3	−21.2	11.9
Total MT	203.1	10.9	8938.8	136.5	1.1	8434.7	80.8	−1.1	7549.4
Total SQT	118.6	1.6	1915.4	64.9	2.4	878.2	21.4	−0.7	231.9

Table 2. Standardized emission potentials (E_{30}, in $ng\,g(dw)^{-1}\,h^{-1}$) and temperature dependencies (β, in K^{-1}) as derived from nonlinear regression analysis (Eq. 5) for the different seasons and light conditions. N is the amount of data used in the calculations and R^2 is the statistical result that expresses the quality of the fitting.

ALL ($N = 16\,200$)	E_{30}	β	R^2
Methanol	119.8 ± 21.9	0.08 ± 0.02	0.35
Acetaldehyde	72 ± 26.1	0.11 ± 0.04	0.41
Acetone	392.7 ± 87.1	0.15 ± 0.04	0.67
Total MT	885.5 ± 149.6	0.11 ± 0.02	0.47
Total SQT	347.2 ± 70.4	0.11 ± 0.02	0.48

Spring ($N = 4391$)	E_{30}	β	R^2
Methanol	217.2 ± 41.7	0.11 ± 0.02	0.45
Acetaldehyde	72.6 ± 25.4	0.11 ± 0.04	0.36
Acetone	325.1 ± 57.9	0.13 ± 0.03	0.62
Total MT	2837.3 ± 368.8	0.14 ± 0.02	0.58
Total SQT	533.8 ± 61.7	0.09 ± 0.01	0.41

Summer ($N = 6625$)	E_{30}	β	R^2
Methanol	123.6 ± 25.1	0.08 ± 0.02	0.49
Acetaldehyde	70.6 ± 22	0.1 ± 0.03	0.33
Acetone	493.4 ± 93.4	0.16 ± 0.03	0.68
Total MT	977.5 ± 140.7	0.12 ± 0.02	0.45
Total SQT	352.9 ± 56.1	0.12 ± 0.02	0.43

Autumn ($N = 5184$)	E_{30}	β	R^2
Methanol	60.9 ± 15.7	0.07 ± 0.02	0.2
Acetaldehyde	38.1 ± 13.4	0.1 ± 0.03	0.55
Acetone	247.8 ± 70.9	0.14 ± 0.04	0.62
Total MT	355.8 ± 66.1	0.08 ± 0.01	0.45
Total SQT	175.5 ± 61.7	0.11 ± 0.01	0.71

Day ($N = 8891$)	E_{30}	β	R^2
Methanol	124.6 ± 24.3	0.09 ± 0.02	0.31
Acetaldehyde	76.5 ± 23.3	0.11 ± 0.03	0.37
Acetone	400.4 ± 71.7	0.15 ± 0.03	0.63
Total MT	1448.5 ± 219.7	0.13 ± 0.03	0.42
Total SQT	365.1 ± 77.1	0.12 ± 0.02	0.37

Night ($N = 7309$)	E_{30}	β	R^2
Methanol	108.9 ± 26.7	0.08 ± 0.02	0.19
Acetaldehyde	52.1 ± 21.5	0.1 ± 0.04	0.27
Acetone	281.1 ± 76.1	0.15 ± 0.04	0.45
Total MT	258.6 ± 45.7	0.06 ± 0.01	0.11
Total SQT	327 ± 57.4	0.11 ± 0.02	0.32

Table 3. Mean ambient mixing ratios (in ppb$_v$) along with their standard deviations for each month.

	spring			summer		autumn		
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Methanol	3.32 ± 1.02	3.70 ± 0.88	4.31 ± 1.11	3.61 ± 1.12	3.62 ± 1.13	3.11 ± 1.11	2.38 ± 0.62	2.18 ± 0.32
Acetaldehyde	1.31 ± 0.58	1.68 ± 0.76	1.78 ± 0.54	1.59 ± 0.58	1.78 ± 0.83	1.19 ± 0.52	0.79 ± 0.22	0.73 ± 0.1
Acetone	1.51 ± 0.51	1.46 ± 0.58	1.93 ± 0.84	1.61 ± 0.61	2.14 ± 1.15	1.28 ± 0.54	0.91 ± 0.55	0.78 ± 0.16
Isoprene	0.30 ± 0.17	0.33 ± 0.27	0.32 ± 0.15	0.32 ± 0.14	0.38 ± 0.28	0.15 ± 0.07	0.11 ± 0.07	0.08 ± 0.04
Nopinone	0.06 ± 0.03	0.08 ± 0.06	0.11 ± 0.06	0.08 ± 0.04	0.11 ± 0.06	0.05 ± 0.02	0.03 ± 0.02	0.03 ± 0.01
Linalool	0.06 ± 0.04	0.06 ± 0.05	0.07 ± 0.05	0.07 ± 0.04	0.09 ± 0.07	0.04 ± 0.03	0.03 ± 0.02	0.02 ± 0.02
Pinonaldehyde	0.04 ± 0.03	0.04 ± 0.03	0.05 ± 0.03	0.04 ± 0.03	0.06 ± 0.05	0.02 ± 0.02	0.02 ± 0.02	0.01 ± 0.01
Total MT	0.35 ± 0.22	0.45 ± 0.35	0.46 ± 0.2	0.38 ± 0.17	0.51 ± 0.32	0.26 ± 0.15	0.17 ± 0.1	0.13 ± 0.06
Total SQT	0.15 ± 0.09	0.11 ± 0.07	0.08 ± 0.07	0.09 ± 0.06	0.09 ± 0.05	0.04 ± 0.02	0.03 ± 0.02	0.02 ± 0.06
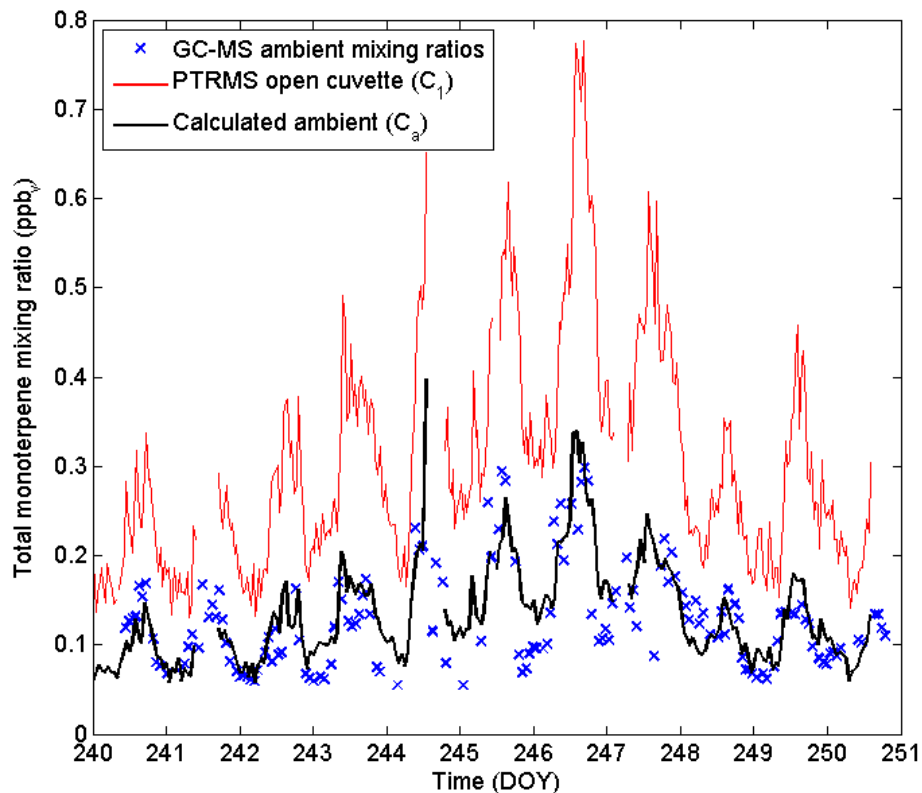
Fig. 1. Comparison between the PTR-MS signal with open cuvette (red line), the GC-MS measurements conducted in the ambient atmosphere (blue cross) and the box model calculations of Eq. (4).

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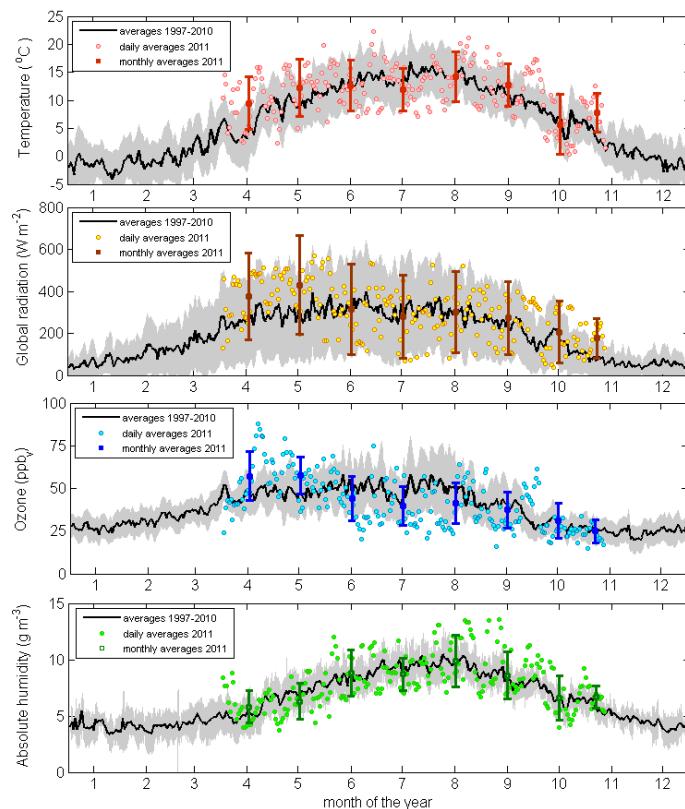
Fig. 2. Climatological observations of temperature, global radiation, ozone and absolute humidity. The black continuous line represents the daily average from the years 1997 to 2010 and the shadow their standard deviation. Daily means of the year 2011 are given with cycles while the errorbars represent the monthly means with the respective standard deviations.
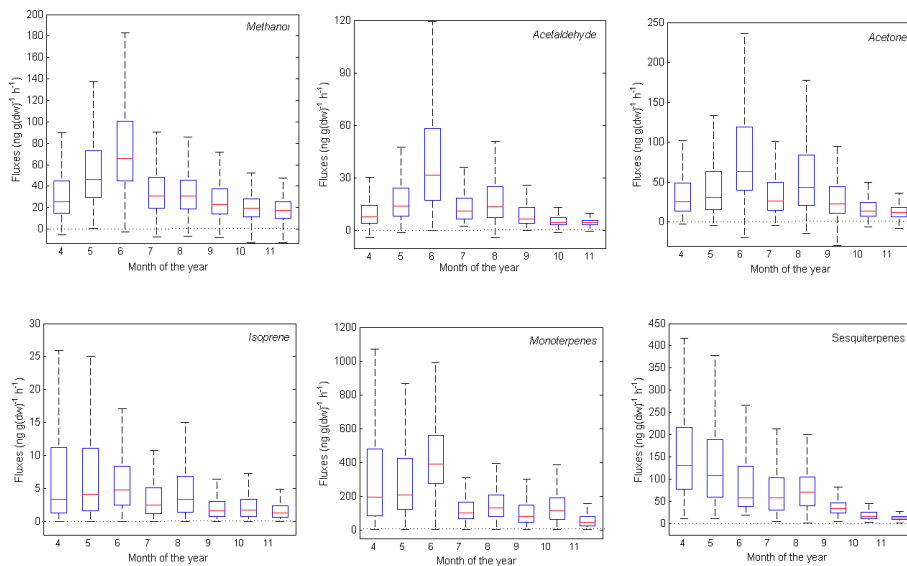
Fig. 3. Boxplot for the fluxes of the main oxVOC investigated (top) and for isoprenoids (bottom). On each box, the central mark is the median and the edges of the box are the 25th and 75th percentiles.
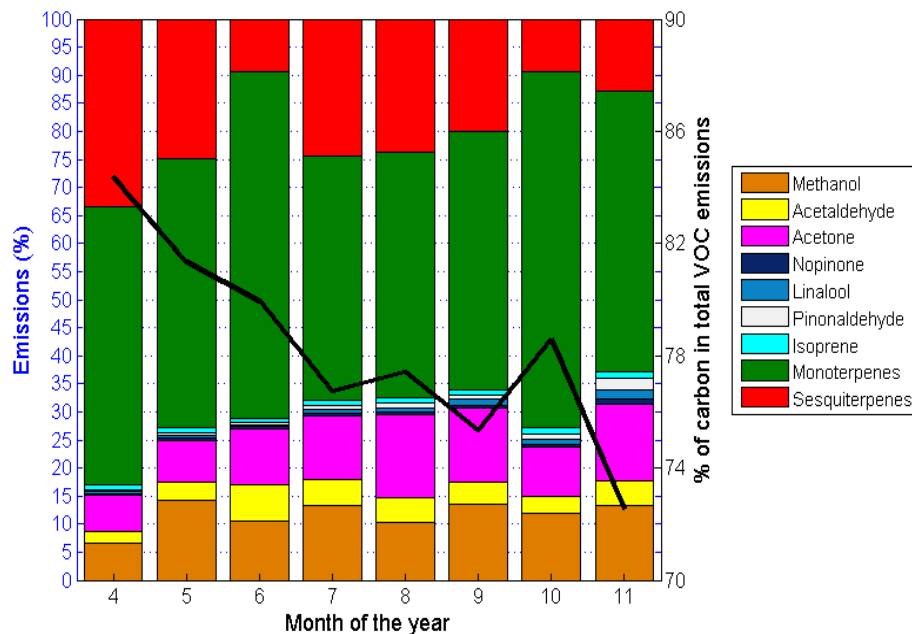
Fig. 4. Normalized contribution of each VOC measured to the total sum of emission rates (left axis) along with the percentage of carbon in the total VOC emissions (right axis) for each month.

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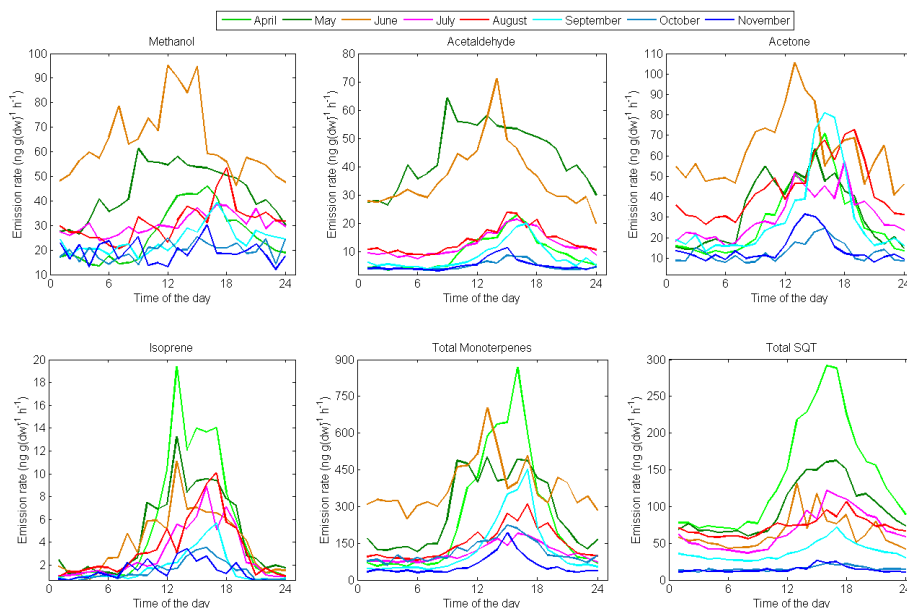
Fig. 5. Diurnal patters for the most abundant emissions from Norway spruce including both oxVOC (top) and isoprenoids (bottom).
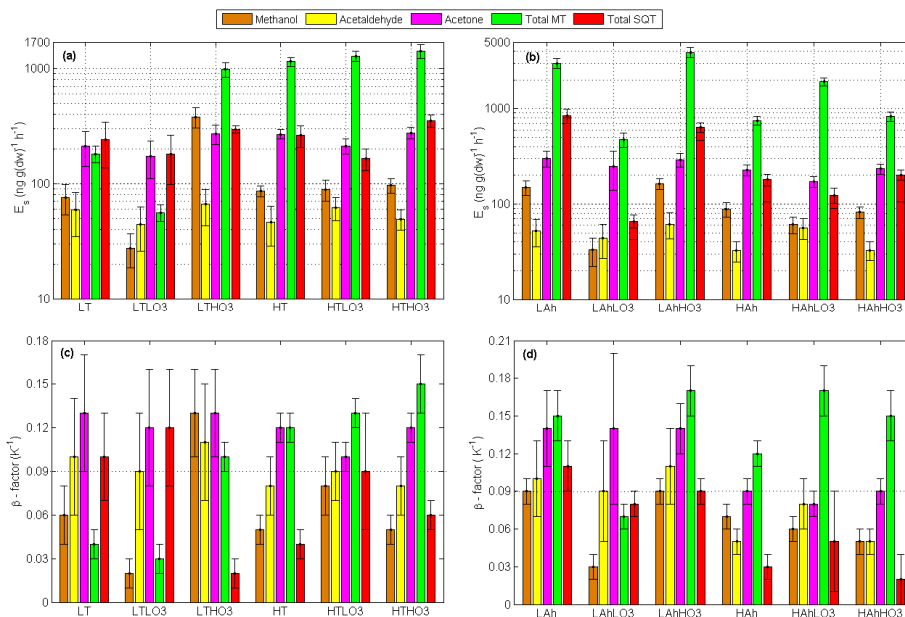
Fig. 6. Standardized emission potentials (E_{30}, in $ng\,g(dw)^{-1}\,h^{-1}$) and temperature dependencies (β, in K^{-1}) as derived from nonlinear regression analysis for 12 different atmospheric conditions (LT: low temperature; LTLO$_3$: low temperature and low ozone; LTHO$_3$: low temperature and high ozone; HT: high temperature; HTLO$_3$: high temperature and low ozone; HTHO$_3$: high temperature and high ozone; LAh: low absolute humidity; LAhLO$_3$: low absolute humidity and low ozone; HAh: high absolute humidity; HAhLO$_3$: high absolute humidity and low ozone; HAhHO$_3$: high absolute humidity and high ozone).
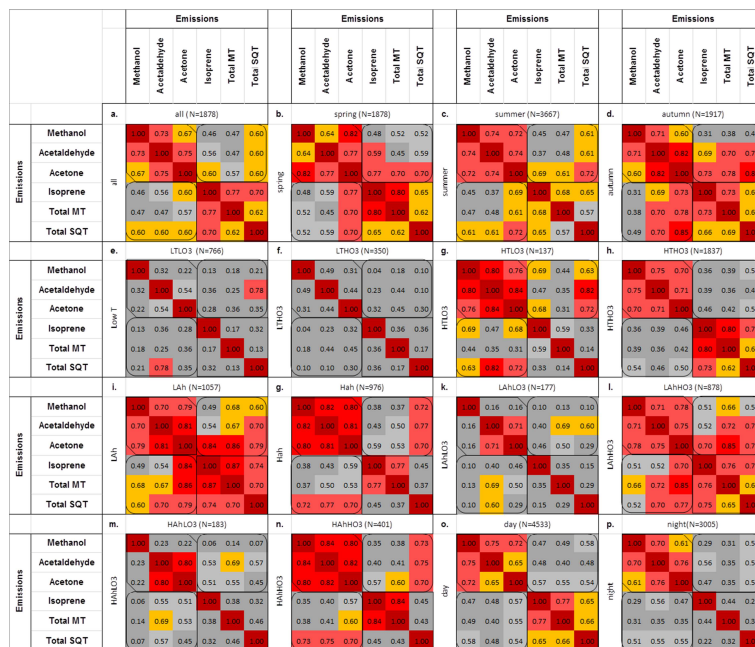
Fig. 7. Correlation coefficient between the main oxVOC and isoprenoids under different seasons, atmospheric conditions and light abundance. **(a)** all data considered, **(b)** spring, **(c)** summer, **(d)** autumn, **(e)** LTLO$_3$: low temperature and low ozone, **(f)** LTHO$_3$: low temperature and high ozone, **(g)** HTLO$_3$: high temperature and low ozone, **(h)** HTHO$_3$: high temperature and high ozone, **(i)** LAh: low absolute humidity, **(j)** HAh: high absolute humidity, **(k)** LAhLO$_3$: low absolute humidity and low ozone, **(l)** LAhHO$_3$: low absolute humidity and high ozone, **(m)** HAhLO$_3$: high absolute humidity and low ozone, **(n)** HAhHO$_3$: high absolute humidity and high ozone, **(o)** day, **(p)** night.

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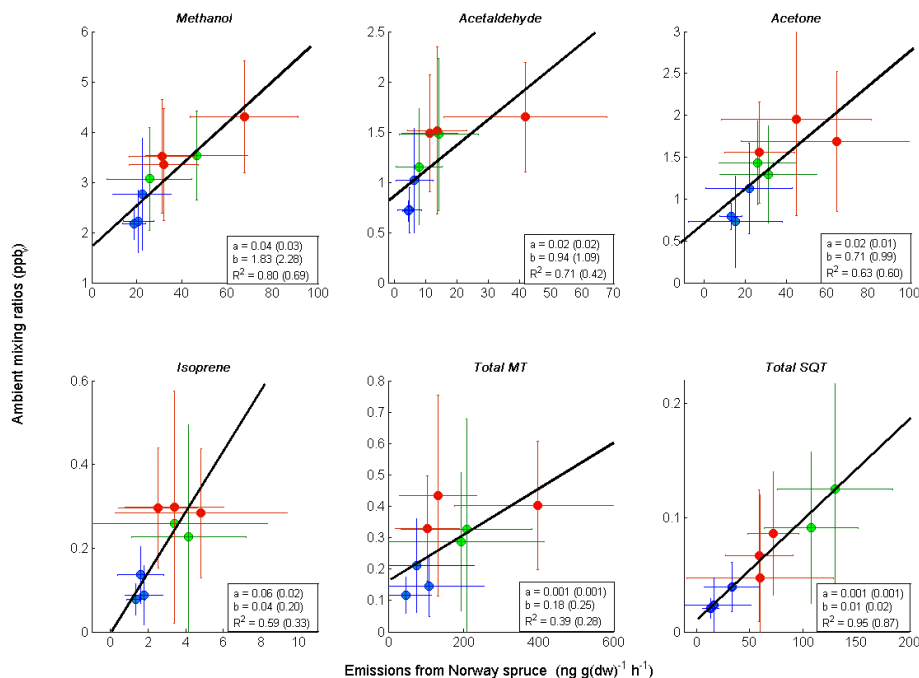◄◄   ►►

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Fig. 8. Monthly mean emissions from Norway spruce against the ambient mixing ratios. The linear fitting is in the form of $y = ax + b$, where y is the ambient mixing ratios and x the emissions. The parameters a and b are defined in the boxes of each plot. R^2 is the statistical result that expresses the quality of the fitting. Inside the brackets are the values obtained when considering all the data.

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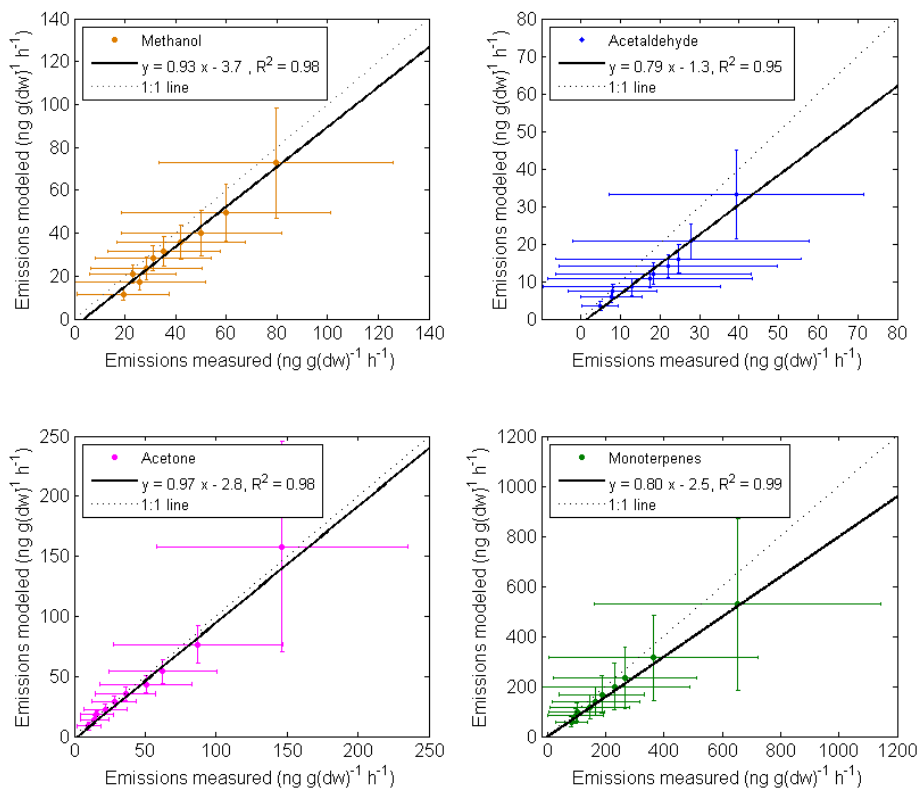
Fig. 9. Measured against modeled emission rates for 10 different temperature regimes with the same probability between the limits.