Isoprene and monoterpene emissions from a mixed temperate forest

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Abstract

We measured the isoprene and monoterpene fluxes continuously above a mixed forest site at Vielsalm in the eastern part of Belgium, using the disjunct eddy covariance technique with proton transfer reaction-mass spectrometry. Simultaneously, we also measured the carbon dioxide fluxes in order to deduce the gross primary production. The measurements were conducted from July to September 2009.

During the day, the seasonal evolution of the isoprene/monoterpene emissions was studied using a monthly temperature and light dependence function deduced from our results to standardize the fluxes. A seasonal decrease in the standard emission factors was observed, probably linked to acclimation or senescence. The standard emission factor for isoprene fluxes (30°C, 1000 μmol m^{-2} s^{-1}) fell from 0.91 ± 0.01 to 0.56 ± 0.02 μg m^{-2} s^{-1} and for monoterpene fluxes from 0.74 ± 0.03 to 0.27 ± 0.03 μg m^{-2} s^{-1}.

During the night, a slight positive flux of monoterpenes was observed that seemed to be driven by air temperature. The standard emission factor (30°C) for night-time monoterpene fluxes was equal to 0.093 ± 0.019 μg $m^{-2}s^{-1}$.

Finally, we studied the seasonal evolution of the relationship between the gross primary production and the isoprene/monoterpenes fluxes. A linear relationship was observed, highlighting the strong link between carbon assimilation and isoprene/monoterpene emissions.

Key words:

Forest ecosystems, monoterpenes, isoprene, disjunct eddy-covariance, PTR-MS

1. Introduction

Isoprene and monoterpenes are the most abundant biogenic volatile organic compounds (BVOCs) emitted by terrestrial vegetation, particularly by forests. Global isoprene and monoterpene emissions are estimated to be 460 TgC yr^{-1} and 117 TgC yr^{-1}, respectively, representing 80% of the total BVOC emissions (Lathière et al., 2006). Isoprene and monoterpenes have a significant impact on atmospheric chemistry and physics. The degradation of BVOCs can lead to an increase/decrease in the production of tropospheric ozone (O_3), depending on the nitrogen oxide (NO_x) concentration (Atkinson, 2000). Their very short reaction time (Atkinson, 2000) with hydroxyl (OH) radicals can modify the oxidative capacity of the atmosphere and increase the lifetime of other chemical compounds such as methane (Ortega et al., 2007). Isoprene and monoterpene oxidation initiates and favours the production of secondary organic aerosols (Kanakidou et al., 2005), compounds that can have a direct and indirect influence on the Earth's radiative budget (Peñuelas and Staudt, 2010).

BVOCs are produced mainly by bio-chemical processes in leaves. Isoprene and monoterpene biosynthesis takes place in chloroplasts (Wildermuth and Fall, 1996) through the 1-deoxy-D-xylulose 4-phosphate/2-C-methylerythritol 5-phosphate (DOXP/MEP) pathway (Eisenreich et al., 2004; Lichtenthaler, 2007). The first enzyme in this biosynthesis pathway catalyses the formation of DOXP from D-glyceraldehyde 3-phosphate and pyruvate, both intermediate products of photosynthesis. After six other enzymatic reactions, DOXP is transformed in isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMADP). This DMADP is transformed into isoprene by the isoprene synthase enzyme (ISPS) and monoterpenes are synthesized as a product of DMAPD and IPP condensation through the enzymatic monoterpene synthase (Croteau et al., 1988). There is another IPP and DMADP synthesis pathway in the cytosol (Lichtenthaler, 2007; 1997) leading to the formation of sesquiterpenes, triterpenes and polyterpenes, but the IPP exchange between the two biosynthesis pathways apparently does not occur under physiological standard conditions (Lichtenthaler, 2007). Several studies (Delwiche and Sharkey, 1993; Funk et al., 2004; Karl et al., 2002a) have shown that photosynthetically assimilated carbon is the principal source of carbon used in the formation of isoprene (more than 80%: Funk et al. (2004)) in the absence of drought and thermal stress. Brüggemann and Schnitzler (2002) showed a positive correlation between net carbon assimilation and DMADP content in leaves, as well as between DMADP content in leaves and isoprene emission. Isoprene (monoterpene) production is therefore regulated by the ISPS (monoterpene synthase) activity and by the availability of DMADP in leaves, the latter depending on the enzymatic activity of the MEP pathway (Brüggemann and Schnitzler, 2002; Fischbach et al., 2002; Wiberley et al., 2008).

In addition, under conditions of drought and thermal stress, it has been observed that the *de novo* carbon constituting the BVOC skeleton is partly replaced by carbon coming from alternative sources that are not directly dependent on photosynthesis (Funk et al., 2004). In addition, in the case of isoprene, Owen and Penuelas (2005) formulated the hypothesis that if other BVOCs such as diterpenes and tetraterpenes are synthesized episodically by the plant (thermal protection, defence against pathogens,...) via the DOXP/MEP pathway, available DMADP can be reduced, leading to a decrease in isoprene emission.

After their production, isoprene and monoterpenes are emitted directly to the atmosphere mainly through the stomata. In the case of monoterpenes, a fraction of the production can be stored temporarily in the plant before progressively diffusing in the plant tissues and being emitted into the atmosphere (Fuentes et al., 2000; Kesselmeier and Staudt, 1999).

To date, very few studies have presented simultaneous ecosystem-scale micrometeorological measurements of isoprene, monoterpenes and CO_2 fluxes over several months (Fuentes et al., 1999; Holst et al., 2010; Holzinger et al., 2006; Pressley et al., 2006). Such measurements performed over shorter periods, from several days to several weeks (Gallagher et al., 2000; Grabmer et al., 2004; Greenberg et al., 2003; Rinne et al., 2001; 2007; 2000; Spirig et al., 2005), cannot cover the seasonal evolution of BVOC emissions. Knowing this evolution, however, is crucial for reducing uncertainties in regional emission models and for a better understanding of the emission mechanisms. There are also numerous studies of BVOC emissions using cuvettes (Kesselmeier and Staudt, 1999) which allow, under controlled conditions, to pinpoint the drivers of these emissions. These studies are often limited in time and it is more difficult to obtain statistically reliable relationships at the ecosystem spatial scale due to the challenge of having enough replica.

In this study, we present ecosystem-scale flux measurements of isoprene and monoterpenes between a mixed forest and the atmosphere, using the disjunct eddy-covariance (DEC) technique (Rinne et al., 2001). This technique is the best suited for long-term monitoring in real conditions and at the ecosystem scale without disturbing the ecosystem. Our dataset extends from July to October 2009, thus covering the Belgian summer and the first part of autumn.

Our objectives were to (i) describe and quantify the climatic control of these emissions, (ii) derive standard emission factors, (iii) investigate the coupling between BVOC emissions and assimilated CO_2 and (iv) investigate the seasonal evolution of the above-mentioned parameters in order to see how BVOC production pathways within the plant can alter over time.

2. Material and methods

2.1 The Vielsalm site

The forested site is at Vielsalm in the Belgian Ardenne forest (50°18’18.20’’N, 5°59’53.15’’E altitude: 450 m). Its topography is smoothly sloping (3%) in a north-westerly direction. The climate is temperate maritime. The soil is 50-100 cm deep and is classified as a dystric cambisol. The vegetation is a mixture of coniferous species, mainly Douglas fir (*Pseudotsuga menziesii* [Mirb.] Franco) about 40 m high, Norway spruce (*Picea Abies* [L.] Karst.) about 32 m high, Silver fir (*Abies alba* Miller) about 32 m high, and deciduous species, mainly beeches (*Fagus sylvatica* L.) about 28 m high. Figure 1 represents the vegetation distribution around the tower. There are more details about the site in (Aubinet et al., 2001; 2002) and (Laitat et al., 1999).

2.2 Disjunct eddy covariance

The technique used to measure ecosystem BVOC fluxes is the disjunct eddy-covariance (DEC) derived from the eddy covariance method (Ammann et al., 2006; Karl et al., 2001; 2004; 2002b; Rinne et al., 2001; Spirig et al., 2005) which is generally used to measure CO_2 and H_2O fluxes (Aubinet et al., 1999). The flux is computed as the covariance of vertical wind velocity component and BVOC concentration. These two components must be measured with a short instrumental time response in order to take into account the high frequency fluctuations contributing to the flux. For BVOC fluxes, proton transfer reaction-mass spectrometry (PTR-MS) allows the concentration fluctuations of BVOCs to be measured in real time with a fast instrumental response time (see below). Conventional PTR-MS instrument with a quadrupole mass spectrometer (used in this study) does not enable ion intensities to be measured at more than one mass at a time; the ion signal intensities in the masses of interest are measured in a cyclical way, which produces a disjunct concentration time series for each mass. Two methods can then be used to compute the turbulent flux (Hörtnagl et al., 2010). The first (Spirig et al., 2005) consists of filling the missing data in the concentration time series by simply repeating the closer measured concentration with a sampling frequency identical to the one of the vertical velocity component. The second (Karl et al., 2002b) consists of under-sampling the vertical velocity component time series with a sampling frequency identical to the PTR-MS cycle. The first method will act as a low-pass filter and the use of an empirical correction function can be contemplated (Bamberger et al., 2010). The second method increases the random error on the fluxes but does not increase the systematic error (Lenschow et al., 1994) as long as the under-sampling period is shorter than the turbulent integral time scale (typically between 15 and 60 s over forests). In this study, we used the second method (under-sampling) for flux computation, with an under-sampling period of 2 s. From the empirical relationship deduced by Turnipseed et al. (2009), the additional random error originating from this under-sampling was 10%.

Our system comprised a sonic anemometer (model SOLENT 1012R2, Gill Instruments Ltd, Lymington, UK) and an hs-PTR-MS (Ionicon Analytick GmbH, Innsbruck, Austria). The sonic anemometer was placed at the top of a tower at a height of 52 m and measured the three wind velocity components continuously at a sampling frequency of 20.8 Hz. Ambient air was continuously sampled close to the sonic anemometer through a main sampling line (PFA tubing: Fluortechnik-Wolf)

60 m long and 6.4 mm inner diameter, with a flow rate of 9 STP L min^{-1} (Standard Pressure and Temperature conditions corresponded to 1013.25 hPa and 273.15 K) and was slightly heated above ambient temperature. A part of this air flow (0.1 STP L min^{-1}) was drawn into the PTR-MS through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The time lag between the sonic anemometer measurements and the PTR-MS measurements was computed for each half-hour by shifting one-time series relative to the other until the absolute maximum covariance between the two-time series was determined. We used the filled-time series as proposed by Spirig et al. (2005) and described above to determine the time lag (but not to compute fluxes as already mentioned). This approach allowed an easier timelag determination and is similar to the averaging approach proposed by Taipale (2010). The mean time lag found using this method was 14.8 s, close to 12.9 s, the theoretical value computed from the flow rate and the inlet line volume. This experimental mean time lag was used as the default value when we didn't found a maximum in the covariance function inside the [10 s, 18 s] time window. The data streams coming from the two instruments were logged on a single computer in order to optimise synchronization. We measured the ion signals at mass to charge ratio m/z 21 (primary hydronium ions: $\mathrm{H}_3^{18}\mathrm{O}^+$), m/z 33 (methanol), m/z 39 (water cluster ion), m/z 45 (acetaldehyde), m/z 59 (acetone), m/z 69 (isoprene), m/z 71 (methyl vinyl ketone and methacrolein), m/z 81 (fragment of monoterpenes), m/z 87 (methylbutenol and possibly others) and m/z 137 (monoterpenes). The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. This dwell time was required for limiting significant noise contribution from the PTR-MS. The dwell time had little influence on flux loss (Hörtnagl et al., 2010). BVOC fluxes were computed using the EUROFLUX methodology (Aubinet et al., 1999). Means were computed

using block average over 30 min periods, and 2D rotation was applied. High frequency losses due mainly to the damping of concentration fluctuations in the sampling line were corrected experimentally following the method reported by Aubinet et al. (2001) using a transfer function determined by a comparison of the sensible heat flux co-spectra and the m/z 69 flux co-spectra. From this unique transfer function, a correction factor was deduced which was applied to the BVOC fluxes. For example, for a wind speed of 3 m s^{-1} (mean value of our dataset), we obtained a correction factor of 1.49.

2.3 PTR-MS operation

There are detailed descriptions of the PTR-MS technique in Lindinger et al. (1998), de Gouw et al. (2007) and Ammann (2004). In our study, PTR-MS was operated at a drift tube pressure of 2.1 hPa, a drift tube temperature of 333 K and a drift voltage of 600 V, resulting in an E/N of 143 Townsend (1 Td = 10^{-17} V cm^2), with E the electric field and N the ambient air number density in the flow/drift tube. During the measurements, the instrumental background was determined every 4 hours by sampling BVOC-free air, obtained by sending ambient air through a heated catalytic converter for 15 min (the last 8 min being used for the calculation of the mean background values). The sensitivity of the instrument was calibrated for the main target compounds (isoprene, sum of monoterpenes, methanol, acetone and acetaldehyde) every two or three days using a gravimetrically prepared mixture of these gases in N_2 (Apel-Riemer Environmental, Denver, CO, USA) that contained approximately 500 ppbv isoprene, α-pinene and sabinene and about 1 ppmv methanol, acetaldehyde and acetone, with an accuracy of 5%. The compounds were further diluted (2-12 ppbv range) using a dynamic dilution system.

The ion signal at m/z 87 was followed because it is typical for C_5 alcohols, which might interfere with the detection of isoprene because these alcohols are known to have an important fragment ion at the same m/z value of protonated isoprene (m/z 69) (de Gouw and Warneke, 2007; Demarcke et al., 2010a). A comparison of measured fluxes and concentrations calculated from the ion signals at m/z 69 and 87, however, indicated (data not shown) that there is no important contribution of C_5 alcohols to the ion signal at m/z 69. The ion signal at m/z 137 has always been considered to be a good estimator ion of the sum of monoterpenes (de Gouw and Warneke, 2007).

2.4 Meteorological measurements

Measurements of relevant meteorological variables were performed as half-hourly averages, including total and diffuse fraction of photosynthetically active radiation (Sunshine sensor type BF3, Delta-T Devices Ltd, Cambridge, UK), air temperature and humidity (RHT2, Delta-T Devices Ltd, Cambridge, UK) at a height of 50 m, soil humidity (ThetaProbe, Delta-T Devices Ltd, Cambridge, UK) at a depth of 20 cm, and precipitation and atmospheric pressure (MPX4115A, Motorola, Phoenix, USA).

2.5 Data filtering

Throughout the measurement period, in some cases, mixing ratios of methanol and monoterpenes were abnormally high for the wind direction sector 230-270° (Figure 2), which was also the main wind direction. In this direction, a wood panel factory was 3 km from the tower. This industrial process is known to emit high levels of monoterpenes (due to wood grinding). The factory was not located inside the main day flux footprint (90%), but this source was probably so important, compared with biogenic sources, that it influenced our measurements. The suspected anthropogenic origin of these monoterpene emissions was confirmed by the lack of a relationship between wind direction and mixing ratios of isoprene (Figure 2). The measurements spoiled by anthropogenic emissions should therefore be rejected from the dataset. A filtering criterion based on wind direction only would have been too restrictive in view of the intermittent activity of the factory and the huge amount of data that would have been lost. We therefore used a filtering criterion based on the variance of the monoterpene mixing ratio. When the factory was functioning, this variance was very high for the 230°-270° wind sector compared with other sectors, where it never exceeded 0.08 ppbv^2 during the day and 0.03 ppbv^2 during the night (data not shown). These high values must be the consequence of the huge difference in monoterpene mixing ratios between air emitted by the factory and ambient air. The relatively short distance between the factory and the tower did not allow complete mixing of the air, resulting in important mixing ratio fluctuations and therefore in strong disturbances of the ecosystem flux measurements. The application of the flux variance criterion rejected 17% of the monoterpene data. The isoprene data were not affected by the factory activity and were therefore not filtered.

The system detection limit was estimated using a procedure proposed by Wienhold et al. (1994) and Spirig et al. (2005). They proposed computing the covariances of concentrations and vertical velocities delayed by time lags so large that the covariance should theoretically have been zero. The detection limit was then defined as three times the standard deviation of the covariance for these time lag ranges. In practice, we used -180 s to -160 s and 160 s to 180 s as the time lag ranges. These confidence intervals were useful as quality criteria for individual flux estimations, but became useless when flux estimations were treated as statistical means in order to get rid of the noise.

2.6 Data treatment and analysis

2.6.1 Emission algorithm

To analyse the meteorological responses of isoprene and monoterpene emissions, we used an algorithm derived from those proposed by Guenther et al. (1993). We modelled the temperature and radiation dependence of isoprene and monoterpene emissions as:

$$\text{Emission} = SEF.C_L.C_T \qquad (1)$$

where *SEF* is the standard emission factor describing emissions under standard conditions (PPFD = 1000 µmol m^{-2} s^{-1}, T_a = 30°C), and C_L and C_T are functions describing the photosynthetic photon flux density (PPFD) and the air temperature (T_a) dependence, respectively. In this study, air temperature was used as a surrogate for leaf temperature.

C_T was modelled as:

$$C_T = \exp(\beta.(T_a - 303.15)) \qquad (2)$$

where β [K^{-1}] is the temperature dependence parameter,

and C_L as:

$$C_L = \frac{C_{L1}Q}{\sqrt{1000^2({C_{L1}}^2 - 1) + Q^2}} \qquad (3)$$

where Q [µmol m^{-2} s^{-1}] is the PPFD and C_{L1} [µmol m^{-2} s^{-1}] is the saturation C_L value. The expression 2 is generally used to describe the monoterpene emissions from storage pools. The temperature response of isoprene/monoterpenes emission from *de novo* production is commonly represented by a temperature response of enzymatic activity that decreases above 40°C due to the enzyme denaturation

(Guenther et al., 1993). These temperatures were never observed in our dataset therefore we used the expression 2 in our data adjustment to represent both the temperature response of *de novo* isoprene/monoterpene production and monoterpene emissions form pools.

Expression 3 from Guenther et al. (1993) was rearranged in order to depend on only one parameter, C_{L1}.

We adjusted these equations to our data by using non-linear least square fitting based on the Levenberg-Marquardt algorithm from Origin software 7.0 (OriginLab Corporation).

2.6.2 Footprint model

The footprint analyses were performed with a two-dimensional analytical footprint software tool proposed by Neftel et al. (2008) according to the Kormann-Meixner footprint model (Kormann and Meixner, 2001). The inputs of the model are information provided by the eddy covariance system (friction velocity, Obukhov length, standard deviation of lateral wind speed, measurement height and horizontal wind speed).

2.6.3 Gross primary production computation

The gross primary production (GPP) was inferred by deducting the total ecosystem respiration (TER) to the net ecosystem exchange (NEE) measured by eddy covariance. TER was inferred by extrapolation to the whole day of night-time NEE measurements, since plant assimilation can be considered to be zero at night. An algorithm proposed by Reichstein et al. (2005) for the respiration response to soil temperature based on night flux measurements was used for the extrapolation.

3. Results

3.1 Micrometeorological and flux seasonal evolutions

The seasonal evolution of air temperature, PPFD, wind direction, friction velocity (u*), soil moisture (S_W) and precipitation are given in Figure 3. Mean air temperature was 16.8°C, 13.6°C and 8.4°C for July-August, September and October 2009, respectively. Maximum temperature (30.3°C) was reached on 20 August and minimum temperature (–1.7°C) on 15 October (the first frost appeared on 14 October). In July, the noon PPFD values went up to 1500 and 300 µmol m^{-2} s^{-1} under sunny and cloudy conditions, respectively. In October they reached 800 and 150 µmol m^{-2} s^{-1}, respectively. The main wind direction was W-SW (50%), but E-SE (15%) and NE (10%) directions were also observed. Soil moisture measured at 0.2 m below the soil surface diminished progressively in August and September, from 0.38 m^3 m^{-3} to 0.26 m^3 m^{-3} (field capacity: 0.43 m^3 m^{-3}, wilting point: 0.15 m^3 m^{-3}). During this period, precipitation was quite sparse, occurring on about one or two days every 10 days. More intense precipitation in early October increased soil moisture rapidly up to 0.33 m^3 m^{-3}.

Time series of measured isoprene and monoterpene fluxes are presented in Figure 4. The measurements covered 88% of the period, data gaps being due either to partial or total system failures or to background noise measurement and PTR-MS calibration (12%). The grey lines correspond to data that could not be considered as different from zero on the basis of the detection limit criterion described in section 2.5.

Both fluxes were always positive, which indicates that the flux was always oriented from the surface towards the atmosphere, and presented a diurnal cycle. At night, isoprene fluxes were close to zero, whereas monoterpene fluxes remained slightly positive. Maximum flux values were observed for both components on 20 August (isoprene: 1.96 µg m^{-2} s^{-1}; monoterpenes: 0.69 µg m^{-2} s^{-1}), which corresponded to the warmest day of the 2009 season. The last significant fluxes of isoprene and monoterpenes were observed on 28 September and 7 October, respectively, the latter date corresponding to the last day of the season where the temperature slightly exceeded 20°C. Only data measured between July and September were used in the rest of the study. During this measurement period, no biotic stress on trees was visually detected, nor was any alteration of the GPP signal observed.

The land cover map and footprint climatology corresponding to the July-September period are shown in Figure 1. The contribution to the flux from the NE wind direction (Douglas fir) appears small compared with that of *Fagus sylvatica*, *Picea abies* and *Abies alba*.

A two-way analysis of variance (ANOVA) was performed in order to analyse the relative impact of radiation and temperature on the fluxes. Response to temperature appeared dominant as it contributed up to 44% and 22% of the isoprene and monoterpene flux variance, respectively, whereas the PPFD response contributed up to 14% and 10%, respectively.

3.2 BVOC flux response to temperature

The relationships between BVOC fluxes and air temperature are shown in Figure 5 for July, August and September. They show that both isoprene and monoterpene emissions increased with temperature. Fitting Equations 1 and 2 to the data allowed the temperature sensitivity, β, to be estimated and the emission factor to be standardized at 30°C, $SEF.C_L$. Their mean values for each month and each compound are given in Table 1.

Isoprene fluxes were characterized by systematically larger temperature sensitivities and standardization factors than monoterpene fluxes. Below 30°C, these two parameters affected the relationship in opposite ways, so that isoprene fluxes were larger than monoterpene fluxes at high temperatures but lower at low temperatures. In addition, the temperature sensitivities of both components and the isoprene temperature standardized emission factor ($SEF.C_L$) did not evolve significantly with season.

Under night-time conditions, the isoprene flux was zero but there was still a slight monoterpene flux. This emission appeared to be related to temperature, as shown in Figure 6. By adjusting Equation 2 to the measurements, a temperature sensitivity of $0.061 \pm 0.017\ \mathrm{K}^{-1}$ was found with an SEF (C_L=1) equal to $0.093 \pm 0.019\ \mu\mathrm{g\ m}^{-2}\mathrm{s}^{-1}$ (estimate ± standard error).

3.3 BVOC response to PPFD and GPP

Figure 7 represents the response to PPFD of monoterpene and isoprene fluxes standardized with temperature. To this end, each flux was divided by Equation 2 parameterized with the temperature sensitivities given in Table 1. The increase of fluxes with PPFD was clear. Saturation coefficients, C_{L1}, were deduced by fitting Equation 3 on these relationships. The results are given in Table 1.

Both saturation fluxes tended to decrease during the season. For monoterpene fluxes, the decrease was quite regular, whereas for isoprene it was not significant between July and August but was more pronounced in September. Saturation of the flux response to PPFD, however, was observed only once, in September, for the monoterpene fluxes.

Finally, there was a clear response of temperature-standardised BVOC fluxes to GPP (Figure 8). Both fluxes were found to increase linearly with absolute GPP in July. The slopes and their standard errors were $-5.54\ 10^{-4} \pm 1.69\ 10^{-5}$ (intercept: $-1.310^{-3} \pm 3.67\ 10^{-4}$ μmol m^{-2} s^{-1}) and $-1.99\ 10^{-4} \pm 9.70\ 10^{-6}$ mol mol^{-1} (intercept: $-2.53\ 10^{-4} \pm 2.10\ 10^{-4}$ μmol m^{-2} s^{-1}) for isoprene and monoterpenes, respectively. In September, the isoprene flux response to GPP (slope: $-2.78\ 10^{-4} \pm 2.84\ 10^{-5}$ mol mol^{-1}; intercept: $-2.13\ 10^{-4} \pm 5.37\ 10^{-4}$ μmol m^{-2} s^{-1}) was still linear, whereas that of monoterpene saturated rapidly.

3.4 Standard emission factors

The seasonal evolution of *SEF* is presented in Figure 9. The *SEF* for both isoprene and monoterpenes decreased during the season. The decrease was clearer for monoterpenes than for isoprene, the *SEF* remaining quite stable and lower than 0.5 μg m^{-2} s^{-1} after the end of August. This trend was also significant for isoprene but less pronounced and partly masked by a larger day-to-day variability.

Finally, an *SEF* dependence on friction velocity was also found, as shown in Figure 10. In both cases, fluxes were found to increase with u*, the increase being more pronounced for isoprene than for monoterpenes and showing saturation at high u* (see below).

4. Discussion

4.1 Impact of tree species on fluxes

The footprint climatology (Figure 1) suggested that, during the observation period, the fluxes originated mainly from the south-west, a zone covered predominantly by *Fagus sylvatica* and *Picea abies*/*Abies alba,* and to a lesser extent from the northeast, where Douglas fir predominated. Footprint analysis (data not shown) suggested that the flux measured by the eddy covariance system never came from a unique source, but more often from a mixture of species. Under these conditions, it was difficult to characterize univocally the emission characteristics of each emitting species. By combining the footprint analysis (Figure 1b) with the land use map (Figure 1a), we found that monoterpene flux increased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%. This suggests that *Fagus sylvatica* emits more monoterpenes than the other species of the ecosystem, which accords with previous studies (Holzke et al., 2006; Moukhtar et al., 2005; Tollsten and Müller, 1996). Other species could also contribute to the emissions of monoterpenes, such as *Abies alba* (Moukhtar et al., 2006) or *Picea abies* (Filella et al., 2007). However, Moukhtar (2006) showed that *Fagus sylvatica* should emit at least 10 times more than *Picea abies* or *Abies alba*, which accords with our footprint analysis.

The analysis also showed that the isoprene flux decreased linearly with the *Fagus sylvatica* flux contribution when it exceeded 40%, suggesting that this beech is not an isoprene source, as already reported by Moukhtar et al. (2005) and Tollsten and Müller (1996). Moukhtar et al. (2006) also found that *Abies alba* was not an isoprene source, but Filella et al. (2007) showed that *Picea abies* could be one. This would suggest that *Picea abies* was the sole species on the site emitting isoprene. This is not incompatible with our results, but cannot be validated by the footprint analysis because the contribution of this species to the measured flux never exceeded 40%. Given these results, in the following discussion we will consider the forest as a whole without trying to discriminate between the emitting species. The changing fluxes contribution of the major emitters due to the spatial heterogeneity combined with the changing wind direction and atmospheric stability will introduce variability on the flux that can be seen as a random error. This additional source of random error is compensated by the fact that given the important data coverage, our further analyses will always be performed on statistics containing an important number of realisations. A systematic error could also potentially be introduced in our seasonal evolution analyses if the flux footprint also presents a seasonal evolution. This effect, although present, is rather limited since the flux species contribution for each month (July, August and September) was respectively equal to 66.2 ± 2.0; 60.1 ± 1.6 and 49.8 ± 2.6 % for *Fagus sylvatica* and was respectively equal to 19.3 ± 1.1; 21.5 ± 1.1 and 24.1 ± 1.3 % for *Picea abies*/*Abies alba*.

4.2 Temperature response of BVOC emissions

BVOC flux temperature dependency is characteristic of an enzymatic reaction and could therefore characterize the isoprene or monoterpene synthases as well as the enzymatic reactions of the DOXP/MEP pathway. It is unlikely to be related to photosynthesis because this process is not very sensitive to temperature in the investigated range. No seasonal evolution of temperature sensitivity was observed, suggesting that this factor is an enzyme property that is independent of climatic conditions or leaf age. During the measurement period, it is possible that the β values were slightly distorted by the correlation that could exist between warm and sunny conditions. This effect is limited because we have shown that temperature is the main driving emission parameters. The values we observed for monoterpenes were close to those reported by Guenther et al. (1993), which varied between 0.057 and 0.144 K^{-1}. For isoprene, temperature sensitivity was slightly larger than 0.13 K^{-1}, the value obtained by adjustment of expression 2 on the Guenther et al. (1993) C_T relation.

4.3 Night-time monoterpene flux

There could be several reasons for the observed night-time monoterpene flux. First, it could result from de-storage. Unlike isoprene, some of the monoterpene production can be stored in plant tissues from which it can diffuse progressively to the atmosphere where it is volatilized (Lerdau et al., 1994; 1997; Tingey et al., 1991). The release of monoterpenes is controlled by their concentration within tissues and by their temperature-dependent vapor pressures. This process is much slower than the direct diffusion that follows production and could therefore be responsible for the flux observed at night. However, several studies (Demarcke et al., 2010b; Dindorf et al., 2005; Holzke et al., 2006; Moukhtar et al., 2005) have shown that, in the absence of light, emissions of monoterpenes from *Fagus sylvatica* were small or, in some cases, close to zero, suggesting that storage pools play only a marginal role in *Fagus sylvatica*. For coniferous species, storage pools are known to be located in resin ducts (Fuentes et al., 2000). Night-time monoterpene fluxes have never been observed in *Abies alba*, so far as we know, but they have been observed by Grabmer et al. (2004) using DEC above a *Picea abies* forest (Germany). They found fluxes of about 0.02 µg m^{-2} s^{-1} at T_a ~ 15°C, which is comparable in magnitude with those observed in our study for a similar temperature. With regard to storage pool capacity, we did not observe significant differences between monoterpene fluxes at the beginning and the end of the night (data not shown), suggesting that the fluxes are not rapidly depleted and therefore storage pools could be important. Ghirardo et al. (2010) also showed that the contribution of pool emissions to total monoterpene emissions may be significant for *Picea abies* (66.5%).

A second reason for monoterpene night-time fluxes could be soil production through various mechanisms. Litter decomposition has the potential to contribute significantly to these fluxes (Isidorov et al., 2010), especially fresh litter (Hayward et al., 2001). An emission from the storage pools of the roots with a mechanism similar to needle storage emissions can also contribute to monoterpene emissions (Janson, 1993; Lin et al., 2007), as well as the activity of specific micro-organisms (Schulz and Dickschat, 2007). Hayward et al. (2001) observed 30°C standardized emissions (July) varying between 0.008 and 0.01 µg m^{-2} s^{-1} from an undisturbed forested soil under Sitka spruce (United Kingdom). Hellén et al. (2006) observed fluxes between the detection limit and 0.1 µg m^{-2} s^{-1} for a forested soil under Scots pine (Finland), the maximum value being observed during spring and average values below 0.007 µg m^{-2} s^{-1} being observed in summer. However, our fluxes were at least one order of magnitude higher than those observed by Hayward et al. (2001) and Hellén et al. (2006).

Night-time emission processes were also present during the day, but their contribution to fluxes was at least 10 times lower than the contribution of *de novo* synthesized monoterpene emissions. The C_T obtained for each month was therefore influenced mainly by the biosynthesis process of monoterpenes. In summary, it is likely that night-time monoterpene fluxes resulted from both de-storage in the conifers and soil emission. However, the results of the literature survey suggest that de-storage fluxes would be at least one order of magnitude larger than those of soil emission.

4.4 BVOC flux response to PPFD/GPP

There are strong correlations of BVOC fluxes with PPFD and GPP, as the latter two variables themselves are well correlated. It is therefore not easy to determine the true causal relations.

A direct correlation between BVOC fluxes and GPP appears to be the most logical hypothesis because DMADP (the isoprene and monoterpene precursor) is a sub-product of photosynthesis. The linear relationship observed in July would suggest that DMADP (via GPP) was the main limiting factor in BVOC synthesis. Penuelas and Llusià (1999) had already found a linear relationship between monoterpene emission and GPP in a Mediterranean ecosystem during summer. They concluded that monoterpene precursors originated from photosynthetic activity. Under these conditions, the response to PPFD would be a direct consequence of the dependence on GPP.

However, we cannot completely discard the hypothesis of a direct dependence of other synthesis reactions on light. Wildermuth and Fall (1996) discussed the possibility of the direct impact of light on ISPS activity by covalent modifications. However, Lehning et al. (1999) and Brüggemann and Schnitzler (2002) have shown that ISPS activity undergoes no intra-day variation, making it more likely that the light-dependency of isoprene emission results directly from the GPP response to light. The slope of the BVOC/GPP relationship depends on enzymatic activity. It is therefore likely that the decrease in this slope during the season corresponded to a decrease in this activity. Schnitzler et al. (1997) and Mayrofher et al. (2005) stressed a seasonal evolution of ISPS activity in *Quercus robur* and *Populus* X *canescens*, respectively, showing an activity decrease after the summer. Fischbach et al. (2002) observed a similar effect on the monoterpene synthase activity of *Quercus ilex*. This seasonal decrease could be due to a leaf acclimation to temperature and radiation (Lehning et al., 1999) that could affect enzymatic activity over the long term. For *Fagus sylvatica*, leaf senescence could also have contributed to the decrease in monoterpene synthase activity. The non-linearity of the BVOC emissions to GPP responses in September and the appearance of saturation at a large GPP clearly indicates that other factors limit the BVOC synthesis. The limitation appears to be more critical for monoterpenes than for isoprene and could be due to saturation in the substrate of the enzyme activity through the DOXP/MEP pathway and/or saturation in the substrate of the monoterpene synthase activity and (to a lesser extent) of the isoprene synthase activity during the season.

In the case of isoprene, a DMADP reallocation to the production of diterpenes, tetraterpenes and monoterpenes, which eventually results in the decreased production of isoprene, has been proposed by Owen and Penuelas (2005). However, the occurrence of this mechanism is unlikely in our study as it generally takes place when there is stress, but no heat or drought stress was detected during the measurement period.

4.5 Response of SEF to friction velocity

There are several possible explanations for the *SEF* response to friction velocity. In the case of CO_2 fluxes, similar behavior is generally observed that can be explained by the lack of atmospheric turbulence and the development of other transport processes (Aubinet, 2008). This process would affect similarly BVOC fluxes but it can explain CO_2 or BVOC fluxes underestimations for low u* at night-time only because the alternative transport processes do not develop during the day. The two most likely explanations are linked to O_3 transport and the chemical lifetime of BVOCs in the atmospheric boundary layer. The possibility of an adsorption/desorption process on ecosystem surfaces was discarded because neither isoprene nor monoterpene depositions were ever observed in this study.

In the first explanation, an increase of u* would denote an intensification of turbulent mixing in the canopy and therefore an increase in O_3 supply in the canopy, which could activate BVOC synthesis. Several studies have highlighted the existence of a stimulation process of isoprene (Calfapietra et al., 2009; Fares et al., 2006; Velikova et al., 2005) and monoterpene emissions (Loreto et al., 2004) when leaves are exposed to high O_3 concentrations (100-300 ppb). This emission could be a protection mechanism against oxidation. Apart from this, O_3 deposition and O_3 vertical gradients are known to be controlled by the efficiency of turbulent mixing in the canopy that is driven by friction velocity (Jäggi et al., 2006; Karlsson et al., 2006; Pleijel et al., 1996). Ozone concentration in the canopy should therefore increase with u* and tend towards above-canopy concentration at high u* values. This hypothesis was confirmed by independent measurements made at a station 300 m from our site that showed an increase in O_3 concentration with u* during the day (data not shown).

The difference in behaviour between isoprene and monoterpenes could be explained by different sensitivities of the emitting tree species to the stimulation by O_3 due to differences in O_3 absorption capacity or the possible presence of other anti-oxidative compounds.

The second explanation involves the limited BVOC chemical lifetime. Upon emission, a BVOC might be oxidized (degraded) through reaction with other atmospheric compounds, mainly OH and to a lesser extent O_3 and the nitrate radical, before reaching the measurement point. As the footprint zone expands under low u*, the distance between the BVOC source point and the measurement system generally increases, increasing the extent of chemical degradation. By combining a footprint model with a chemical degradation model, and assuming an abundance of 0.25 ppt (i.e., 6 x 10^6 molec. cm^{-3}) for OH, Rinne et al. (2007) showed that when u* was equal to 0.5 m s^{-1} (measurement height: 22 m; source height: 11.2 m), the flux loss could reach 10%. This value of OH is typically observed in summer in the USA (Ren et al., 2008) or in August, in Germany, near Jülich (Dlugi et al., 2010), and is probably similar at the Vielsalm site. The loss calculated in our case was higher but this could be due to the distance between the emitting canopy and the measurement location, which is about twice as large at Vielsalm than at Hyytiala. However, it is still difficult to quantify the flux loss through chemical degradation in order to validate this hypothesis.

5. Summary and conclusions

This study is one of the first to have collected data on monoterpene, isoprene and CO_2 fluxes simultaneously and continuously over several months. This extensive dataset allowed an analysis to be conducted of the flux responses to climate and their seasonal evolution.

Temperature appeared to be the most important driving variable of BVOC fluxes, followed by solar radiation. During the day, the temperature response was found to be exponential and probably reflected the temperature activation of enzymatic reactions in the DOXP/MEP biosynthetic pathways. The flux response to radiation was probably controlled by the GPP/PPFD response. This was confirmed by the linearity of the relationship between BVOC fluxes and GPP. The slope of this relationship, characterizing the enzyme activity through the biosynthesis pathway decreased during the season. This was probably modulated by leaf acclimation to environmental conditions. For monoterpenes, leaf senescence and acclimation might take place simultaneously, especially in September. In September, at high GPP, BVOC fluxes no longer depended on GPP. The seasonal decrease in the enzymatic activity and the saturation in the substrate of this enzymatic activity at a given GPP threshold could explain this behavior.

During the night, the isoprene flux was zero but small emissions of monoterpenes were found, showing a temperature dependency. These emissions were probably due to the volatility of monoterpenes stored in the needle resin ducts of coniferous species. There could also be a contribution from the soil through litter decomposition, from roots or from micro-organisms.

An increase in temperature- and radiation-standardized BVOC fluxes (mainly isoprene) with u* was found. This surprising relationship could be due to a stimulation of isoprene emissions by exposure to O_3, the O_3 concentration in the canopy increasing with u*. Complementary measurements of O_3 fluxes should be performed to test this hypothesis. The relation BVOC fluxes/u* could be also due to the distance between the BVOC source point and the measurement system that generally increases under low u* thereby increasing the extent of BVOC oxidation.

Finally, long-term measurements of BVOC fluxes at the ecosystem scale allowed a temperature dependence function and a PPFD dependence function necessary to compute a standard emission factor to be deduced for each month. In this study, the PPFD dependence function has been transformed from Guenther et al. (1993) by using only one fitting parameter, making it easier to study the seasonal variation of the standard emission factor. These factors are crucial for regional emission modelling, and a more in-depth analysis of their seasonal evolution for different ecosystems in real-field conditions would help to improve these emission predictions.

Acknowledgements

This work was supported financially by the Belgian Science Policy Office (BELSPO) (contract number SD/TE/03A) for funding the IMPECVOC (Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems) research project, and by the Fonds National de la Recherche Scientifique (FNRS) for the building of a new flux tower in Vielsalm.

The authors would like to thank Gerardo Fratini (Laboratory of Forest Ecology of the University of Tuscia) who shared the EC flux computation software developed within the framework of the IMECC project (Infrastructure for Measurements of the European Carbon Cycle, European Commission, Contract Nbr.: 026188). We adapted this software to compute DEC BVOC fluxes. We also wish to thank Elisabeth Jerome who computed the GPP, as well as the technical personnel at the Unit of Biosystem Physics of the University of Liege, Gembloux Agro-Bio Tech (Michel Yernaux, Alain Debacq and Henri Chopin) and the technical personnel at the Belgian Institute for Space Aeronomy.

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Table captions

Table 1. Fitting coefficients of *Ta* and PPFD dependence according to Equation 1, 2 and 3.

Figure captions

Figure 1. Left: Land-use map around the tower. Right: Normalised and cumulated day footprint from July to September superimposed on the vegetation map (red colour corresponds to the region that contribute the most to the flux). Tower location: (0,0) , North direction: (0,Y).

Figure 2. Wind direction dependence of m/z 69 and m/z 137 mixing ratios.

Figure 3. Temporal evolution of relevant meteorological parameters between 10 July 2009 and 31 October 2009: air temperature (T_a), Photosynthetic Photon Flux Density (PPFD), wind direction, friction velocity (u*), soil humidity (S_W) and precipitation.

Figure 4. Temporal evolution of isoprene (m/z 69) and monoterpene (m/z 137) fluxes throughout the measurement period. The grey parts of the curves represent measured fluxes that are not significantly different from zero.

Figure 5. Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes in relation to the air temperature (n≥14, error bars are 95% confidence intervals) for July (light grey), August (grey) and September (dark grey) during the day.

Figure 6. Bin average of monoterpene (m/z 137) fluxes ($u^* > 0.3$ m s^{-1}) in relation to the air temperature (n≥14, error bars are 95% confidence intervals) during the night from July to September.

Figure 7. Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C in relation to PPFD (n≥14, error bars are 95% confidence intervals) for July (light grey), August (grey) and September (dark grey).

Figure 8. Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized at 30°C (n≥14, error bars are 95% confidence intervals) in relation to the gross primary production (GPP) for July (light grey) and September (dark grey).

Figure 9. Mean diurnal evolution (PPFD > 300 μmol m^{-2} s^{-1}) of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PPFD (1000 μmol m^{-2} s^{-1}). The grey area represents the 95% confidence intervals.

Figure 10. Bin average of isoprene (m/z 69) and monoterpene (m/z 137) fluxes standardized for temperature (30°C) and PFFD (1000 μmol m^{-2} s^{-1}) in relation to the friction velocity (u*).

Table 1

	Isoprene			***Monoterpenes***		
	July	**August**	**September**	**July**	**August**	**September**
β[a]	0.16±0.01	0.15±0.01	0.18±0.02	0.10±0.01	0.11±0.01	0.10±0.02
$SEF.C_L$[b]	1.07±0.08	0.93±0.10	0.90±0.09	0.65±0.02	0.51±0.03	0.38±0.09
C_{L1}[c]	2.35±0.20	2.10±0.43	1.55±0.24	1.65±0.08	1.37±0.08	1.03±0.08
SEF[d]	0.91±0.01	0.83±0.02	0.56±0.02	0.74±0.03	0.54±0.03	0.27±0.03

[a] units of β: K^{-1}

[b] units of $SEF.C_L$: $\mu g\ m^{-2}\ s^{-1}$

[c] units of C_{L1}: $\mu mol\ m^{-2}\ s^{-1}$

[d] units of SEF: $\mu g\ m^{-2}\ s^{-1}$

Figure 1

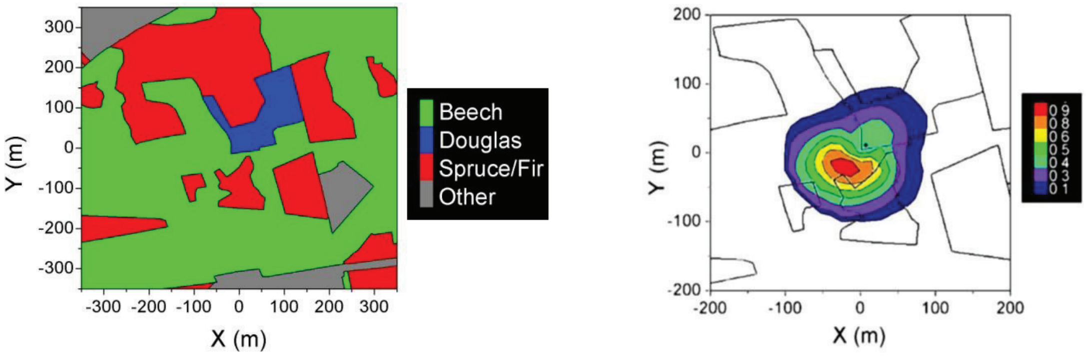
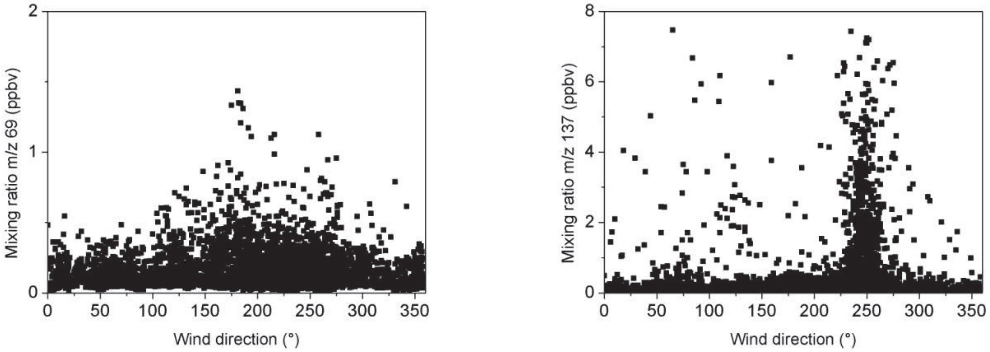
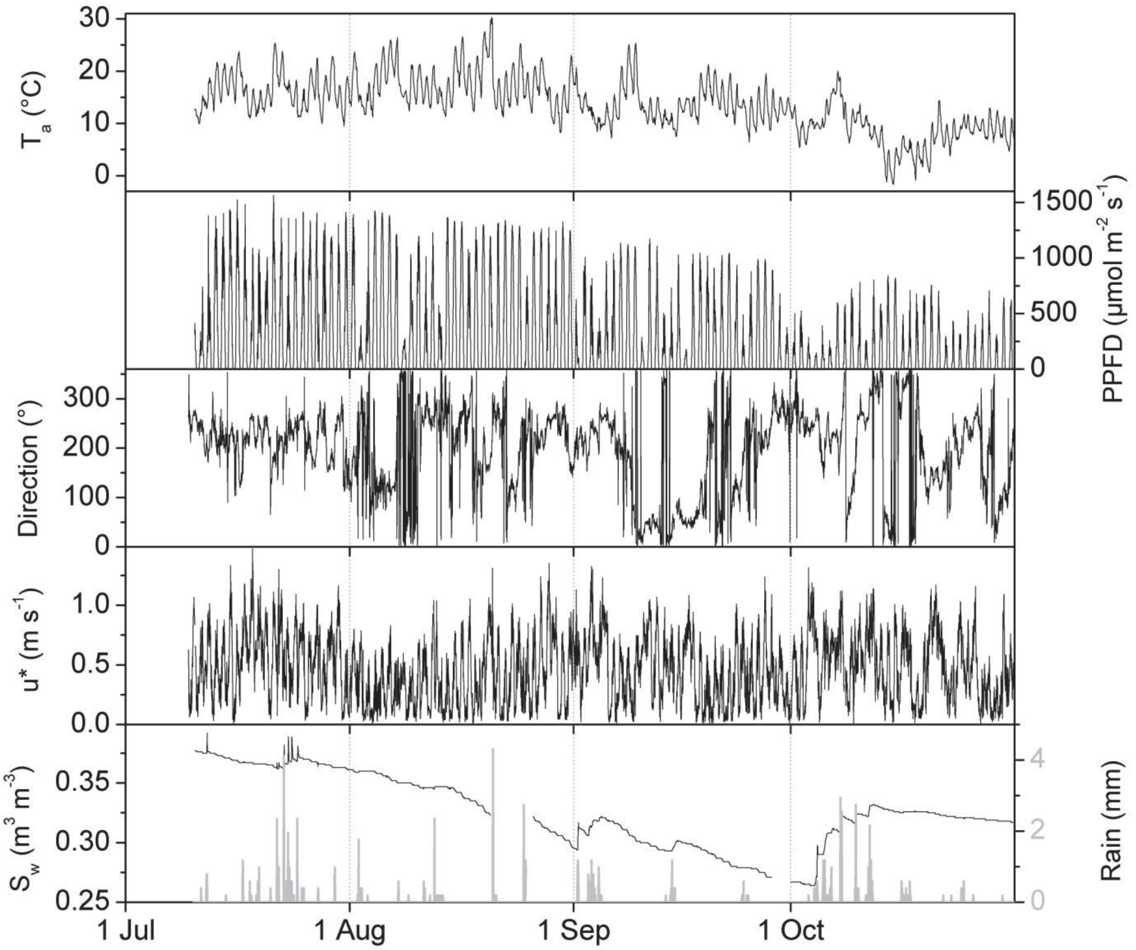

300
200
100
0
-100
-200
-300
Y (m)
-300 -200 -100 0 100 200 300
X (m)
🟩 Beech
🟦 Douglas
🟥 Spruce/Fir
⬛ Other
200
100
0
-100
-200
Y (m)
-200 -100 0 100 200
X (m)
0 9
0 8
0 6
0 5
0 4
0 3
0 1

Figure 2



Mixing ratio m/z 69 (ppbv)
2
1
0
0
50
100
150
200
250
300
350
Wind direction (°)
Mixing ratio m/z 137 (ppbv)
8
6
4
2
0
0
50
100
150
200
250
300
350
Wind direction (°)

Figure 3



T_a (°C)
30
20
10
0
1500
1000
500
0
PPFD (µmol m^{-2} s^{-1})
Direction (°)
300
200
100
0
u* (m s^{-1})
1.0
0.5
0.0
S_w (m^3 m^{-3})
0.35
0.30
0.25
4
2
0
Rain (mm)
1 Jul
1 Aug
1 Sep
1 Oct

Figure 4

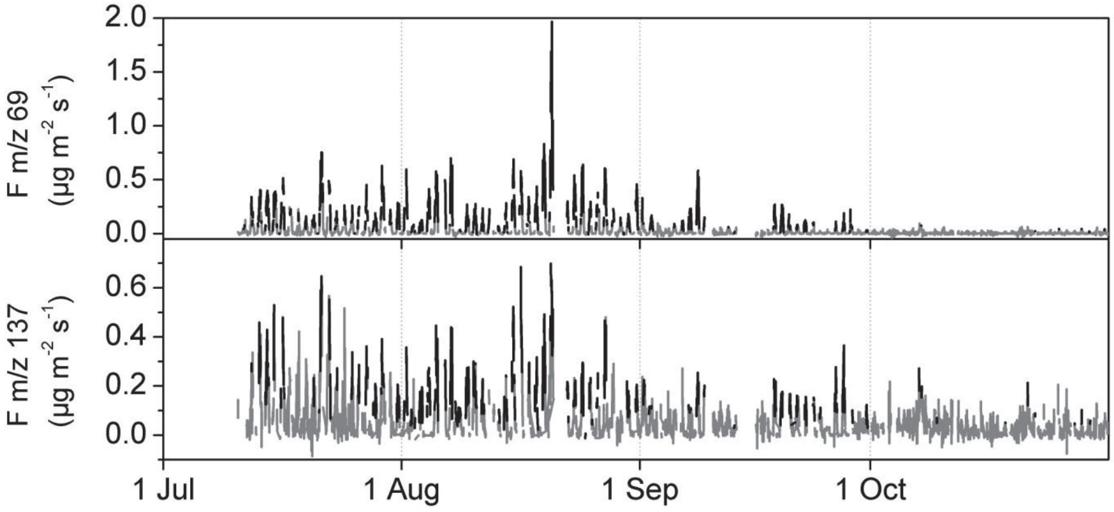
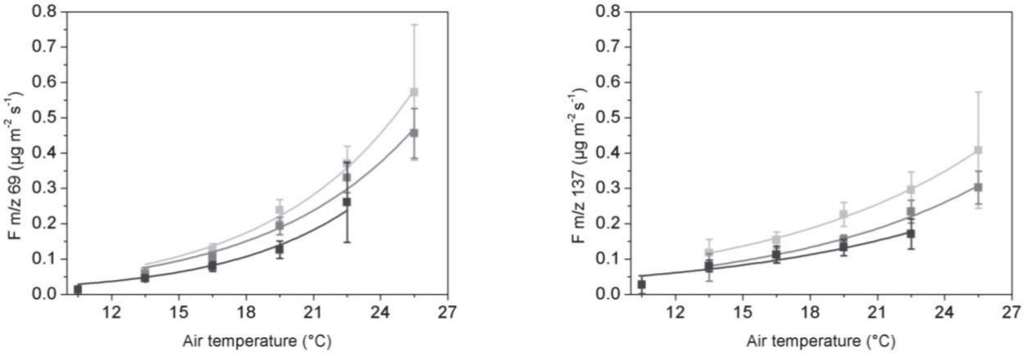

2.0
1.5
1.0
0.5
0.0
F m/z 69
(μg m^{-2} s^{-1})
0.6
0.4
0.2
0.0
F m/z 137
(μg m^{-2} s^{-1})
1 Jul
1 Aug
1 Sep
1 Oct

Figure 5



0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
F m/z 69 (μg m⁻² s⁻¹)
12
15
18
21
24
27
Air temperature (°C)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
F m/z 137 (μg m⁻² s⁻¹)
12
15
18
21
24
27
Air temperature (°C)

Figure 6

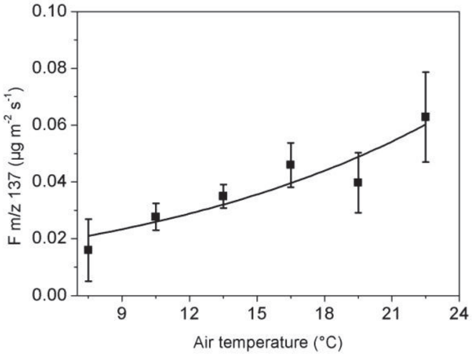
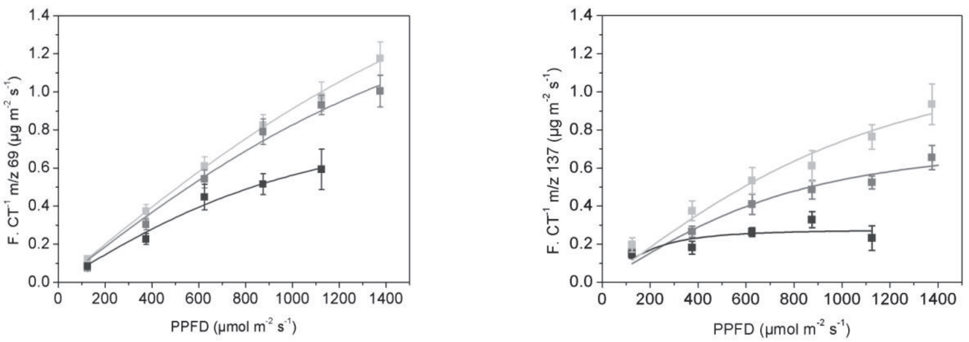

0.10
0.08
0.06
0.04
0.02
0.00
F m/z 137 (µg m^{-2} s^{-1})
9
12
15
18
21
24
Air temperature (°C)

Figure 7



F. CT^{-1} m/z 69 (µg m^{-2} s^{-1})
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
PPFD (µmol m^{-2} s^{-1})
F. CT^{-1} m/z 137 (µg m^{-2} s^{-1})
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
PPFD (µmol m^{-2} s^{-1})

Figure 8

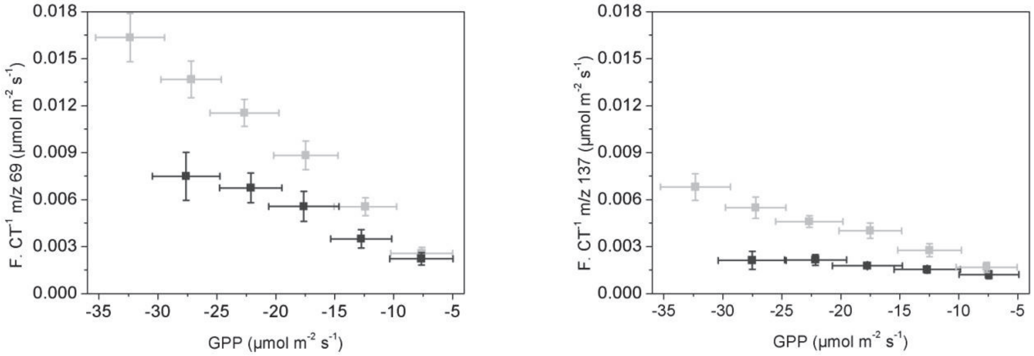
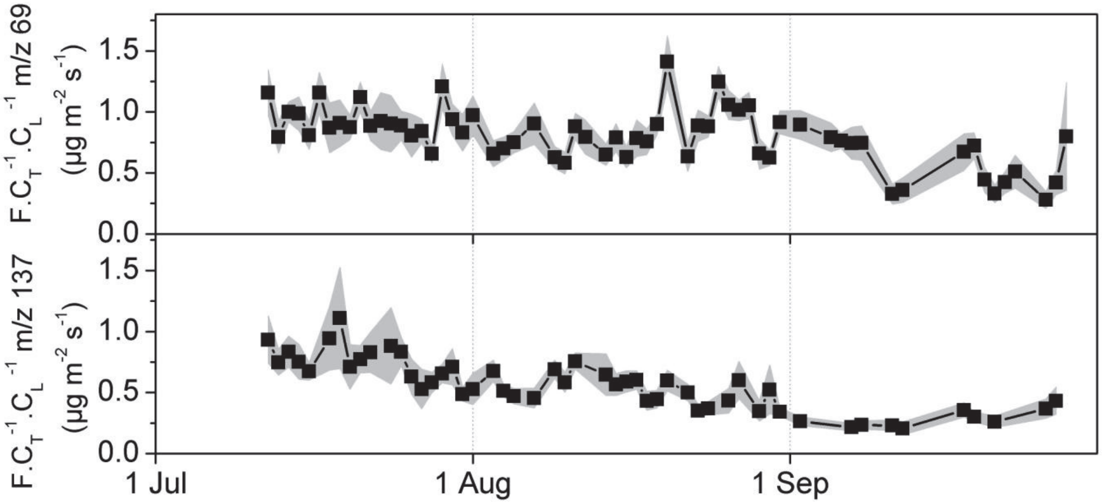
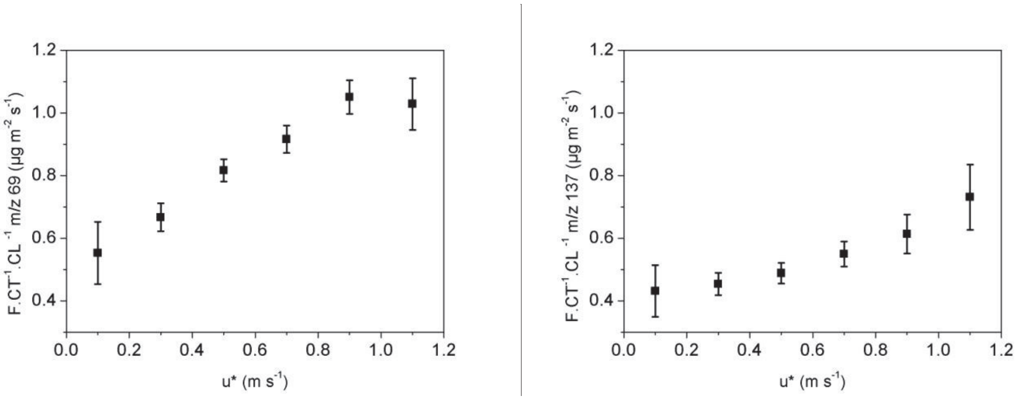

0.018
0.015
0.012
0.009
0.006
0.003
0.000
F. CT^{-1} m/z 69 (µmol m^{-2} s^{-1})
-35
-30
-25
-20
-15
-10
-5
GPP (µmol m^{-2} s^{-1})
0.018
0.015
0.012
0.009
0.006
0.003
0.000
F. CT^{-1} m/z 137 (µmol m^{-2} s^{-1})
-35
-30
-25
-20
-15
-10
-5
GPP (µmol m^{-2} s^{-1})

Figure 9



F.C$_T^{-1}$.C$_L^{-1}$ m/z 69
(µg m^{-2} s^{-1})
1.5
1.0
0.5
0.0
F.C$_T^{-1}$.C$_L^{-1}$ m/z 137
(µg m^{-2} s^{-1})
1.5
1.0
0.5
0.0
1 Jul
1 Aug
1 Sep

Figure 10



F.CT^{-1}.CL^{-1} m/z 69 (µg m^{-2} s^{-1})
1.2
1.0
0.8
0.6
0.4
0.0
0.2
0.4
0.6
0.8
1.0
1.2
u* (m s^{-1})
F.CT^{-1}.CL^{-1} m/z 137 (µg m^{-2} s^{-1})
1.2
1.0
0.8
0.6
0.4
0.0
0.2
0.4
0.6
0.8
1.0
1.2
u* (m s^{-1})

Research Highlights

►Isoprene and monoterpene emissions during the day are driven by temperature and light

►Monoterpene emissions during the night seems to be driven by temperature

►Isoprene and monoterpene emissions are strongly linked with the carbon assimilation

►Standard emission factors for isoprene and monoterpenes decrease with the season

►Standard emission factor seems to be linked to the friction velocity