

**Abiotic and biotic
control of methanol
exchanges**

Q. Laffineur et al.

Abiotic and biotic control of methanol exchanges in a temperate mixed forest

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Methanol exchanges over a mixed temperate forest in the Belgian Ardennes were measured for more than one vegetation season using disjunct eddy-covariance by a mass scanning technique and Proton Transfer Reaction Mass Spectrometry (PTR-MS). Half-hourly methanol fluxes were measured in the range of -0.6 to $0.6 \mu\text{g m}^{-2} \text{s}^{-1}$, and net daily methanol fluxes were generally negative in summer and autumn and positive in spring. On average, the negative fluxes dominated (i.e. the site behaved as a net sink), in contrast to what had been found in previous studies.

An original model describing the adsorption/desorption of methanol in water films present in the forest ecosystem and the methanol degradation process was developed. Its calibration, based on field measurements, predicted a mean methanol degradation rate of $-0.0074 \mu\text{g m}^{-2} \text{s}^{-1}$ and a half lifetime for methanol in water films of 57.4 h. Biogenic emissions dominated the exchange only in spring, with a standard emission factor of $0.76 \mu\text{g m}^{-2} \text{s}^{-1}$.

The great ability of the model to reproduce the long-term evolution, as well as the diurnal variation of the fluxes, suggests that the adsorption/desorption and degradation processes play an important role in the global methanol budget. This result underlines the need to conduct long-term measurements in order to accurately capture these processes and to better estimate methanol fluxes at the ecosystem scale.

1 Introduction

Methanol is the second most abundant organic gas in the atmosphere after methane (Jacob et al., 2005; Singh et al., 2001). Its mixing ratio can easily exceed 10 ppbv above forests during the growing season (Karl et al., 2003; Schade and Goldstein, 2001, 2006). Methanol plays a minor but non-negligible role in atmospheric chemistry (Harley et al., 2007; Jacob et al., 2005). It reduces atmospheric oxidation capacity due to its reactions with hydroxyl radicals (OH), producing formaldehyde (CH_2O) and

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



hydroperoxyl radicals (HO_2), thereby increasing the tropospheric ozone concentration (Tie et al., 2003). The chemical atmospheric lifetime of methanol is from 5 to 12 days (Atkinson, 2000; Galbally and Kirstine, 2002; Jacob et al., 2005; Millet et al., 2008; Tie et al., 2003). Several modelling studies (Galbally and Kirstine, 2002; Heikes et al., 2002; Jacob et al., 2005; Singh et al., 2000; Stavrakou et al., 2011; Tie et al., 2003) have focused on the global methanol budget. These studies show that the principal methanol source in the atmosphere is vegetation (60–80 %) and that the major sinks are the reaction with OH in gas-phase (40–70 %) and dry deposition on land (20–30 %). These modelling efforts, however, remain characterized by huge uncertainties. Estimations of global emission by plants vary between 75 (Singh et al., 2000) and 280 (Heikes et al., 2002) Tg yr^{-1} and estimations of global sinks through OH reaction and dry deposition vary between 133 (Galbally and Kirstine, 2002) and 234 (Tie et al., 2003) Tg yr^{-1} . These uncertainties are due mainly to a lack of available measurements, which are typically limited in terms of temporal and spatial resolution, leading to limited knowledge about emission and deposition mechanisms. To date, about 15 studies (see a partial review of them in Seco et al., 2007) have measured and quantified methanol exchange above a variety of ecosystems (mainly forests and grasslands) using a variety of techniques (relaxed eddy accumulation and disjunct eddy-covariance). These studies usually cover only a small part of the vegetation season, centred on time periods when biogenic emissions are thought to be important, and are still too limited in terms of the variety of ecosystems that are potential methanol emitters. Among these techniques, disjunct eddy-covariance is the most suitable for long-term monitoring of the ecosystem exchange in real-undisturbed conditions (Rinne et al., 2001). It has been used in several methanol studies (Bamberger et al., 2010; Brunner et al., 2007; Custer and Schade, 2007; Holst et al., 2010; Karl et al., 2001, 2002, 2003, 2004, 2005; Langford et al., 2010; Spirig et al., 2005), but none of them proposed a year-round follow-up of the exchange. In addition, although methanol dry deposition has been observed occasionally or more regularly in some studies (Custer and Schade, 2007; Holst et al., 2010; Karl et al., 2004, 2005; Langford et al., 2010; Schade et al., 2011;

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Spirig et al., 2005), very few of these studies paid detailed attention to the underlying mechanisms.

In this study, we present long-term ecosystem-scale measurements of methanol fluxes exchanged between a heterogeneous temperate forest and the atmosphere, obtained using the disjunct eddy-covariance by mass scanning. Our dataset covers more than one vegetation period (winter is not included), with a total composite coverage of 10 months. The main result of the study is that, on a long-term scale, the site behaved as a methanol sink in contrast to what has been found at other sites. In order to better understand these results, abiotic and biotic drivers of the methanol emissions/depositions were disentangled. An original model was developed in order to estimate the respective contributions to the net flux of the methanol adsorption/desorption in water films present in the ecosystem and of methanol degradation. Model residuals were then used to isolate biogenic emissions and to identify their driving variables.

2 Material and methods

2.1 Measurement site

The experimental site is a forest ecosystem located at Vielsalm in the Belgian Ardennes 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 in the tower flux footprint 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. A more detailed description of this site is given by Aubinet et al. (2001, 2002) and Laitat et al. (1999).

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2 Instrumentation and BVOC sampling

An ultrasonic anemometer (model SOLENT 1012 R2, Gill Instruments Ltd, Lymington, UK) was placed at the top of a tower at a height of 52 m, and it continuously measured the three wind velocity components 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: Fluorteknik-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); the line was slightly heated above ambient temperature. Part of this air flow (0.1 STP l min⁻¹) was drawn into a gas analyser through a 1.2 m long heated capillary inlet line (333 K) with an inner diameter of 1 mm. The data streams coming from the two instruments were logged on a single computer in order to optimise synchronization.

Measurements of relevant meteorological variables were performed at a sampling frequency of 0.04 Hz and averaged over half an hour, including total and diffuse fraction of photosynthetically active radiation: PPFd (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 moisture content (ThetaProbe, Delta-T Devices Ltd, Cambridge, UK) at a depth of 20 cm, and precipitation and atmospheric pressure (MPX4115A, Motorola, Phoenix, USA). A global Vegetation Area Index (VAI) was deduced from PPFd measurements above and below the canopy, as described by Aubinet et al. (2002).

VOC concentrations were measured by a conventional hs-PTR-MS (Ionicon Analytick GmbH, Innsbruck, Austria) equipped with a quadrupole mass spectrometer. Detailed descriptions of the PTR-MS technique are given by Lindinger et al. (1998), de Gouw et al. (2007) and Ammann (2004). The 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 ($1 \text{ Td} = 10^{-17} \text{ V cm}^2$), where E is the electric field and N the ambient air number density in the flow/drift tube. The ion signals were

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



measured in a cyclic way (which produces a disjunct time series for each mass) at mass to charge ratio m/z 21 (primary hydronium ions: $\text{H}_3^{18}\text{O}^+$), m/z 33 (protonated methanol), m/z 39 (water cluster ion), m/z 45 (protonated acetaldehyde), m/z 59 (protonated acetone), m/z 69 (protonated isoprene), m/z 71 (protonated methyl vinyl ketone and methacrolein), m/z 81 (fragment of protonated monoterpenes), m/z 87 (protonated methylbutenol and possibly others) and m/z 137 (protonated monoterpenes). In 2010, m/z 47 (protonated formic acid) and m/z 61 (protonated acetic acid) were added. The dwell time for each mass was 0.2 s, ending in a 2 s measurement cycle length. More details can be found in Laffineur et al. (2011).

2.3 Disjunct eddy-covariance

The technique used to measure ecosystem BVOC fluxes is disjunct eddy-covariance by mass scanning (Karl et al., 2002; Rinne et al., 2001). The flux (F_{VOC}) is determined by the covariance of the discrete function between the time series of vertical wind velocity $w(t)$ and VOC concentration $C_{\text{VOC}}(t)$ over an averaging period of 30 min (T):

$$F_{\text{VOC}} = \frac{1}{N} \sum_{i=1}^N w'(t_i - t_{\text{lag}}) \cdot C'_{\text{VOC}}(t_i)$$

with w' , C'_{VOC} , the instantaneous deviations from the mean value of w and C_{VOC} respectively, N the number of disjunct PTR-MS samples during T and t_{lag} the lag time between w and C_{VOC} induced by the distance between inlet and PTR-MS. More details on the flux computation methodology are given by Laffineur et al. (2011).

2.4 Data filtering

In the 230–270° wind direction sector, which was also the main wind direction, methanol fluxes could be contaminated by the activities of a wood panel factory, 3 km from the tower. Wood panel production is known to emit high levels of monoterpenes and methanol (Nicholson, 2003). Although not located inside the main day

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



flux footprint, defined as the 90 % level contribution to the total flux (footprint analyses were performed with a two-dimensional analytical footprint software tool proposed by Neftel et al. (2008) in line with the Kormann-Meixner footprint model; Kormann and Meixner, 2001), this source was probably so important compared with forested ecosystem sources that it influenced our measurements. Flux measurements spoiled by anthropogenic emissions were therefore rejected, using a filtering criterion based on the variance of the monoterpene mixing ratio. This procedure was described in detail by Laffineur et al. (2011).

In contrast with CO₂ fluxes (Aubinet et al., 1999), u^* filtering was not applied here. The methanol flux is not controlled by a continuous production process (like respiration in the case of CO₂) that works independently of the presence or absence of turbulent transport. The dependence of the methanol flux on turbulence (see Sect. 4.2.) corresponds here to a real process (not a measurement artefact), so that any data filtering with a criterion based on turbulence could lead to flux overestimation (Aubinet et al., 2011).

3 Methanol adsorption/desorption model

The empirical adsorption/desorption model is represented by the electrical analog scheme presented in Fig. 1. Net methanol flux exchange by the ecosystem with the atmosphere is characterized by F_1 [$\mu\text{g m}^{-2} \text{s}^{-1}$]. This flux consists of two components: the first one (F_3) corresponds to adsorption/desorption in water films present in the ecosystem; and the second one (F_2) corresponds to methanol degradation in aqueous phase, possibly by methylotrophic organisms. This sink was postulated to deal with the negative methanol budget on a long-term time scale (see Sect. 4.3.2).

The net flux with the atmosphere is written as:

$$F_1 = \frac{1}{R_t} (M_{\text{aw}} - M_{\text{aa}}), \quad (1)$$

where M_{aw} [$\mu\text{g m}^{-3}$] and M_{aa} [$\mu\text{g m}^{-3}$] represent the methanol concentration in the air at the water film surface and in the atmosphere, respectively, and R_t [s m^{-1}] represents the gas-phase resistance to the methanol transfer in the surface boundary layer. Sign convention is that a positive flux is directed towards to the atmosphere and a negative flux towards the surface. Considering that molecular diffusion transport is negligible compared to turbulent transport, R_t might be approximated by the aerodynamic resistance of in-canopy air space (Mihailovic et al., 2009; Pul and Jacobs, 1994) in a very straightforward way:

$$R_t = \frac{1}{A \cdot u^*}, \quad (2)$$

where A is an empirical parameter and u^* [m s^{-1}] is the friction velocity. The aerodynamic resistance above the canopy can be considered negligible compared with this resistance.

In this model, we consider that the methanol reservoir in the ecosystem is made of water films present on leaves and wet soil surfaces that can adsorp/desorp methanol. In these conditions, M_{aw} can be related to the total methanol content in the water film reservoirs of the ecosystem (q [$\mu\text{g m}^{-2}$]) by:

$$M_{aw} = \frac{q}{C}, \quad (3)$$

where C [$\text{m}^3 \text{m}^{-2}$] represents the capacity of the water films to store methanol as suggested by Sutton et al. (1998) in the context of ammonia exchange. This constant depends on Henry's law constant, K_H [dimensionless (water/air partition ratio)], and on the free water present in the ecosystem. The dimensionless Henry's law constant of methanol is given by (Warneck, 2006):

$$K_H = \frac{1000 \cdot R \cdot 298 \cdot 15 [e^{-12.46} e^{5312.4/T}]}{101\,325}, \quad (4)$$

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

where R [$\text{J mol}^{-1} \text{K}^{-1}$] is the gas constant and T [K] represents the temperature that we have considered to be the air temperature (T_a).

A complete description of the free water content would require establishing a detailed ecosystem water balance, which is not available here. We therefore approximated it by a function of air humidity as suggested by Van Hove and Adema (1996), Burkhardt and Eiden (1994) and Burkhardt et al. (2009) and the precipitation during the preceding days. Dependence on air humidity (see Sect. 4.3.1) was computed by:

$$C = K_H \cdot \frac{C_R}{[1 - \exp(-\frac{D}{\alpha})]}, \quad (5)$$

where D [Pa] is the water vapour pressure deficit, α [Pa] is an empirical parameter and C_R [m] is the component of the capacity that depends on the precipitation (P [mm]) of the preceding days. Without information on the leaf/soil water balance from precipitation, C_R was computed simply by a linear dependence on cumulated precipitation of the 10 preceding days (480 half-hours):

$$C_R = C_{R0} + \sum_{i=0}^{480} P_i, \quad (6)$$

with C_{R0} a residual capacity.

Methanol degradation is described by a diffusion flux (F_2) and characterized by a resistance τ/C :

$$F_2 = -\frac{q}{\tau}, \quad (7)$$

where τ [s] represents a time constant, characteristic of the methanol lifetime in the water films in the absence of adsorption or desorption.

Using Kirchhoff's circuit law, we can write:

$$F_3 = F_1 - F_2 = -\frac{dq}{dt}. \quad (8)$$

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

By introducing Eqs. (1)–(3) and (7) in (8) and approximating the equation by finite differences, we get:

$$q_j = q_{j-1} - \Delta t \left[A \cdot u^* \cdot \left(\frac{q_{j-1}}{C} - M_{aa} \right) + \frac{q_{j-1}}{\tau} \right], \quad (9)$$

where Δt is the integration time, fixed in this study to one half-hour (1800 s) and index j denotes successive time period intervals.

By introducing expression (9) of q into (3) and then into (1), we then get:

$$F_{1,j} = A \cdot u^* \cdot \left[\frac{q_j}{K_H \cdot \frac{C_{R0} + \sum_{i=0}^{480} P_i}{[1 - \exp(-\frac{D}{\alpha})]}} - M_{aa} \right]. \quad (10)$$

Finally, the complete model given by Eq. (10) depends on four empirical parameters: A , τ , C_{R0} and α .

4 Results

4.1 Micrometeorological and methanol flux evolutions

The seasonal evolution of air temperature (T_a), photosynthetically active radiation (PPFD), water vapour pressure deficit (D), precipitation (P), friction velocity (u^*), methanol ambient mixing ratio and methanol flux is shown in Fig. 2.

Summer and autumn 2009 were characterized by high temperatures (mean temperature in July-August-September 15.7 °C) for the region, except at the end of October. August and September were relatively dry with cumulated rain close to only 50 mm. The temperature conditions during spring 2010 were normal for the region, except during the first half of May, which followed the bud break of *Fagus sylvatica* on 1 May and was colder and cloudier than average. The April-May-June period was, however, dry,

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



with cumulated rain of only 86 mm. Summer 2010 was also characterized by high temperatures (mean temperature in July-August-September 15.2 °C), especially between 7 and 14 July. The highest D (>0.8 kPa) were observed mainly between the end of June and the end of July 2010. In contrast with 2009, August 2010 was very rainy, with cumulated rain of 215 mm.

The atmospheric methanol concentration course in the spring and summer periods was similar and varied between 0.8 and 8.7 ppbv (5th centile and 95th centile), with a mean of 3.5 ppbv. In autumn, the methanol concentration was close to 2.0 ppbv. Methanol fluxes were bi-directional. The highest deposition fluxes were observed in July 2009 and in August–September 2010 (up to $-0.6 \mu\text{g m}^{-2} \text{s}^{-1}$), while the highest emissions (up to $0.6 \mu\text{g m}^{-2} \text{s}^{-1}$) were observed during the second half of May 2010 and the beginning of June 2010. To a lesser extent, emissions were observed during July–August 2009 and during the second half of April 2010 and the end of June 2010.

Figure 3 shows the mean diurnal evolution of the methanol flux in the summer in 2009 and 2010 and in spring 2010. In both cases, the flux was generally positive during the day and negative at night, but in spring the fluxes shifted towards more positive values compared with summer, the net daily flux being roughly twice as large in spring as in summer. As a result, the net daily flux was negative in summer (deposition dominates) and positive in spring (emission dominates). For the whole measurement period, deposition was generally less pronounced in the beginning of the night than at the end.

4.2 Main drivers of methanol flux

In order to determine the main drivers of methanol fluxes, their relationships with the main meteorological variables (radiation, air temperature, water vapour pressure deficit, friction velocity, atmospheric methanol concentration) were tested. Only the most relevant relationships are presented here. The clearest response of methanol flux to climatic variables is the one to water vapour pressure deficit (Fig. 4). At low D , fluxes are mainly negative, indicating methanol deposition. The flux increases with D ,

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and tends towards a positive and constant value above $D = 1$ kPa. The influence of humidity on the methanol exchange can be seen in Fig. 2 where deposition is systematically observed during or following precipitation.

A linear dependence between the ratio of F to M_{aa} and u^* was also found (Fig. 5), only when wet conditions ($D < 0.15$ kPa) were selected (and $R_{net} > -20$ W m⁻², explanation below). In these wet conditions, M_{aw} can be close to zero, the ratio F to M_{aa} thereby representing a deposition velocity (see Sect. 4.3.1 and Foken et al., 2008). Similar relationships were observed for day and night. Slope (parameter $-A$ in the model) and intercept coefficients were equal to -0.055 ± 0.004 and -0.0018 ± 0.0022 m s⁻¹ ($R^2 = 0.36$), respectively, for the day and equal to -0.060 ± 0.002 and -0.0043 ± 0.0011 m s⁻¹ ($R^2 = 0.58$), respectively, for the night. For the whole measurement period, the mean u^* was 0.4 m s⁻¹, which corresponds to a deposition velocity of 2.4 cm s⁻¹.

The relationship between methanol exchange and temperature appeared to be complex (Fig. 6), with the most important negative fluxes being observed between 10 and 20°C and the most important positive fluxes between 15 and 25°C.

4.3 Bi-directional methanol flux modelling

The methanol deposition quantities increased strongly with increasing air humidity, indicating that water on the leaf and/or soil surface plays a major role in the interaction of methanol with leaf and/or soil surfaces. This is due to microscale liquid water films and/or droplets formed on external plant/soil surfaces through condensation of water vapour on the leaf/soil surface or through rain or fog droplets from the atmosphere. The dependence of methanol deposition on u^* indicates that turbulent transport is the main resistance driving deposition. The complex response of deposition to air temperature could be due to the interaction between the temperature dependency of methanol solubility (Henry's law) in water and of air saturation deficit.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Our observations therefore strongly suggest that methanol fluxes could be driven by the adsorption/desorption process of methanol in water films that are present in the ecosystem. We have used the model developed in Sect. 3 to prove this hypothesis.

The model has 5 input variables (T_a , u^* , M_{aa} , D and P) and 4 site-specific parameters (A , τ , C_{R0} and α). In this section, the model will first be calibrated (Sect. 4.3.1) and validated (Sect. 4.3.2) on data sets where the abiotic processes appear dominant (i.e. in summer). The model will then be used (Sect. 4.3.3) to compute the abiotic component in spring. Finally, abiotic flux simulations will be combined with measurements in order to isolate the biogenic contributions to the fluxes and these fluxes will be analysed more deeply. Calibration will be performed on summer 2009 data (July to September) and validation on summer 2010 data.

4.3.1 Model calibration (summer 2009)

The calibration was performed in three steps. First, for parameter A , the value found in Sect. 4.2 (Fig. 5) above was retained, selecting night conditions when stomata are closed to limit the possible effect of biogenic emissions on the parameter A . Second, α was also deduced from the results of Sect. 4.2 (Fig. 4). A function of the type:

$$f(\alpha) = \psi \cdot \left[1 - \exp\left(-\frac{D}{\alpha}\right) \right]$$

was adjusted on the relationship between $M_{aw} \cdot K_H(T_a)$ and D (Fig. 7), $\psi = \frac{q}{C_R}$ being a free parameter (corresponding to a residual concentration) and M_{aw} being deduced from Eq. (1) by using our measurements (M_{aa} , u^* and $F_1 = F_{\text{measured}}$). We obtained $\alpha = 588 \pm 69 \text{ Pa}$ ($R^2 = 0.44$).

Third, the last two parameters (τ , C_{R0}) were estimated by minimising the square root differences between modelled and measured cumulated fluxes. This provided $C_{R0} = 0.176 \text{ m}$ and $\tau = 82.8 \text{ h}$, the latter corresponding to a half lifetime of 57.4 h. If C_{R0} is interpreted as the minimum total height of water films in the ecosystem, its value may look unrealistically high. This is probably because we use air temperature for the

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



computation of the Henry's law constant instead of the temperature of the water films at the soil surface. This latter temperature is not available, but is usually lower than the air temperature, leading to a systematic underestimation of K_H compensated by a high fitted C_{R0} .

5 In the above calibration and in the subsequent validation phase, we rejected data with net radiation below -20 W m^{-2} because in these atmospheric conditions (26 % of the dataset) the oversimplified parameterisation chosen for R_t in Eq. (2) underestimates the in-canopy aerodynamic resistance (Pul and Jacobs, 1994). In summer, the comparison between measured mean diurnal evolution of methanol fluxes without
10 (Fig. 3) and with R_{net} filtering (Fig. 8a) shows that, under stable atmospheric conditions, the turbulent exchange is dampened, therefore limiting the exchange. Without R_{net} filtering, the model would have predicted unrealistically strong deposition (result not shown) during these events.

In the case of long data gaps (more than 10 days), the model lacks information on
15 the temporal evolution of total methanol content in the water films. Several days are needed after the measurement recovery to allow reliable modelling. Such data gaps did, for instance, occur in 2010, the first one in July and the second at the beginning of August. In these cases, we discarded the results obtained less than 4 days after the measurement recovery.

20 After calibration, the model was able to reproduce the intra-day (Fig. 8a) as well as the long-term (Fig. 8b) flux dynamics. The frequency distribution of the differences between measurements and simulations (Fig. 8c) is characterized by a mean and a median close to zero and by a standard deviation of $0.065 \mu\text{g m}^{-2} \text{ s}^{-1}$. This standard deviation probably originates from the random errors introduced by the DEC method
25 (Hörtnagl et al., 2010) and by the spatial distribution of sources/sinks that can affect measurements, especially at low wind speed (Richardson et al., 2006). The effect of these random errors was limited in time by performing the model calibration on cumulated fluxes instead of using individual half-hours. The cumulated flux shows a linear decrease with time (Fig. 8b). This decrease is due to methanol degradation that

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

affects the long-term evolution of the modelled flux. The slope of this long-term evolution, representing the mean degradation methanol flux, is $-7.42 \times 10^{-3} \mu\text{g m}^{-2} \text{s}^{-1}$. The fluctuations of the cumulated flux around this linear decrease are due to adsorption/desorption mechanisms that, unlike degradation, are short-term effects.

5 4.3.2 Model validation (summer 2010)

Once calibrated with the summer 2009 data, the model reproduced faithfully the observed mean diurnal flux evolution in summer 2010 (Fig. 8d). Measured and modelled cumulated fluxes were also in good agreement (Fig. 8e) and were characterized by a linear decrease similar to that in the calibration phase. In the period from 28 August to 5 September, the model first under-estimated and later over-estimated the depositions. At the beginning of this period, heavy rains occurred and the effect of this is probably poorly represented by the model through Eq. (6) on a short-time scale (<10 days). The frequency distribution of the deviation measurements-model (Fig. 8f) is characterized by a mean and a median close to zero and by a standard deviation of $0.057 \mu\text{g m}^{-2} \text{s}^{-1}$.

15 Other divergences were observed in autumn 2009, from 15 October onwards, and also in April 2010 (data not shown), during which the model over-estimated the deposition. One reason could be that during both these periods the deciduous trees are leafless, while the model had been parameterised (Eq. 5) on the basis of measurements taken during the full-leaf period. This could lead to an overestimation of the water film capacities during these periods.

20 4.3.3 Flux partitioning during transitional phenological phases (spring 2010)

The model was then applied to spring (May 2010, Fig. 9). As the model computes only the abiotic contribution to the fluxes and the methanol degradation, its residuals (measurement minus modelling) during this period should therefore represent the biogenic emissions. Time evolutions of the residuals and their driving variables have been investigated.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The model residuals during the day become increasingly significant from 20 to 27 May, reaching a maximum value of $0.6 \mu\text{g m}^{-2} \text{s}^{-1}$. During this period, when leaves are almost at their full development stage (see VAI, Fig. 2), the model residuals cannot be explained by an overestimation of the water film capacities as suggested for the divergence observed in autumn. Indeed, a possible increase in foliar surface should instead reduce these residuals.

As the biogenic fluxes are known to respond mainly to temperature (Custer and Schade, 2007; Filella et al., 2007; Folkers et al., 2008; Harley et al., 2007) and to PPFD (Brunner et al., 2007; Harley et al., 2007), we investigated the relationships of the model residuals to these two variables. The results are presented in Fig. 10.

Residuals increase with temperature (Fig. 10a) and can be fitted using an exponential relation:

$$F_{\text{Methanol}} = \text{SEF}_{30^{\circ}\text{C}} \cdot \exp(\beta \cdot (T_a - 303.15))$$

where $\text{SEF}_{30^{\circ}\text{C}}$, the standard emission factor at 30°C was found to be $0.76 \pm 0.11 \mu\text{g m}^{-2} \text{s}^{-1}$ and β , the temperature dependence parameter, $0.12 \pm 0.01 \text{ }^{\circ}\text{C}^{-1}$ ($R^2 = 0.38$).

On the other hand, no obvious relationship (slope coefficient not significantly different from zero, $p = 0.1$) between the model residuals standardized with air temperature and PPFD was found (Fig. 10b).

5 Discussion

5.1 Comparison with previous flux studies at the ecosystem scale

This study reports a temperate forest behaving as a net methanol sink ($-0.057 \pm 0.012 \text{ mg m}^{-2} \text{ h}^{-1}$) over a 7-month period (April to September 2010) and, given the fact that net emissions are not expected during winter, most probably as a sink on an annual basis. This result contradicts most studies published on methanol exchange by

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 forests to date (Karl et al., 2004, 2005; Schade et al., 2011; Spirig et al., 2005), which reported generally positive fluxes and a positive net budget during their measurement periods. Methanol deposition was observed only occasionally in these studies, with a maximum deposition up to $0.15 \mu\text{g m}^{-2} \text{s}^{-1}$ for Spirig et al. (2005) over a temperate forest, still four times lower than our maximum deposition. The sole negative net budget over two measurement periods (April–May 2008: $-0.02 \pm 0.02 \text{ mg m}^{-2} \text{ h}^{-1}$ and June–July 2008: $-0.04 \pm 0.02 \text{ mg m}^{-2} \text{ h}^{-1}$) was observed by Langford et al. (2010) above a tropical rainforest.

10 One of the main reasons for these differences is probably that most of these studies were conducted over short periods corresponding with sunny weather conditions and vegetation development, during which biogenic emission dominated. If our study had been limited to spring, it would also have reported such a positive methanol net budget with occasional depositions. The detection of the alternation between day emission and night deposition and of the long-term methanol degradation was possible only because of long-term measurements performed after the single production period.

15 MEGANv2.1, the state-of-the-art empirical upscaling emission algorithm (Stavrakou et al., 2011), is parameterised using emission factors and deposition velocities derived from a compilation of the above-mentioned ecosystem-scale studies. The proposed standard emission factor for growing leaves of northern temperate forests ($0.67 \mu\text{g m}^{-2} \text{s}^{-1}$) is close to our result ($0.76 \mu\text{g m}^{-2} \text{s}^{-1}$).

20 In this model, dry depositions are accounted for by using a linear dependence of the deposition velocity on the LAI, increasing from 0 to 0.75 cm s^{-1} when LAI increases from 0 to $6 \text{ m}^2 \text{ m}^{-2}$. Our results contrast with this parameterisation. Our calculated average deposition velocity (2.4 cm s^{-1}) is 10 times higher than the mean deposition velocity observed by Karl et al. (2004) above a tropical rain forest ($0.27 \pm 0.14 \text{ cm s}^{-1}$) and more than twice as high than the maximum velocity of 1.0 cm s^{-1} observed by Karl et al. (2005) above a *Pinus taeda* plantation and than the deposition velocity of $1.1 \pm 0.9 \text{ cm s}^{-1}$ observed by Schade et al. (2011) above a *Fagus sylvatica* forest. However, it is worth mentioning that in our study we selected only wet atmospheric conditions

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

(and $R_{\text{net}} > -20 \text{ W m}^{-2}$) for the deposition velocity calculation (see Sect. 4.2), whereas other studies used their whole dataset. For comparison, we obtained a deposition velocity of $1.78 \pm 0.08 \text{ cm s}^{-1}$ without filtering, still higher than in previous studies.

Our study therefore questions the measured and modelled net methanol budget in forest ecosystems. The presence of an adsorption/desorption process of methanol in water films and of a methanol degradation process could significantly modify the methanol budget on short- and long-term scales.

5.2 Processes responsible for methanol depositions/emissions

5.2.1 Adsorption/desorption process

The good agreement between our simulations and the measurements in summer, especially the good reproduction of the intra-day variability of the methanol exchange, suggests that methanol adsorption/desorption in water films is the main process controlling net methanol ecosystem exchange in the short-term. This is due to the high solubility of this compound in water compared with other BVOCs (Sander, 1999).

5.2.2 Degradation processes

In addition, the observation of a negative cumulated flux on a long-term scale in summer reflects the existence of methanol degradation processes in the ecosystem. Several degradation mechanisms have been identified in literature.

The possibility of stomatal deposition during the day followed by the oxidation of methanol into formaldehyde in the leaf was reported by Gout et al. (2000). However, this process would imply a higher deposition velocity during the day than at night, because the stomata are closed at night. Since no significant difference was observed in the deposition velocity during the day or night (Fig. 5), we assume that this process was negligible at our site compared with the adsorption/desorption mechanism in water films.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Another possibility would be consumption by methylotrophic bacteria, organisms that preferentially use methanol as source of energy and carbon through an enzymatic reaction (Duine and Frank, 1980). These organisms are known to be common on leaf surfaces (Holland and Polacco, 1994) and soil (Hiraishi et al., 1995). Romanovskaya et al. (2001) reported a natural colonization of methylotrophic bacteria on leaves, occurring mainly via air transfer. The degradation of methanol could also be due to the reaction of methanol in the aqueous-phase with OH radicals (Elliot and McCracken, 1989). This chemical reaction might occur in water films present on leaf and soil surfaces. Based on our sole dataset, we were not able to identify the precise origin of this degradation mechanism and whether it occurs on leaf and/or soil surfaces. Nevertheless, we found a mean degradation rate of $-7.42 \times 10^{-3} \mu\text{g m}^{-2} \text{s}^{-1}$ and a half lifetime for methanol in water films of 57.4 h. This latter value is in agreement with Howard et al. (1991) who found a half lifetime in a wet soil of between 1 and 7 days.

5.2.3 Biogenic emission processes

We considered that biogenic emissions occur mainly in spring. Leaf methanol emission is usually considered to be two to three times lower for mature leaves than for young leaves (Karl et al., 2003; Nemecek-Marshall et al., 1995). It is therefore likely that, in summer, leaf emissions might be negligible compared with the methanol adsorption/desorption in water films. We therefore associated biogenic emission with the model residual only for spring.

Between 20 and 27 May (Fig. 9), these residuals showed an exponential increase with temperature (Fig. 10a), indicating an enzymatic mechanism and/or destorage from an internal pool. This enzymatic mechanism can be attributed to the demethylation of pectin that occurs during the leaf/needle cell wall expansion (Fall and Benson, 1996) and also to root growth (Folkers et al., 2008), this entire methanol production being emitted through the stomata (Galbally and Kirstine, 2002). In support of this hypothesis, the fitted temperature sensitivity factor was found to be $0.12 \pm 0.01 \text{ } ^\circ\text{C}^{-1}$, comparable with previous enclosure studies ($\beta = 0.06 \pm 0.003 \text{ } ^\circ\text{C}^{-1}$ (*Fagus sylvatica*) for Fillela et

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



al., 2007 and $\beta = 0.082\text{ }^{\circ}\text{C}^{-1}$ (*Picea abies*) for Folkers et al., 2008) (Filella et al., 2007; Folkers et al., 2008; Harley et al., 2007).

The attribution of biogenic emissions due to leaf/needle growth to a specific tree species is a difficult exercise because of the mixed composition of the stand. In the 20–27 May period, during which the most significant emissions were observed, footprint analysis reveals that a contribution to the total flux of 40% or more by *Fagus sylvatica*, *Pseudotsuga menziesii* and *Picea abies/Abies alba* occurred during 50, 36 and 24% of the time, respectively. Since *Fagus sylvatica* was the main contributor during this period and since its leaves were still not at their full development stage at that time, we attribute the main part of the growth-linked biogenic emission to that species, but we cannot exclude a contribution of *Pseudotsuga menziesii* and *Picea abies/Abies alba*, since they also contribute to flux and are known to have their bud break at the end of April and mid-May, respectively (Lebourgeois et al., 2002).

The emission we observed (Fig. 10) did not coincide exactly with the *Fagus sylvatica* bud break, which started on 1 May 2010. This is probably because the following 15 days were characterized by cold conditions ($T_a < 9\text{ }^{\circ}\text{C}$) which hindered biogenic emissions (Fig. 10). From 15 May onwards, the air temperature increased and the highest residuals were found.

Methanol can also be produced through litter decomposition occurring mainly in autumn (Gray et al., 2010; Warneke et al., 1999). This would agree with an increase of the model residuals observed in autumn, but we have already noted that our model was not designed to handle the LAI change occurring during this period. In the absence of trustworthy information produced by the model, it was not possible to determine if methanol production from the litter was really present in autumn and/or if a seasonal decrease of methanol degradation occurred.

In contrast to the enclosure study of Folkers et al. (2008) (*Fagus sylvatica*) and the DEC study of Brunner et al. (2007) (grassland), we did not observe any clear dependence of the biogenic emissions on PPFD, whereas PPFD is known to regulate stomatal conductance, which in turn controls leaf emissions for soluble compounds such as

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



methanol (MacDonald and Fall, 1993; Niinemets et al., 2004). This dependence could have been blurred by two processes: (i) the biogenic emission computation procedure as model residuals standardised with air temperature and (ii) the leaf development dynamics that occurred throughout the period when biogenic emissions were analysed.

6 Summary and conclusions

This study presented and analysed long-term measurements of ecosystem-scale methanol exchange over a forest. It showed that the site behaved as a methanol sink for most of the measurement period, which contradicts results generally reported in experimental studies and the estimates of methanol exchanges based on emission modelling.

A simple model was developed in order to identify the mechanisms responsible for this sink. The results suggest that the main processes controlling methanol exchanges in summer are on a short-term scale, the methanol adsorption/desorption by water films and, at longer term, the methanol degradation.

The production of methanol associated with leaf development, as generally observed in some preceding studies, was also detected at our site, but it was limited to a short period in spring and did not constitute the largest contribution to the net ecosystem exchange. This would suggest that abiotic and methanol degradation processes play a more important role than previously assumed and that measurements focusing only on the growing period could strongly bias the annual methanol budget of ecosystems by neglecting these processes. This highlights the need to develop long-term measurements in order to obtain accurate estimates of net methanol exchanges at the ecosystem level.

Different processes responsible for methanol degradation and operating at the soil or leaf level were suggested, but none of them could ultimately be retained. Additional measurements are needed to elucidate the precise origin of this degradation.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



These results suggest that the adsorption/desorption and degradation processes play a more important role than previously expected in the site methanol balance. In addition, these processes could affect other organic compounds that are similarly or more soluble than methanol as, for example, the precursors to secondary organic aerosol issue from isoprene oxidation, from aromatic compounds. This needs to be investigated for different types of ecosystems using long-term (at least one season) continuous measurements. The model and the procedure presented here could be adapted for each site and each compound in order to separate the abiotic and biogenic component of the fluxes.

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Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Q. Laffineur et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

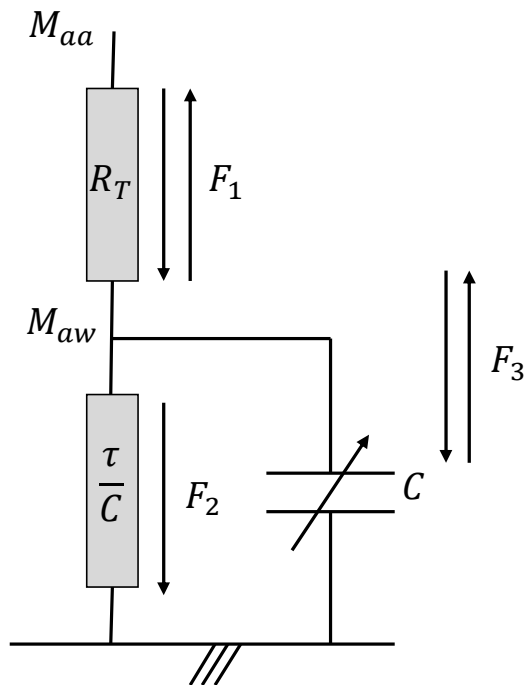


Fig. 1. Electrical analogy for methanol adsorption/desorption/degradation processes.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

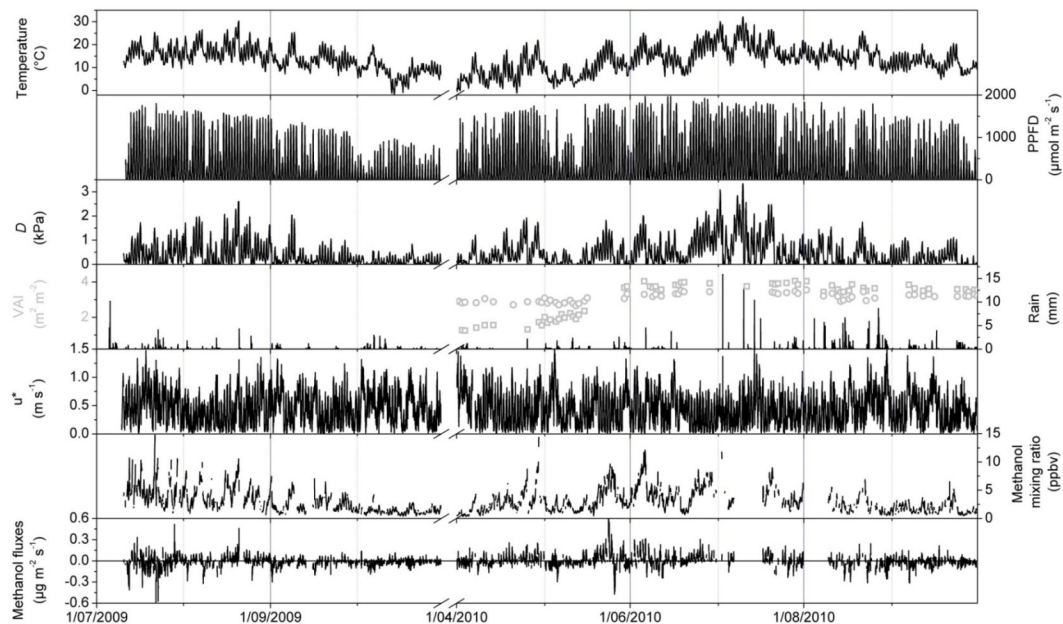
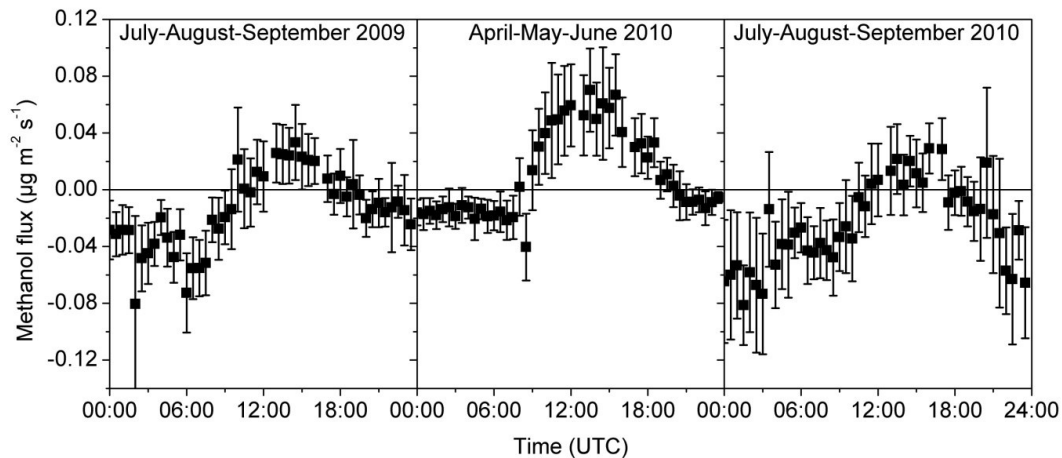


Fig. 2. Temporal evolution of meteorological variables, methanol mixing ratio and methanol flux between 10 July and 31 October 2009 and between 1 April and 30 September 2010: air temperature (T_a), PPF, vapour pressure deficit (D), precipitation, vegetation area index (VAI) of beeches (\square) and Douglas (\circ), friction velocity (u^*), ambient methanol mixing ratio and methanol fluxes.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

**Fig. 3.** Mean diurnal evolutions of methanol flux (error bars are 95 % confidence intervals).[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

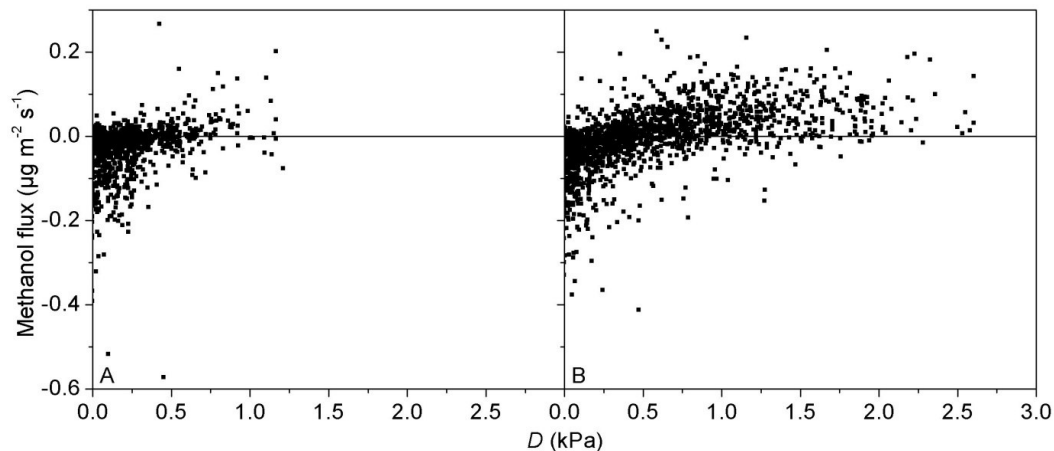


Fig. 4. Vapour pressure deficit (D) dependence of methanol flux in night (**A**) and day (**B**) conditions for July-August-September 2009.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

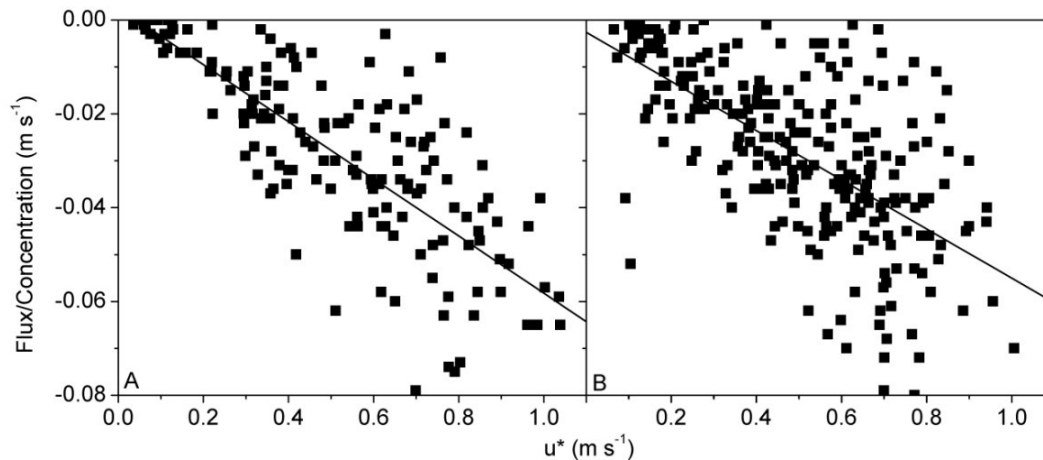


Fig. 5. Relationship between the ratio methanol flux/ambient methanol concentration and the friction velocity (u^*) in night (**A**) and day (**B**) conditions for July-August-September 2009, respecting these conditions: flux $< 0 \mu\text{g m}^{-2} \text{s}^{-1}$, $D < 0.15 \text{ kPa}$ and $R_{\text{net}} > -20 \text{ W m}^{-2}$.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

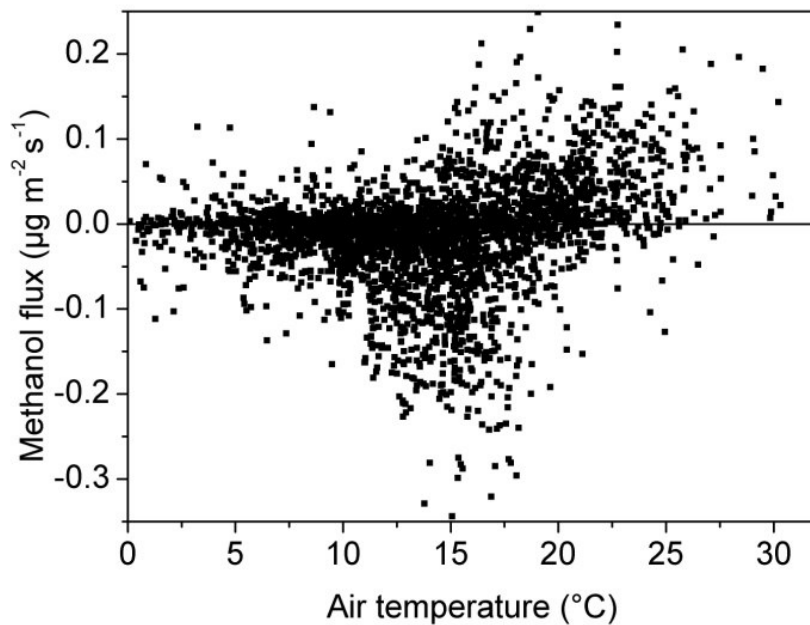


Fig. 6. Methanol flux in relation with the air temperature for July-August-September 2009.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



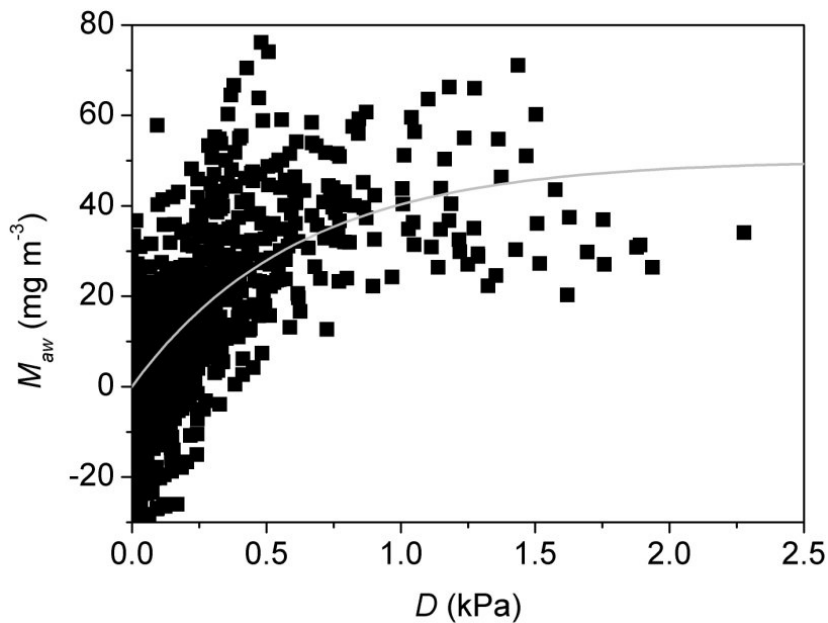


Fig. 7. Relationship between the concentration of methanol (M_{aw}) in the water films and the vapour pressure deficit (D) for July-August-September 2009.

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

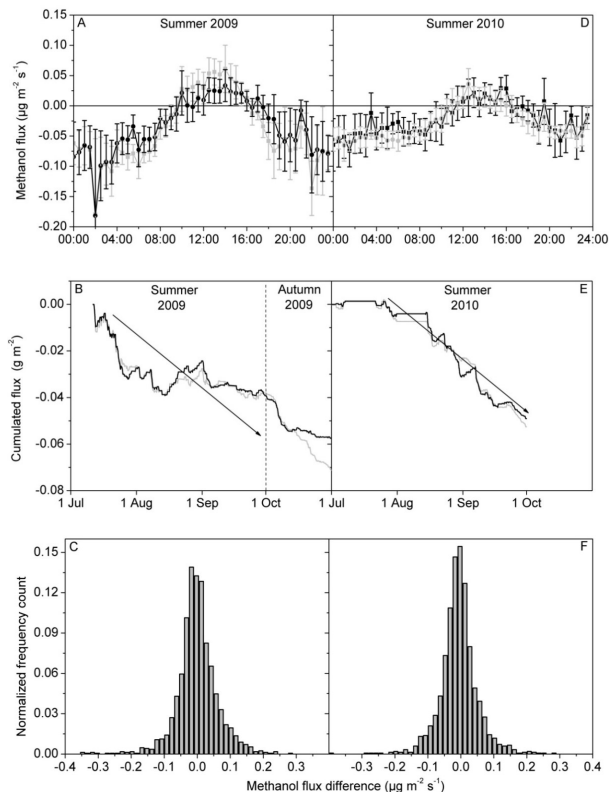


Fig. 8. Mean diurnal flux evolution of modelled (grey line) and measured (black line) methanol flux for the summer 2009 (A) and for the summer 2010 (D) with $R_{\text{net}} > -20 \text{ W m}^{-2}$ (error bars are 95 % confidence intervals), temporal evolution of cumulated measured (black line) and modelled (grey line) methanol flux for the summer 2009 (B) and the summer 2010 (E), distribution of the difference between the measured and modelled methanol flux for the summer 2009 (C) and the summer 2010 (F).

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

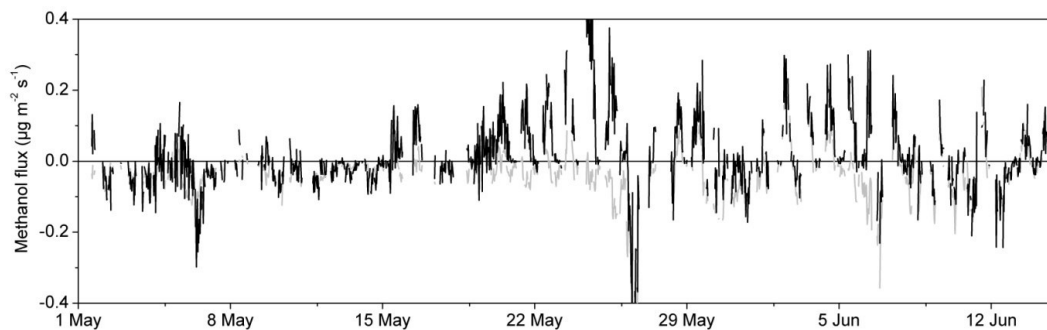


Fig. 9. Temporal evolution of measured (black line) and modeled (grey line) methanol flux between 1 May and 15 June 2010.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Abiotic and biotic control of methanol exchanges

Q. Laffineur et al.

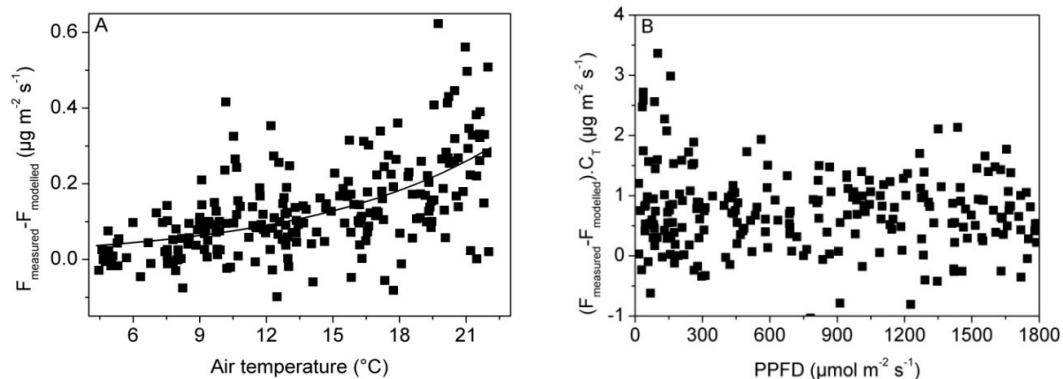


Fig. 10. Relation between the difference of measured/modelled methanol flux and the air temperature **(A)**, relation between the difference of measured/modelled methanol flux standardised at 30 °C and the PPFD **(B)** between 15 and 27 May 2010.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)