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Methanol exchange dynamics between a temperate cropland soil and the atmosphere

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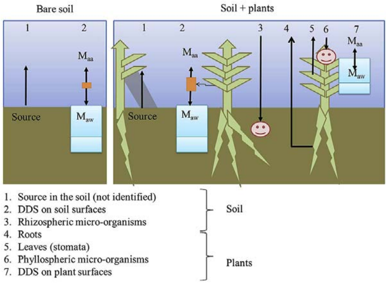
GRAPHICAL ABSTRACT



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ABSTRACT

Soil methanol (CH_3OH) exchange is often considered as several orders of magnitude smaller than plant methanol exchange. However, for some ecosystems, it is significant in regard with plant exchange and worth thus better consideration. Our study sought to gain a better understanding of soil exchange. Methanol flux was measured at the ecosystem scale on a bare agricultural soil over two contrasted periods using the disjunct eddy covariance by mass scanning technique. A proton-transfer-reaction mass spectrometer was used for the methanol ambient mixing ratio measurements. Bi-directional exchange dynamics were observed. Methanol emission occurred under dry and warm conditions and correlated best with soil surface temperature, whereas methanol uptake occurred under wet and mild conditions and correlated well with the methanol ambient concentration. After having tested a physical adsorption-desorption model and by confronting our data with the literature, we propose that the exchange was ruled by both a physical adsorption/desorption mechanism and by a methanol source, which still needs to be identified. The soil emission decreased when the vegetation developed. The reasons for the decrease still need to be determined. Overall, the dynamics observed at our site were similar to those reported by other studies for both cropland and forest ecosystems. The mechanism proposed in our work can thus be possibly applied to other sites or ecosystems. In addition, the methanol exchange rate was in the upper range of the exchange rates reported by other soil studies, suggesting that cropland soils are more important methanol exchangers than those in other ecosystems and should therefore be further investigated.

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1. Introduction

After methane, methanol (CH_3OH) is the most abundant hydrocarbon in the atmosphere. Since it is less reactive than other non-methane volatile organic compounds (NMVOC), such as isoprene or sesquiterpenes (Atkinson and Arey, 2003), it can cross longer distances and affect atmospheric chemistry in remote locations. It influences, *inter alia*, the concentration of tropospheric oxidants (Collins et al., 2002; Tie et al., 2003) and the lifetime of methane (Collins et al., 2002).

Methanol is the main NMVOC compound emitted by soils, but exchange is thought to be 1 to 3 orders of magnitude smaller than plant exchange (Peñuelas et al., 2014). Soil methanol exchange is therefore not directly considered in methanol budgets (Stavrakou et al., 2011) or by atmospheric chemistry models (Collins et al., 2002; Tie et al., 2003), which rely on plant methanol emission models only (with empirical standard emission factors based on ecosystem-scale studies).

Recently, however, in a study conducted in a cropland ecosystem, equally important methanol exchange from bare soil as from well-developed vegetation was detected (Bachy et al., 2016). This means that, for some ecosystems, the soil exchange cannot be considered as negligible. It therefore needs to be better constrained if estimates of global methanol budgets are to have high accuracy.

Soil VOC exchange has been widely studied, and a recent review is available (Peñuelas et al., 2014). So far as we know, however, only one study to date has reported methanol flux on croplands under natural weather conditions (Schade and Custer, 2004). Most studies have focused on non-agricultural ecosystems (Asensio et al., 2008, 2007; Bäck et al., 2010; Gray et al., 2014; Greenberg et al., 2012; Kalender and Akosman, 2004; Ramirez et al., 2009; Schade et al., 2010), mainly forest soils or litter. Some studies have dealt with agricultural soils (Gray et al., 2010; Gray and Fierer, 2012; Mancuso et al., 2015), but they were performed under controlled conditions or did not report methanol flux. This demonstrates the need for more detailed methanol exchange studies on agricultural soils, especially given that these lands cover more than 38% of the land area (Food and Agriculture Organization of the United Nations, Statistics Division, FAOSTATS, 2013) and are dominant in some regions. In addition, the methanol exchange dynamics of cropland soils could differ from that of forest soils, because forest and cropland soils differ in both litter content and micro-organism composition and because these factors influence the VOC exchange composition of soils (Mancuso et al., 2015; Ramirez et al., 2009).

The methanol exchanged by soil is also affected by the presence of vegetation. Gray et al. (2014) showed, for example, that tree roots emit methanol. Conversely, Asensio et al. (2007) observed an increase in methanol uptake in the presence of roots in a forest ecosystem and attributed this to an increase in the activity of methylotrophs (i.e., microorganisms that consume compounds with one atom of carbon [C1 compounds] for their metabolism, including methanol) in the rhizosphere. More measurements focusing on different soils and plant species are needed to better constrain and quantify the vegetation effect on soil methanol exchange.

In our study, we sought to improve the understanding of methanol exchange between agricultural soils and the atmosphere. We measured methanol flux at the ecosystem scale on a bare agricultural soil over two contrasting periods. In this paper, we initially describe the methanol exchange rate and dynamics for each period. We then look at the mechanisms beyond these dynamics and discuss a soil exchange model built in order to test them. In the final part, we evaluate qualitatively the impact of vegetation on the methanol exchanged by the soil by comparing the exchange rate measured on bare soil with that measured at the same site when maize was grown (Bachy et al., 2016).

2. Methods

2.1. Measurement periods

All the flux measurements were carried out at the Lonzée Terrestrial Observatory (LTO). This site is a production field of about 12 ha located in the Hesbaye region of Belgium. It is surrounded by croplands, except in the North-West direction (250–300°N) where a silo and a cowshed are located approx. 300 and 450 m from the measurement mast, respectively. Analyses did however not reveal a significant impact of these surroundings on the measured methanol fluxes. Therefore, we concluded that they were far enough from the mast so that they did not impact the flux measurements. The site is candidate for the Integrated Carbon Observation System Research Infrastructure (ICOS RI) European network (https://www.icos-cp.eu/node/83). The soil is a luvisoil (silty loam) composed of 65% silt, 25% clay and 10% sand, with a SOM content of 2.15 ± 0.03% and a C/N ratio of 9.40 ± 0.01 (MPJ-Jena, pers. comm.). The LTO was described in detail by Moureaux et al. (2006).

The first bare soil flux measurement period, B1, ran from 17 to 28 May 2012, i.e., 262 days after the winter wheat harvest and 247 days after the winter wheat stubble breaking (Fig. 1). There were no measurements between 21 and 24 May because of a power cut. Seedbed preparation and liquid nitrogen application were done 3 days before the start of the B1 period, and maize (*Zea mays* L.) seeds of the varieties Prosil (75%) and Rocket (25%) were sown at that time. Both varieties were homogeneously widespread in the field. The seeds germinated on 25 May 2012. At the end of B1, the leaf area index (*LAI*) of the maize stamps was estimated to be 0.01 $m^2\,m^{-2}$ (Bachy et al., 2016).

After the B1 period, methanol fluxes were measured on growing maize until its harvest, which was on 13 October 2012. The full flux measurements were described in detail by Bachy et al. (2016), who discussed the methanol exchange rate (note that the B1 period is included in that reference and refers to the G stage). The main developmental stages of the maize, and the associated net methanol exchange, are summarized in Fig. 1. In our study, these data were used only to compare the net methanol exchange rate recorded during the maize growing season (i.e., stages L to R2) with that measured on bare soil. Herbicide was applied by 5 June 2012.

The second bare soil flux measurement period, B2, ran from 13 to 27 September 2013, i.e., 29 days after the winter wheat harvest and 17 days after the winter wheat stubble breaking. There were no measurements between 20 and 23 September because of a calibration and technical problems with the data acquisition system. Seedbed preparation was done 6 days before the measurement period, and mustard seeds were sown at that time. They germinated on about 15 September 2013 (exact date unknown). At the end of B2, the mustard biomass ranged between 0.01 and 0.03 $g_{DW}\,m_{soil}^{-2}$ (Bodson B., pers. comm.).

We considered the soil as bare during both B1 and B2, but, as described earlier, small plants were present during both periods. Their possible impact on net ecosystem-scale fluxes is discussed in Sec 3.1.

2.2. Methanol flux measurements

For each measurement period, methanol flux was collected every half an hour using the disjunct eddy covariance by mass scanning technique (Rinne and Ammann, 2012). This technique involves measuring flux as the covariance between the vertical wind speed, measured at high frequency, and the concentration of the scalar required to determine the flux. A 3D-sonic anemometer (Solent Research R3, Gill Instruments Lymington, UK) was used for wind speed measurements, and an high sensitivity proton-transfer-reaction mass spectrometer (hs-PTR-MS, Ionicon Analytick GmbH, Innsbruck, Austria), located in an air-conditioned shelter, was used to measure the methanol ambient mixing ratio.

The experimental set-up (e.g., tubing, filters) and the hs-PTR-MS

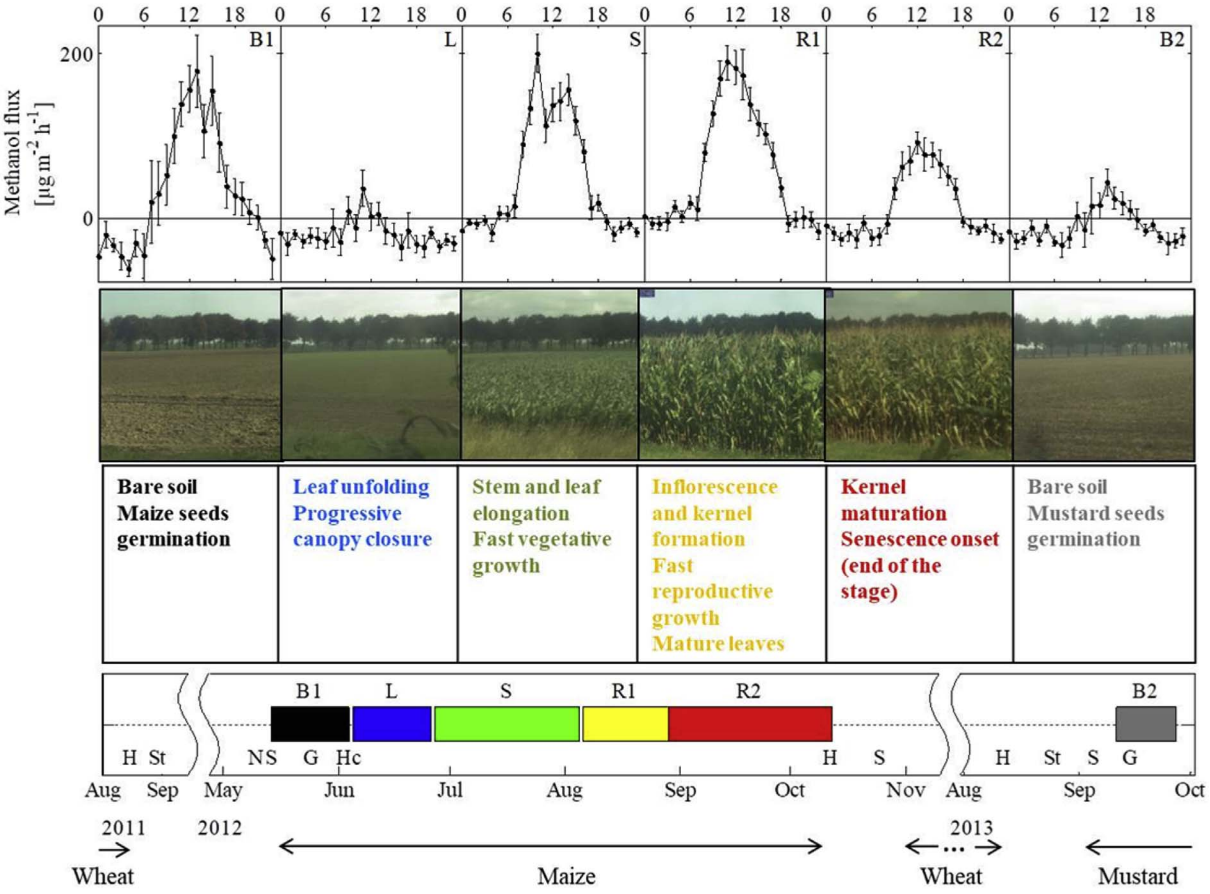

Fig. 1. Top panels: methanol flux circadian dynamics for bare soil periods and each maize phenological stage. Pictures and table: brief description of each period. Bottom panels: timeline of flux measurement periods and stages. The letters above the timeline refer to the stages. Namely: B1 = bare soil (1st period), L = leaf unfolding, S = stem elongation, R1 = 1st reproduction phase (flowering, kernel formation), R2 = 2nd reproduction phase (kernel maturation), B2 = bare soil (2nd period). The letters below the timeline indicate the major events of the crop growing season: H = harvest, St = stubble breaking, S = sowing, G = germination, N = fertilizer application, Hc = herbicide application.

operation (e.g., calibration, mode) used in the B1 period and for the maize measurement have been widely detailed in Bachy et al. (2016) and will not therefore be described here. The protocol used for B2 was identical to that described by Bachy et al. (2016), except for the technical differences listed below. These differences did not reduce flux quality or jeopardize the comparability between B2 and the other measurement exercises (B1 period and maize measurement).

The shelter containing the hs-PTR-MS was oriented north-east from the mast for B2, whereas for B1 and maize measurement it was oriented north-west. The north-east wind direction is the second most dominant wind sector at the LTO, but the comparison of CO_2 and sensible heat flux co-spectra between this sector and the south-west sector (the dominant wind sector at the LTO), under the presence and absence of the shelter, did not reveal any significant effect of the shelter on the fluxes. We concluded that the shelter was far enough from the mast not to disturb the wind flow around it. From 23 September 2013 onwards, the number of compounds measured by the hs-PTR-MS was reduced to two (including methanol) instead of 11, for methodological reasons. This increased the methanol mixing ratio sampling frequency to 1 Hz instead of 0.25 Hz. An increase in this scale reduces the sampling random noise, but does not bias the fluxes. The mast height was kept constant at 2.7 m throughout B2, but when the maize was growing it was elevated up to 4.7 m. These different heights were taken into account when computing the flux frequency correction factors.

The flux calculation procedure, data quality evaluation and error estimation were detailed in Bachy et al. (2016) for the B1 and the maize measurement campaigns, and the same protocol was applied for the B2 campaign. That procedure is thus only shortly described in the following paragraphs.

The methanol fluxes were measured with a data acquisition frequency of 0.25 Hz (1 Hz from 23 September 2013 onwards). The time lag was estimated for each half-hour by covariance maximisation on smoothed curves. The fluxes were corrected for high frequency loss with theoretical transfer functions for deducing a cut-off frequency of the system following Moncrieff et al. (1997), the reference co-spectrum chosen being the one proposed in Kaimal and Finnigan (1994) which was found to be very similar to the local sensible heat co-spectrum. The half-power cut-off frequency was estimated to be 0.4 Hz. The resulting correction factor ranged between 1 and 2, with an average of 1.3 for all measurement periods.

The fluxes were discarded when the field contribution to the total flux footprint (Neftel et al., 2008) was below 70%, during hs-PTR-MS calibration and background measurement periods, or when flux measurement were not available (maintenance operations, power failures, spraying event, …). This resulted in 227 valid flux data for the B1 period, 338 valid flux data for the B2 period and 3365 valid flux data for the maize period. Note that the fluxes were not filtered according to stationarity or friction velocity. Indeed, tests performed on maize fluxes showed that the filtering criteria conventionally based upon these two variables were not relevant for this measurement campaign (Bachy et al., 2016).

The flux random error (σ) was estimated from the detection limit, following the technique described in Spirig et al. (2005). The methanol flux precision (2σ) was on average 20 $\mu g\,m^{-2}\,h^{-1}$ during nighttime and 32 $\mu g\,m^{-2}\,h^{-1}$ during daytime. The error of the flux averages, induced by these individual flux random errors, was estimated as the square root of the mean of the squared individual flux random errors (σ), in accordance with variance additivity properties. It was lower than 1 μg m^{-2} h^{-1} for the flux averages of the stages B1 and B2 (Table 1).

The potential systematic flux error was estimated for all VOC compounds together by analyzing the flux distribution and by comparing the water vapor flux obtained from the measurements with the hs-PTR-MS with that based upon the measurements with an infra-red gas analyzer. First, we did not observe a dip in the flux distribution around zero. We therefore concluded that the chosen time lag method did not select artificially large positive or negative fluxes (this effect is called mirroring effect, see Langford et al., 2015). Then, the slope of the relationship between the water vapor fluxes estimated with both instruments did not significantly differ from 1. We therefore concluded that the fluxes were not biased. More details about the random and systematic error quantification can be found in Bachy et al. (2016).

We also tested the effect of high frequency O_2^+ interferences on the m/z 33 signal and its subsequent impact on estimated methanol mixing ratios and fluxes. Indeed, the isotopic $^{17}O^{16}O^+$ ion signal, which is determined by the water vapor concentration in the drift tube reactor, interferes with the ion signal of protonated methanol measured at the same nominal mass. In our experiment, the methanol background was measured every 1.5 h and subtracted from the measured m/z 33 signal. By doing this, we caught the low frequency (i.e. lower than 1.5 h) O_2^+ contribution to the m/z 33 signal. However, high frequency (i.e. higher than 1.5 h) fluctuations were not taken in account. In order to quantify their effect on measured fluxes, we performed three methanol background calibrations as a function of relative humidity, from which we drew a linear relationship between water vapor concentration and total methanol background. Then, we used that relationship with fast measurements of water vapor concentration (at the m/z 39 nominal mass) to obtain estimation of high frequency O_2^+ contribution to methanol fluxes and mixing ratios. It resulted that these interferences impacted only slightly the value of the methanol mixing ratios and fluxes (less than 4%). They were therefore neglected.

2.3. Ancillary measurements

Apart from the methanol flux, the net sensible heat flux H was gathered every half an hour at the LTO using the eddy covariance technique. The instrumental set-up, flux calculation procedures and filtering criteria have been described by Aubinet et al. (2009).

The relevant micro-meteorological variables for the present study were air temperature T_A and air relative humidity (RH T2, Delta T Devices Ltd, Cambridge, UK), from which the saturation deficit D_{SAT} was calculated, soil temperature at a depth of 3 cm T_S (3 cm) (PT 100, Jumo), soil water content (*SWC*) at depths of 5, 20 and 40 cm (ML2, ThetaProbe, Delta-T Devices Ltd, Cambridge, UK), rainfall P (Collector and Tipping Bucket), global incoming radiation R_G (CM21, Kipp and Zonen, Delft, NL), outgoing longwave radiation L_{UP} (CNR 1, Kipp and Zonen, Delft, NL) and friction velocity u_* (calculated from the sonic anemometer data). All these variables were measured continuously at LTO and averaged over 30 min periods.

In addition to these variables, the soil surface temperature T_S (0 cm) was estimated because the methanol flux dynamics suggested an influence of that variable (Sec 3.2). The soil surface temperature was calculated from L_{UP} by inverting the Stefan-Boltzmann law: $L_{UP} = \varepsilon\,\sigma\,T_S\,(0\,\mathrm{cm})^4$, where ε is the soil emissivity, which is site dependent and varies with soil humidity (Mira et al., 2007), and σ is the Stefan-Boltzmann constant (5.67 x 10^{-8}W m^{-2} K^{-1}). ε was estimated every day by inverting that equation when T_S (0 cm) and T_A were very close to each other, i.e., when the sensible heat flux H and the resistance to heat transfer were both small ($H < 15$ W m^{-2} and $u_* > 0.15$ m s^{-1}, respectively). It ranged from 0.92 (dry conditions) to 0.96 (wet conditions) during B1, which accords with the literature (Mira et al., 2007; Rubio et al., 1997), and from 0.98 to 1.00 during B2.

As methanol is highly soluble in water (Sander, 2015), exchange can also depend on the methanol water-to-gas partitioning coefficient K_h. It was calculated with the parametrization used by Warneck (2006) by taking into account the soil surface temperature.

2.4. Soil exchange model

The dynamics observed at the LTO (Sec 3.2) suggested that methanol exchanges were ruled by physical adsorption and desorption (AD) processes. A dynamic model describing this process has been built by Laffineur et al. (2012) for a forest ecosystem and we adjusted it to the LTO soil flux data. In brief, methanol is exchanged by a diffusive process responding to Fick's law between the gas/liquid interface (represented by the subscript ‘aw’) and the ambient air (represented by the subscript ‘aa’). Depending on the concentration gradient between this interface and the ambient air, methanol is either emitted or captured by the aqueous phase. In addition, the model accounts for the capacity of the aqueous phase to retain methanol according to the methanol solubility and to the water volume in which methanol can dissolve (Eq (1), Fig. 5),

$$F = \frac{1}{R}(M_{aw} - M_{aa}) = \frac{1}{R}\left(\frac{q}{C} - M_{aa}\right) \tag{1}$$

where F is the methanol flux [μg m^{-2} s^{-1}], M_{aw} is the methanol concentration in the air at the water film surface (air/liquid interface) [μg m^{-3}], M_{aa} is the ambient methanol concentration [μg m^{-3}], R is the gas-phase resistance to the methanol transfer in the surface boundary-layer [s m^{-1}], q is the quantity of dissolved methanol [μg m^{-2}] and C is the capacity of the ecosystem (here, the soil) to store methanol [m^3 m^{-2}]. Note that in Eq (1), a positive F value corresponds to an emission, whereas a negative value corresponds to an uptake, similar to the convention applied for the measured flux (Sec 2.5). It should also be noted that in this model there is no methanol production or degradation term, meaning that methanol is stored and released only by the water films. We called this version of the model ‘AD’.

The quantity of methanol stored at time j, $q_{j,}$ depends on the quantity initially present in the soil $q_{j\text{-}1}$ and on the quantity that gets dissolved/re-emitted (Eq (2)),

$$q_j = q_{j-1} - F_j\,\Delta t \tag{2}$$

where Δt is the integration time (fixed here at 1800 s) and j represents successive time periods.

C depends on the methanol solubility and the water volume in which methanol is dissolved. It was estimated from the water to gas partitioning coefficient K_h, the rainfall P and the saturation deficit D_{SAT}, by relying on the parameterization used Laffineur et al. (2012) (Eq (3)),

$$C = K_h\left(\frac{C_{R0} + \sum_{j-480}^{j} P_j}{1 - exp^{-D_{SAT}/\alpha}}\right) \tag{3}$$

where C_{R0} and α are empirical parameters. R was determined empirically from the friction velocity u_*, by relying on the parameterization used by Laffineur et al. (2012) (Eq (4)),

$$\frac{1}{R} = A\,u_* \tag{4}$$

where A is an empirical parameter.

Ultimately, the model relied on three parameters: A, α and C_{R0}. It was calibrated with the flux measured during B1 and validated with the flux measured during B2. A and α were estimated separately from the measured flux, by applying the calibration procedure used by Laffineur et al. (2012). C_{R0}, which was a more sensible parameter, was estimated by minimizing the square root difference between the measured and estimated flux.

A comparison of modeled and experimental data (Sec 3.3.1) quickly led to the conclusion that an important source needed to be added to the ‘AD’ model. As the residuals between the measured flux and the flux estimated with this model were best correlated with the soil surface temperature (linear fit during B1, $R^2 = 0.24$, $p < .001$), this source was parameterized with T_S (0 cm) and was added to the 'AD' model (Eq (5), Fig. 5). The resulting model was called 'AD + source':

$$F = \frac{1}{R}(M_{aw} - M_{aa}) + \max(0,\ (a\,T_s(0\,cm) + b)) \tag{5}$$

As in the case of the 'AD' model, this model was calibrated with the data measured during B1, and validated with the data measured during B2. Initially, we used the values determined in the 'AD' model for A, α and C_{R0}. The parameters a and b were estimated by fitting a linear model between the residuals of the 'AD' model (B1) and T_S (0 cm). We then optimized all these parameters simultaneously by minimizing the square root difference between the measured and estimated flux. The values determined after optimization, however, remained close to those determined in the 'AD' model.

Both models being dynamic, they required an initial value for the dissolved methanol quantity $q_{(j\ =0)}$. This value was estimated by averaging the first four flux measurement data and the meteorological conditions under which these fluxes were measured, and then by inverting Eq (1) and Eq (5) for the 'AD' model and the 'AD + source' model, respectively. The models were re-initialized each time a gap larger than 1 day was observed for at least one environmental condition, in order to avoid a drift in the model caused by a mis-estimation of the missing meteorological variable(s). Such a gap occurred once in B1 and once in B2 (Fig. 2). The models were therefore initialized four times (i.e., once at the beginning of each measurement period, and once after each gap).

The fluxes were estimated every half an hour for both models. We averaged them every 2 consecutive hours before comparing them with the measured flux, in order to reduce the random noise induced by the sampling on the measured flux.

2.5. Flux sign convention

Whatever the scalar, a positive flux indicates an emission from the plant/ecosystem to the atmosphere, whereas a negative flux indicates an uptake. Unless another spatial scale is explicitly mentioned, it is always expressed per m^2 of soil.

2.6. Software

The statistical analyses, charts, model optimization and operation were all done using Matlab 2012b software and its statistical toolbox (Mathworks, Natick, MS, USA). The model was run with the *ode45* function, where the variable q was constrained to be non-negative. The parameters were optimized with the *fminsearch* function.

3. Results and discussion

3.1. Exchange rates

The methanol exchange rates ranged from −306 to 334 $\mu g\ m^{-2}\ h^{-1}$, with an average (± SE) of 35 ± 8 $\mu g\ m^{-2}\ h^{-1}$ for B1 and -9 ± 3 $\mu g\ m^{-2}\ h^{-1}$ for B2. This range and average were higher than those reported by forest and shrubland soil studies, but smaller than those observed on another bare agricultural soil (Table 1).

Small plants were present during both B1 and B2, but the emission rates measured at the LTO for both periods were too high to have originated from them.

The maize germinated during B1, but the maximal *LAI* value reached during that period was estimated at 0.01 $m^2\ m^{-2}$ (Bachy et al., 2016). It was shown that young maize leaves of the variety Prosil, the dominant variety grown at the LTO, emitted an average of 7.1 ± 0.8 $\mu g\ g_{DW}{}^{-1}\ h^{-1}$ for a PPFD of 600 $\mu mol\ m^{-2}\ s^{-1}$ and air temperatures ranging between 23 and 27 °C, for a specific leaf weight of 16.6 $g_{DW}\ m_{leaf}{}^{-2}$ (Mozaffar et al., 2017). The contribution of the maize leaves to ecosystem-scale emissions should therefore amount to 1.2 ± 0.1 $\mu g\ m^{-2}\ h^{-1}$. This is two orders of magnitude lower than the methanol exchange rates observed during B1 and B2 at the LTO under these environmental conditions (132 ± 32 $\mu g\ m^{-2}\ h^{-1}$). Roots can also emit methanol (Gray et al., 2014), although this has not yet been quantified for maize. The root biomass, however, amounted only to a few $g_{DW}\ m_{soil}{}^{-2}$ by the end of B1, so it is highly unlikely that the observed methanol emissions originated from them. The AD exchanges due to water film that might have been present on the young maize leaf surfaces were probably negligible due to their very low *LAI*. In addition, no strong uptake and re-emission processes, which would indicate such AD exchange mechanisms, were observed later on the fully developed maize. We can therefore reasonably assume that the young maize plants did not significantly contribute to the ecosystem-scale exchanges during B1.

The mustard seeds germinated during B2. If we divide the maximal methanol emission rates measured at the LTO for that period (Table 1) by the mustard biomass (between 0.01 and 0.03 $g_{DW}\ m^{-2}$), however,

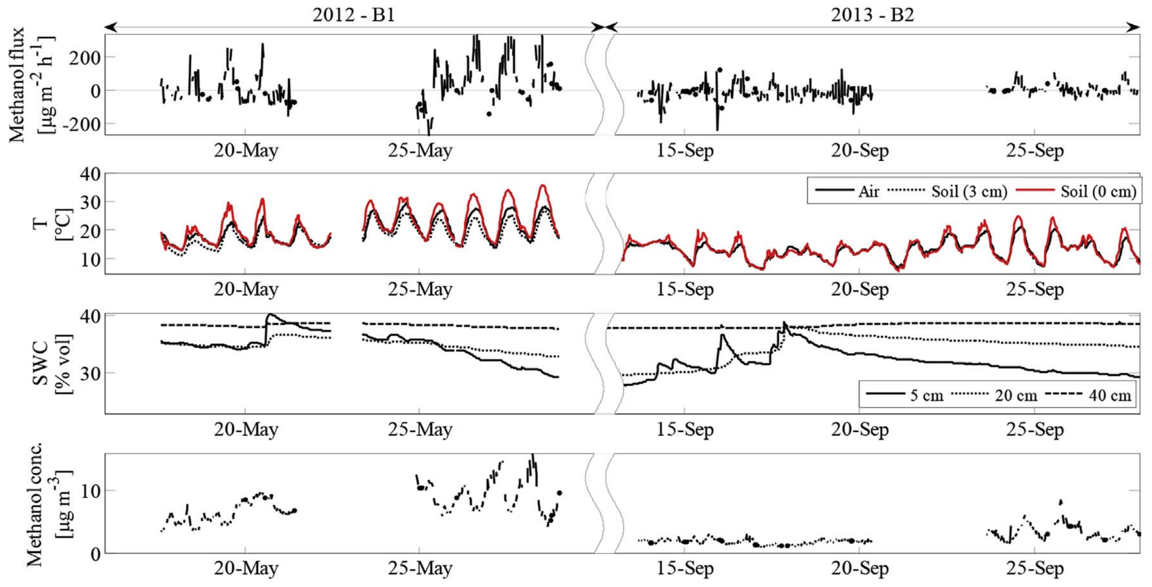

Fig. 2. Methanol flux and micro-meteorological conditions during the two bare soil measurement periods.

Table 1
Methanol flux range and average for bare soil on different ecosystems. ND stands for 'no data available'.

Soil type	Ecosystem	Temperature	Location	Measurement period	Technique	Flux [$\mu g\ m^{-2}\ h^{-1}$]						Authors
						Avg	±	SE	Min	–	Max	
Luvisoil	Cropland	13–28 °C	Belgium	May 2012 (12 days)	vDEC	35	±	8	−306	–	334	This study, B1
		6-21 °C		September 2013 (15 days)	(PTR-MS)	−9	±	3	−243	–	123	This study, B2
Cambisoil	Cropland	Warm	Germany	August 2003 (5 days)	EC (PTR-MS)				0	–	533 ± 30	Schade and Custer, 2004
Petrocalcic Calcixerept	Shrubland, no litter	5-30 °C	Spain	16 days (widespread)	*In situ* chamber (GC-MS)				−12	–	138	Asensio et al., 2008
Sandy	Subalpine forest, with roots	0-25 °C	Colorado (USA)	16 days	*In situ* chamber (PTR-MS)	1.71	±	1				Gray et al., 2014
	Subalpine forest, without roots					0.36	±	0.4				
Mediterranean mountain soil	Oak forest	10-35 °C	Laboratory (Mediterranean climate)	ND	Lab. chamber (PTR-MS)				−93	–	14.28	Asensio et al., 2007
Haplic podzol	Scot pine forest	−5–40 °C	Finland	May–November 2010 (194 days)	*In situ* chamber (PTR-MS)	7.2[b]			−14[b]	–	194[b]	Aaltonen et al., 2013
Loam (haploxeralf)	*Pinus ponderosa*	36 °C [a]	Sierra Nevada (USA)	ND	*In situ* chamber (GC-FID)						267 [a]	Schade and Goldstein, 2001
Cryptogamic soil	*Pinus ponderosa*, with litter	38 °C[a]	Colorado (USA)	June–July 2010 (36 days)	Gradient (PTR-MS)	1.3[c]			0	–	3	Greenberg et al., 2012

[a] Maximum value, taken from Peñuelas et al. (2014).

[b] Value taken from the chamber with the lowest vegetation coverage (9%).

[c] Average midday (10:00–17:00) flux.

we obtain methanol fluxes between 4100 and 12300 µg $g_{DW}^{-1}\ h^{-1}$. This is two to three orders of magnitude higher than the methanol fluxes values reported in the literature for diverse crops and grass species (~1–10 µg $g_{DW}^{-1}\ h^{-1}$) and therefore seems very unrealistic. Consequently, we can reasonably assume that the net methanol exchanges measured during B2 originated mostly from the soil.

Given that the plant contribution to the net methanol exchanges was very small during both B1 and B2, we assumed that the soil was the sole methanol reservoir for both periods, justifying the name 'bare soil' for those periods.

3.2. Dynamics

The average methanol exchange rate ($p < .001$) and its diurnal dynamics changed between B1 and B2. During B1, methanol emission was observed during the day, whereas methanol uptake occurred during the night (Fig. 1). This emission-uptake pattern persisted over several days and the emission amplitude increased during B1 (Fig. 2). In contrast, during B2, methanol uptake was observed both day and night, without any clearly visible dynamics. Daytime methanol emissions occurred at the end of B2, following an increase in temperature (Fig. 2). They always remained smaller than the methanol emissions observed during B1, however.

These differences resulted from differences in temperature rather than from different exchange mechanisms. B1 occurred in warmer conditions than B2 (Fig. 2, Table 1) and the relationships between methanol fluxes and environmental variables were similar during both periods (Fig. 3). We therefore merged the two measurement periods when we performed statistical analyses between the methanol fluxes and the environmental variables (Table 2).

We observed differences in flux dynamics with soil moisture. In order to illustrate it, we split the data into two soil moisture classes, named 'dry conditions' and 'wet conditions'. The value of 35.5% was chosen as the threshold soil moisture from flux dynamics analyses and in order to keep sufficient data in both classes.

Methanol was emitted under dry conditions (SWC [5 cm] < 35.5% vol), and these emissions correlated best with sensible heat fluxes and with a model that combined both air temperature and global radiation (Table 2). In our opinion, these correlations reflected the actual influence of soil surface temperature on the methanol fluxes. This variable varies with both air temperature and light (a bare soil surface is warmer than air during the day because it is radiatively heated). In line with our hypothesis, the methanol fluxes correlated very well with the modeled T_S (0 cm) at LTO, with which they exhibited an Arrhenius type relationship (Table 2, Fig. 3-a). The corresponding activation energy Ea was estimated at 61 ± 18 kJ mol^{-1}. The methanol fluxes were also well correlated linearly with the inverse of the solubility coefficient $1/K_h$. This relationship was expected, however, because $1/K_h$ was calculated from T_S (0 cm) and follows an Arrhenius type relationship with this variable.

Under wet conditions (SWC [5 cm] ≥ 35.5% vol), methanol uptake was observed. It correlated best negatively with methanol concentration (Table 2, Fig. 3-b).

Overall, the relationships and dynamics observed at the LTO accorded well with findings reported from other soil studies. Schade and Custer (2004) had observed methanol emissions on a bare agricultural soil and under dry conditions. As in our study, the fluxes followed clear diurnal dynamics and were very well correlated with sensible heat fluxes (linear function) and with soil surface temperature (Arrhenius function). Our activation energy Ea derived from this Arrhenius expression was in the range of values reported by these authors for diverse soil sites (which spanned from 21 to 82 kJ mol^{-1}), and did not significantly differ from the value estimated by these authors for their agricultural soil (48 ± 3 kJ mol^{-1}, mean ± CI at 95%). Methanol emissions also increased with temperature and under dry conditions in a study reported by Asensio et al. (2008), which was conducted on a

Table 2
Statistics resulting from the regression analyses between soil methanol flux and diverse environmental variables (B1 and B2). The symbols indicate the slope of the relationship (when it is significant). The number of symbols indicates the significance of the relationship. One symbol corresponds to a p-value between 0.05 and 0.01, two symbols to a p-value between 0.01 and 0.001, and three symbols to a p-value below 0.001. ns stands for not significant. Dry and wet conditions were defined for *SWC* (5 cm) below and equal to or above 35.5% vol, respectively. The best determination coefficients are marked in bold.

Soil moisture	Fitted function	Statistics	T_A	T_S (3 cm)	T_S (0 cm)	$1/K_h$	*SWC* (5 cm)	MeOH conc.	R_G	H	u_*	$T_A + R_G$
Dry	Linear	Significance	+ + +	+ + +	+ + +	+ + +	ns	+ + +	+ + +	+ + +	+ + +	+ + +
		R^2	0.37	0.43	0.45	**0.50**		0.10	0.42	**0.49**	0.04	**0.48**
	Arrhenius	Significance	+ + +	+ + +	+ + +							
		R^2	0.44	0.43	**0.51**							
Wet	Linear	Significance	–	ns	–	–	+	**—**	–	ns	ns	
		R^2	0.25		0.22	0.22	0.06	**0.32**	0.08			

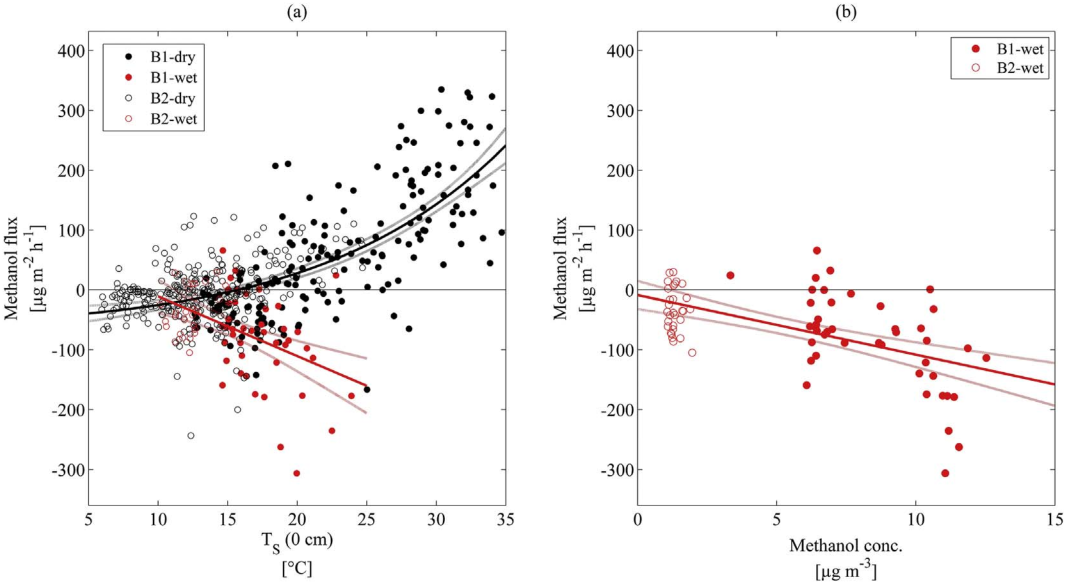

Fig. 3. Methanol flux against soil surface temperature (a) and methanol concentration (b). Dots are the observations. Solid lines represent the fit of the observations for dry and wet conditions, respectively (B1 and B2 merged), with an Arrhenius function (a – dry) or a linear function (other curves). Dotted lines are their confidence interval (α = 0.05). Dry and wet conditions were defined for *SWC* (5 cm) below and equal to or above 35.5% vol, respectively.

partially covered calcic loamy soil without litter, and in studies described by Gray et al. (2014) and Greenberg et al. (2012), which were conducted on a forest soil. Methanol uptake when the soil was wet has been reported in several BVOC studies (Asensio et al., 2007; Kalender and Akosman, 2004; Schade et al., 2010).

In contrast, we did not observe methanol emission bursts after rain events, as reported by Greenberg et al. (2012). These authors suggested that these bursts occur because the sudden increase in soil moisture activates micro-organisms. At the LTO, methanol uptake was observed during wetter periods, and we therefore concluded that these effects were not predominant at our site. This is maybe due to the small litter content at our site. Indeed, the experiment of Greenberg et al. (2012) was conducted on litter. The latter hypothesis should however be confirmed by doing comparative flux measurements on soils with different amounts of litter.

3.3. Sources, sinks and mechanisms

The following methanol sources and sinks have been highlighted or proposed in the literature: abiotic production through SOM degradation (Schade and Custer, 2004), (a)biotic production from the litter (Gray et al., 2010; Gray and Fierer, 2012; Ramirez et al., 2009), and consumption by methylotrophic micro-organisms (Asensio et al., 2007; Ramirez et al., 2009). In addition, because methanol is water soluble, bi-directional methanol exchanges can thus occur between the water phase of the soil and the atmosphere without the presence of any source or sink. That mechanism was called “adsorption and desorption” (Laffineur et al., 2012) and shortened by AD in this paper.

As we will discuss later on, we argue that the methanol fluxes were likely driven by AD mechanisms and by a source.

3.3.1. Physico-chemical exchanges by AD

Both the bi-directional exchange dynamics and the relationships observed at the LTO were consistent with physical adsorption and desorption (AD) mechanism (Laffineur et al., 2012). According to this mechanism, methanol uptake is favored when the soil surface temperature is low or when the soil is wet because the capacity of the ecosystem to dissolve methanol is high. In contrast, dry and warm conditions favor methanol emission by outgassing, because of a decrease in this capacity. These dynamics match those observed at the LTO, where emissions were reported during warm and dry events, whereas small uptakes occurred during wet and/or cold events (Sec 3.2). In addition, methanol fluxes correlated best positively with soil surface temperature (and thereby $1/K_h$) for dry conditions (Fig. 3-a), but best negatively with the ambient methanol concentration when the soil was wet (Fig. 3-b). This is consistent with the equations that rule AD (Eq (1), Eq (2)). $1/K_h$ follows also an Arrhenius function with temperature, with an “activation energy” value of 44 kJ mol^{-1} for methanol which does not significantly differ from the Ea value estimated at LTO (61 ± 18 kJ mol^{-1}).

We therefore compared three models. The first model, ‘AD’, included only the methanol adsorption and desorption processes. In the

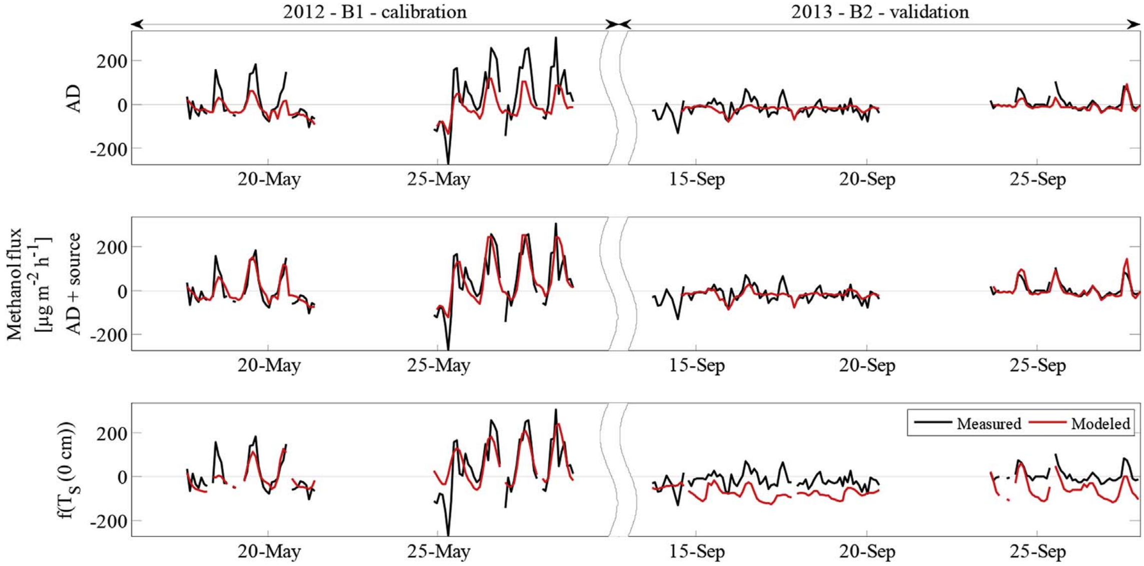

Fig. 4. Ability of the AD models (with or without source) and of the model made of an Arrhenius function with soil surface temperature, f(T_S (0 cm)), to reproduce the methanol exchange dynamics observed at the LTO during B1 and B2 (2 h averaged fluxes).

second model, 'AD + source', an additional methanol source was added to these processes. As the residuals between the fluxes estimated with the 'AD' model and the measured fluxes correlated best linearly with the soil surface temperature, a linear dependence of this source on that variable was put forward in the model (Sec 2.4). The third model, 'f(T_S (0 cm))', consisted of a simple static Arrhenius function of soil surface temperature. We chose this variable and this function because they correlated best with the measured fluxes (Table 2).

Each model was calibrated with the flux data measured during B1 and validated with the flux data measured during B2. The 'AD' models (with or without source) are described in Sec 2.4, where details on the parameter optimization procedure are also given. The parameters of the 'f(T_S (0 cm))' model were adjusted with a non-linear regression model. The statistics associated with each model are given in supplementary material (Table A1).

The 'AD + source' model reproduced best the bi-directional methanol exchange dynamics observed at the LTO (Fig. 4) and had the highest R^2 values for both B1 and B2 (Table A1). The modeled fluxes were not biased during B1, whereas the model slightly over-estimated them during B2. In contrast, the 'AD' model under-estimated the methanol fluxes for both B1 and B2. The 'f(T_S (0 cm))' model reproduced the dynamics observed during the warm period of B1 (i.e., after 25 May 2012) quite well, but its simulation of the uptake events was poor. Therefore, even if the flux was not biased, the determination coefficient between the measured and predicted fluxes was lower than that observed for the two other models. Its estimate of the methanol exchange during B2 was also poor.

Ultimately, only the 'AD + source' model was able to reproduce the methanol exchange at the LTO properly. We therefore suggest that these exchanges were driven by two combined processes: methanol emission from a source driven by the soil surface temperature, and uptake-outgassing effects between the methanol reservoirs present in the soil and the atmosphere. The source strength should have varied between 0 and 147 $\mu g\ m^{-2}\ h^{-1}$ (average: 26 ± 2 $\mu g\ m^{-2}\ h^{-1}$), with an average contribution to the net methanol exchange of 29 ± 1%. As it was correlated with the soil surface temperature, it should be located at or near the soil surface.

3.3.2. Abiotic production from SOM

Abiotic methanol production was proposed by Schade and Custer (2004) as the most plausible hypothesis to explain methanol exchanged between an agricultural soil and the atmosphere. Indeed, abiotic carbon degradation follows an Arrhenius function with the temperature (Schade and Custer, 2004).

The flux dynamics reported in their study was very similar to ours, with the same dependance to soil surface temperature than that observed at LTO, and an activation energy value not significantly different from the one estimated at our site. We also showed that an Arrhenius-type equation was able to reproduce the methanol emissions observed during the warm events (Fig. 4).

Nevertheless, although we do not completely discard their hypothesis, we have some reservations about the importance of abiotic SOM degradation at our site. Indeed, the rate of carbon photo- (King et al., 2012) and thermo-degradation (van Asperen et al., 2015) is higher in warm climatic zones with high amounts of UV-B light (Monson and Baldocchi, 2014), typically tropical areas (King et al., 2012), Mediterranean or arid zones (Monson and Baldocchi, 2014) and on soils with dicot residues (King et al., 2012) and high C/N ratio (King et al., 2012). It is thus expected to be low at LTO, given that the site is located in a temperate climatic zone, that the crop harvested before both B1 and B2 was winter wheat, a monocotyledonous species, and that the C/N ratio of the site is below 10. In addition, the LTO soil contained low amounts of SOM, and SOM degradation is even lower in clay and silt rich soils like the LTO soil (both textures represented indeed 90% of the soil mineral fraction), because it is adsorbed on the soil particles (Six et al., 2002). All these arguments reinforce the hypothesis of small abiotic SOM degradation.

As a consequence, we should expect lower methanol emissions from our site than from sites located in Mediterranean areas and with a higher SOM content, like the experimental site used for the methanol measurements by Asensio et al. (2008). However, we reported higher methanol emission rates from our site (Table 1). For that reason we think that is quite unlikely that the observed methanol emissions resulted solely from abiotic carbon degradation.

3.3.3. (A) Biotic production from the litter

Several studies have reported biotic and abiotic methanol emissions from the soil caused by the degradation of plant residues (Bäck et al., 2010; Gray et al., 2010; Gray and Fierer, 2012), including crop species (Gray et al., 2010; Gray and Fierer, 2012). These litter-induced BVOC emissions, however, among which methanol is the main compound emitted, decrease exponentially over time to become negligible less than 20 days after the litter generation, independently of the litter-induced CO_2 emissions (Gray and Fierer, 2012). Because both B1 and B2 occurred several weeks or months after the winter wheat harvest and stubble breaking, this emission source could be ruled out. One could argue that the experiments reported by Gray and Fierer (2012) were conducted in the laboratory and that the soil was undisturbed throughout their experiment. In contrast, at the LTO the soil was tilled at a depth of 10 cm some days before both B1 and B2, in order to prepare the seedbed, and in particular 3 days before the beginning of B1. Some crop residues could therefore have been brought to the soil surface after the tillage, and released methanol. This scenario implies, however, an exponential decrease in methanol emission amplitude throughout B1. The opposite trend was observed at the LTO (Fig. 2) and we therefore concluded that the methanol emissions observed at our site did not result from litter decomposition.

3.3.4. *Production by pectinolytic micro-organisms*

Micro-organisms that produce the pectinesterase enzyme are able to demethylate the pectin contained in plants or litter (Jayani et al., 2005). By doing this, they produce methanol. However, pectinolytic micro-organisms are rather plant pathogens (Hayat et al., 2010; Jayani et al., 2005) or micro-organisms present in the litter (Gray et al., 2010; Ramirez et al., 2009). Therefore, they were not likely present at LTO, which is conventionally managed and is therefore protected against plant pathogens.

3.3.5. *Consumption by methylotrophic micro-organisms*

Methylotrophs comprise the group of micro-organisms (mostly aerobic bacteria) which are able to consume C1 compounds as the sole source of carbon and energy (Kolb, 2009). Most of them are able to grow on methanol (Kolb, 2009), even under ambient concentrations (Stacheter et al., 2013). In addition, more than 70% of them are facultative, i.e. they are able to consume other carbon sources (Kolb, 2009). The methylotrophic bacteria belong to the classes α-Proteobacteria, β-Proteobacteria, ϒ-Proteobacteria (in particular the Methylbacterium spp), Verrucomicrobia, Firmicutes and Actinobacteria (Chistoserdova, 2011; Eyice and Schäfer, 2015; Kolb, 2009; Stacheter et al., 2013). Most identified methylotrophic species belonging to the α-Proteobacteria, β-Proteobacteria, ϒ-Proteobacteria and Actinobacteria classes are mesophilic (Kolb, 2009). They can thus potentially be found in temperate soils like LTO.

According to Kolb (2009), most studies performed on methylotrophic bacteria were done in the lab, so that little is known about their ecological niches in the soil. To our knowledge, two studies focused on environmental driving factors of methanol oxidation by soil micro-organisms (Morawe et al., 2017; Stacheter et al., 2013). It was found that the soil methylotrophic community varied with vegetation type (Stacheter et al., 2013) and pH (Morawe et al., 2017; Stacheter et al., 2013), even if methylotrophs were found for diverse vegetation types and broad pH ranges. Furthermore, the methanol oxidation activity was more important under the presence of roots (Stacheter et al., 2013). This latter finding is supported by the study of Asensio et al. (2007) who measured higher methanol uptakes from root-containing soil and concluded that rhizospheric micro-organisms should consume methanol. It is also in agreement with the study of García-Salamanca et al. (2013) who reported a much higher abundance of Proteobacteria, in particular of ϒ-Proteobacteria, from the maize rhizosphere than from the bulk soil.

At LTO, net methanol uptakes were observed from bare soil. Because the methylotrophic activity seems to be enhanced by the presence of roots, it was thus probably limited for these periods. For that reason we argue that the uptakes were more likely driven by 'AD' mechanisms. In addition, the field was fertilized a few days before the beginning of the B1 stage. Fertilizer application favors the development of nitrifying bacteria against other micro-organisms including methylotrophs. Consequently, N addition is conducive to modify the methanotroph community and to decrease its importance, and thereby to decrease methanol consumption by the soil. For that reason we argue that the uptakes were more likely driven by 'AD' mechanisms. Measurements of the microbiological composition and of the effect of N on methanol consumption are however needed to confirm this.

3.3.6. *Presumed mechanism(s)*

In conclusion, the good agreement between the fluxes and the 'AD + source' model and the confrontation of our results with the literature led to the conclusion that the methanol exchanges at LTO were likely driven by 'AD' mechanisms combined with a source. Our experimental set-up did not allow us to draw firm conclusions about the physical or biological origin of the methanol source, though. Indeed, by confronting our data with the literature, we had some reservations about the sources proposed in the literature. It is possible that other (unknown) methanol sources were present, but it is also possible that, even if the sources proposed in the literature were expected to be minor at the LTO, they acted conjointly and resulted in non-negligible methanol emission from the soil. We therefore prefer not to draw any conclusions about the origin of the methanol source at our site and would advise that future BVOC studies on agricultural soils include ancillary analyses apart from methanol flux measurements, such as soil microbial composition analyses or abiotic SOM degradation analyses, in order to constrain it.

3.4. *Effect of vegetation on soil exchanges*

When the plants grew, the methanol reservoirs present in the ecosystem became multiple (Fig. 5). Apart from the soil (Fig. 5 – pathways 1–3), the plants exchanged methanol (Fig. 5 – pathways 4, 5 and 7). In addition, methylotrophs may have appeared on the maize leaves (Fig. 5 – pathway 6) and consumed methanol (Farré-Armengol et al., 2016; Iguchi et al., 2015; Kutschera, 2007). With the methanol fluxes measured at the LTO being net exchanges, and the maize leaves emitting methanol (Mozaffar et al., 2017), it was not possible to quantify soil exchanges during the maize growing season accurately. When we compared the net methanol exchange rate measured on the bare soil to that measured during the maize growing season, however, we were able to conclude that the soil methanol emissions decreased when the maize developed. When the weather conditions were warm (T_A between 25 °C and 30 °C) and dry (*SWC* [5 cm] < 35.5% vol), no significant difference in exchange was observed between the bare soil and various maize phenological stages ($p = 0.288$ when the soil exchanges were compared with those of stage S, and $p = 0.054$ when compared with those of stage R1; the L and R2 periods were not compared with the bare soil periods because of a lack of data on the selected weather conditions). For these weather conditions, net methanol uptake by the plants is very unlikely because maize leaves emit methanol during the day (Mozaffar et al., 2017) and because the water film likely to be present on the maize surfaces should have re-emitted rather than taken up methanol. Therefore, the fact that the methanol exchange rate was similar during the day in the presence and absence of plants can be explained either by a decrease in soil methanol emissions when the plants developed or by the apparition of phyllospheric micro-organisms.

The reason for this decrease needs to be further evaluated. The most plausible hypothesis is that the soil surface temperature was dampened by the vegetation (Fig. 5 - pathway 1), so that the amplitude of the methanol source and possible methanol outgassing was reduced. In addition, a methanol sink might have appeared when the maize developed (Fig. 5 - pathway 3). The presence of this sink could explain why no significant exchange was observed during the night for stages S and R1 (Fig. 1), although it was warm and dry during these periods and therefore soil emissions were expected. Rhizospheric (i.e., organisms whose activity is enhanced by the development of roots [Hargreaves et al., 2015]) methylotrophic micro-organisms might then have caused this sink. This was proposed by Asensio et al. (2007) to explain an increase in soil methanol uptake in the presence of vegetation, and several studies have shown an higher abundance of these micro-organisms

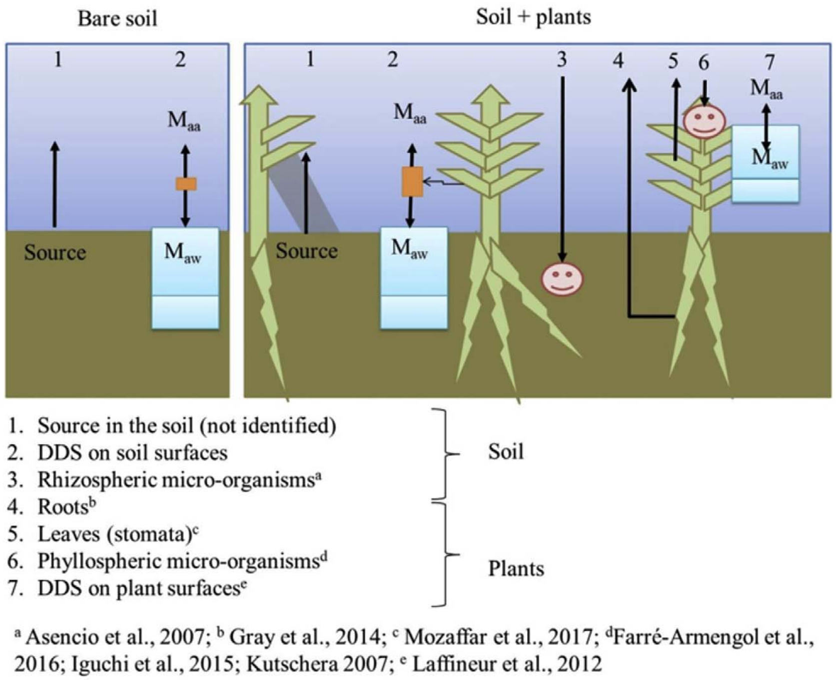

Fig. 5. Left: methanol exchange pathways identified at the LTO between a bare soil and the atmosphere. Right: possible methanol exchange pathways for an ecosystem with plants, based on the exchange pathways determined at the LTO for the soil and on the pathways described in the literature.

in the rhizosphere than in the bulk soil (Sec 3.3.5). The microbiological composition reported by these authors, however, might differ from the one that actually occurred at the LTO, given the differences in the sites and maize varieties. Microbiological analyses would therefore be needed to confirm the presence of this sink. Third, the development of the plant canopy might have significantly increased the aerodynamic resistance to methanol transfer between the soil and the atmosphere (Fig. 5 - pathway 2) and thereby reduced the soil methanol exchanges by AD (hence the methanol outgassing when the weather conditions were warm and dry).

4. Conclusions

This study investigated methanol fluxes from a temperate bare agricultural soil. Methanol emission occurred under dry and warm conditions, whereas methanol uptake was observed under colder and wetter conditions. Fluxes correlated best positively with soil surface temperature under dry conditions, but best negatively with methanol concentration under wet conditions.

The dynamics observed at our site were well reproduced by a model that included both a methanol source and methanol adsorption and desorption mechanisms. We propose that the exchanges were ruled by both a methanol source near or at the soil surface, driven by soil surface temperature, and by physical deposition and outgassing processes. Future work is needed to identify this source and to localize the methanol reservoirs. This work could include abiotic carbon degradation analyses coupled with microbiological analyses and with methanol concentration measurements in the soil water at different times and depths.

In our study the soil methanol emission decreased when the vegetation developed. More experiments are needed to evaluate the reasons for this decrease, but this observation suggests that the vegetation could have affected the methanol exchange from the soil. This implies that the soil exchange model established at this site for the bare soil periods in this study cannot be extended to the vegetation periods.

Overall, the dynamics observed at the LTO were similar to those reported by studies investigating both agricultural and forest soils. The mechanisms identified in this study could probably therefore be extrapolated to other cropland sites or ecosystems. In contrast, we did not observe the methanol emission bursts after rain events (instead, methanol was taken up by the soil) that had been reported in some studies, and concluded that this effect did not apply at our site. Future studies should investigate these events to better understand where the methanol emission bursts occur.

Finally, the methanol exchange rates reported at the LTO were higher than the fluxes reported for soil in different ecosystems and lower than those reported for other croplands. This suggests that cropland soils are more important methanol exchangers than other kinds of soil, and should therefore be more intensively investigated.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2017.12.016.

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