Disentangling soil from plant methanol exchanges in a maize field: a first step

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Context :

- Maize is the second most important crop in the world, but maize BVOCs exchanges have been poorly studied (Das et al, 2003; Graus et al, 2011, Bachy et al., 2016).
- Maize emits mainly methanol (Graus et al, 2011, Bachy et al., 2016).
- At ecosystem-scale (Figure 1), methanol exchange rates of the same order of magnitude on bare soil (B1) as on developped vegetation (B2) (Bachy et al., 2016) ↔ soil exchanges are smaller than plant exchanges (Penuelas et al., 2014).

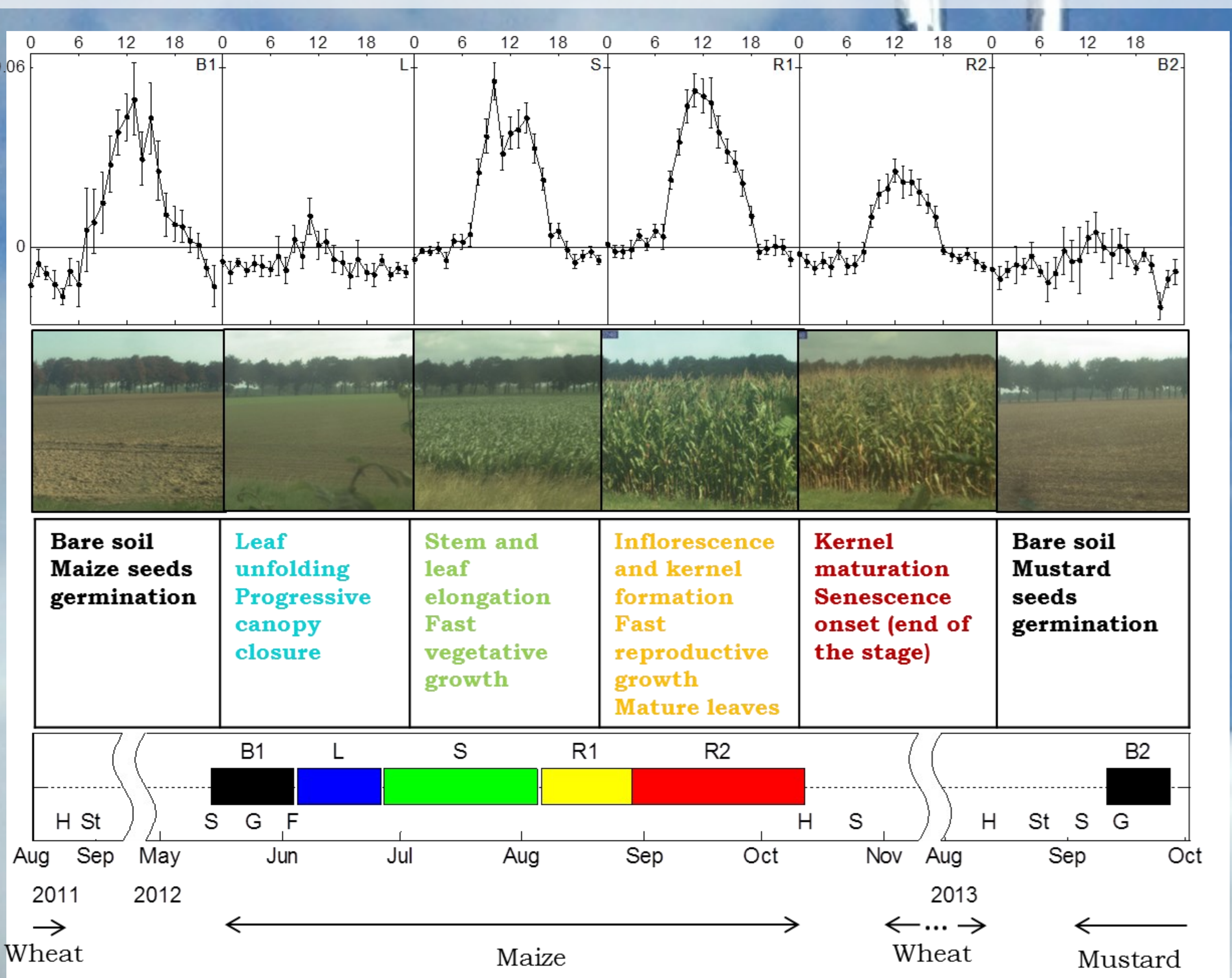

Figure 1. Top panels: methanol fluxes circadian dynamics on bare soil (B1 and B2) and for each main maize developmental periods (L to R2). Middle picture and table: brief description of each stage. Bottom panels: temporal frame of measurement campaigns, divided by phenological periods. The letters indicate major events in the crop growing season: H = harvest, St = ploughing and stubble breaking, S=sowing, G = germination, F = fertilisation.

→ Why were the methanol emissions similar on bare soil and on developped vegetation?

- Did maize actually emit methanol ?
- If so, why did the soil exchanges reduce along the growing season ?

Comparison of methanol exchanges measured from maize leaves in controlled chambers (Mozaffar et al., 2016, poster presented at this GRC) and measured at ecosystem-scale, so including both soil and plants (Figure 2) :

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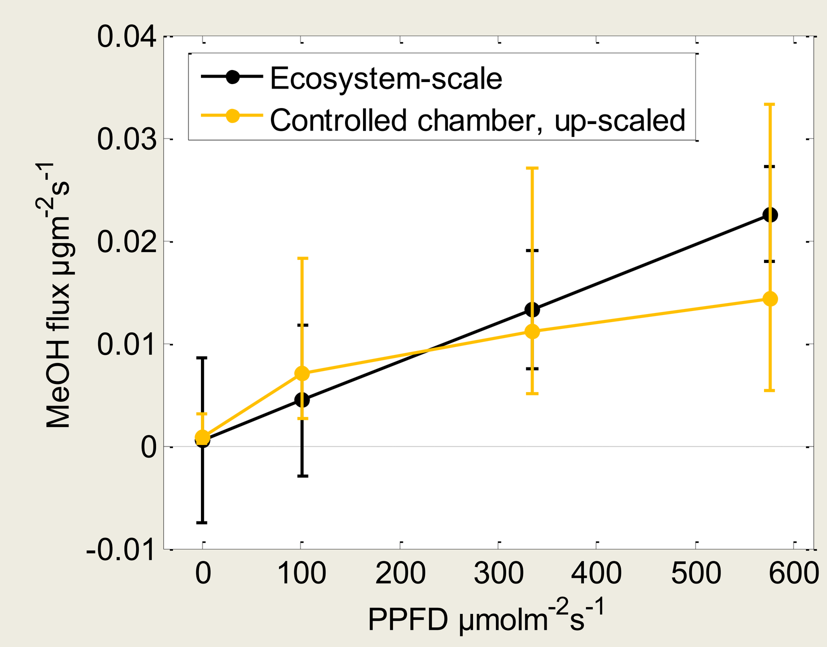


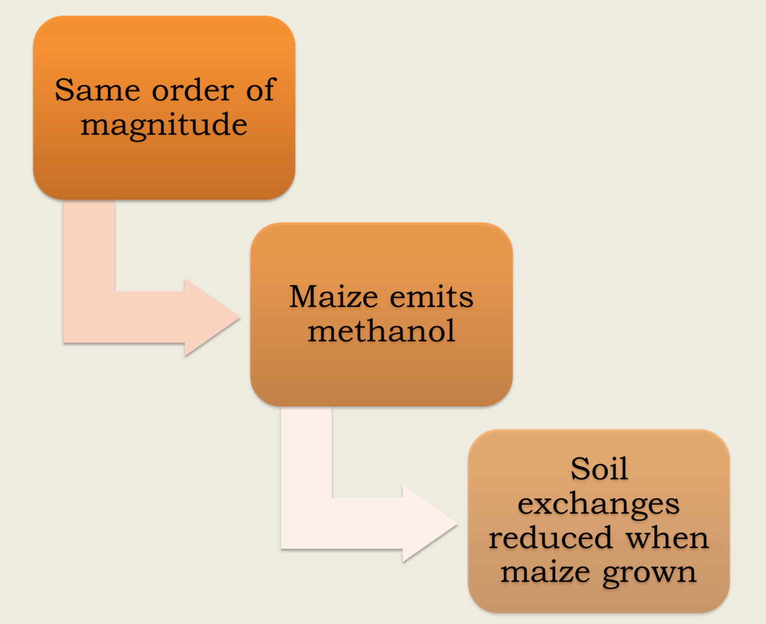


Figure 2. Comparison between methanol fluxes measured on the maize field when leaves were mature (R1), and on mature maize leaves directly (controlled chamber). Temperature ranged between 24 and 27°C for both experiments. Average methanol fluxes for ecosystem-scale were estimated by first drawing a linear relationship between methanol fluxes and PPFD (R^2=0.41), and then by predicting the methanol fluxes for the prescribed PPFD values. Error bars indicate the 95% confidence interval of the prediction. For chamber experiment, error bars correspond to the standard mean error. LAI of 5.06m^2m^{-2} was used for up-scaling, in accordance with LAI value measured in the field during the stage R1.

Maize emits methanol

Our hypothesis about soil methanol emission decrease when the maize developed:

3 Canopy → Less light reaching the soil surface → Decrease in mid-day surface T → Less soil methanol emissions

2 Soil emissions vary with surface T

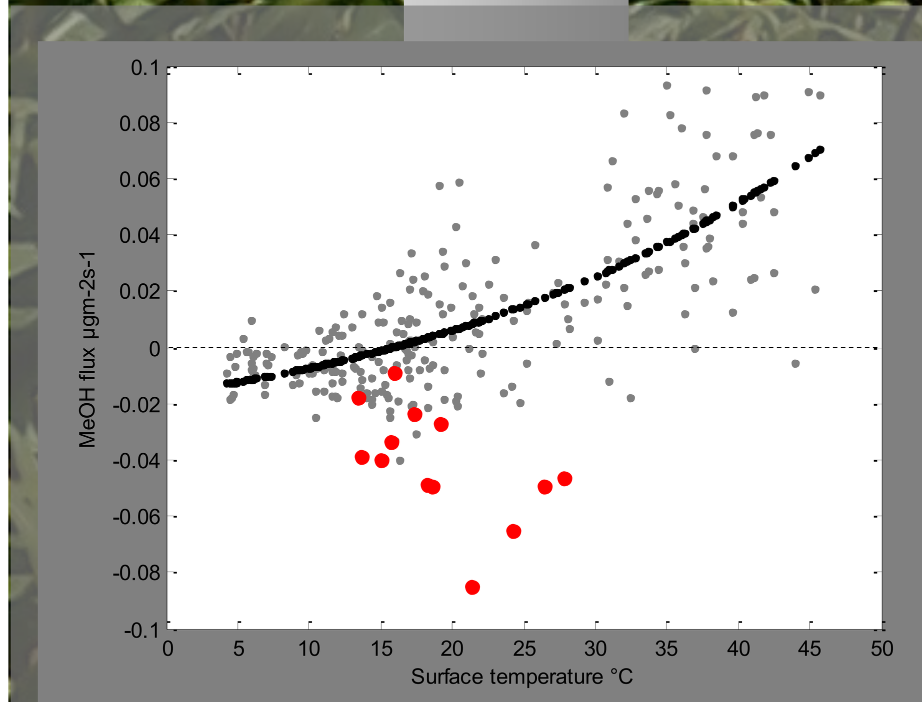
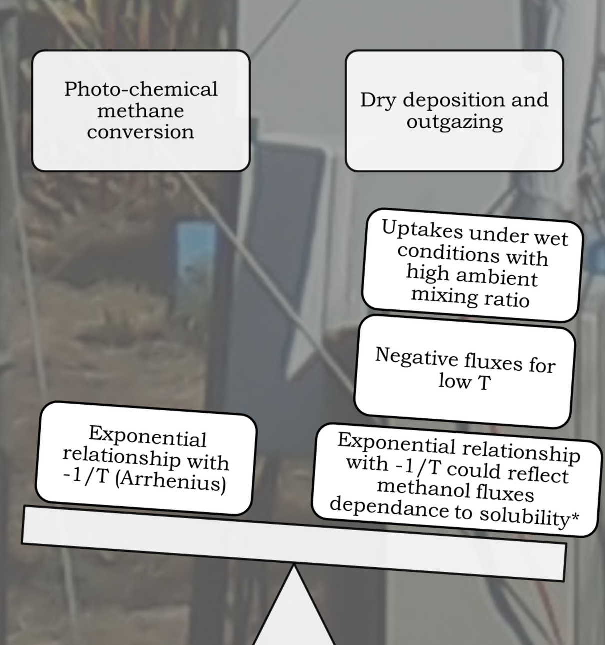


Figure 3 Relationship between surface temperature (estimated from sensible heat fluxes) and methanol fluxes measured on bare soil (B1 + B2). Grey dots: raw data; Line: fit to the Arrhenius equation. (R^2=0.63, Ea=30 $kJmol^{-1}$); Red dots: wet data with high ambient mixing ratio, not used for the fit.

- Bare soil methanol emissions during the day and under warm conditions (Figure 1, compare B1 which occurred under warmer conditions than B2).
- Exponential relationship (Arrhenius shape) between bare soil fluxes and the surface temperature (Figure 3, grey dots) :
- Relationship already observed on another agricultural soil (Schade et al., 2004) during a heat wave event. However, in contrast with their study, methanol uptakes were observed for low surface temperatures. In addition, when ambient mixing ratio were high and the soil wet, methanol fluxes did not follow the exponential relationship anymore (**red dots**).

→ Mechanism: Schade et al. (2004) proposed that methanol resulted from methane converted photo-chemically into methanol. We argue that dry deposition and physical outgazing (Laffineur et al., 2012) could also explain the observed pattern.



* Relationship between methanol solubility and methanol dry deposition/outgazing :

The methanol solubility coefficient Kh is an exponential function of 1/T (Laffineur et al., 2012, Eq 1). Then, the rate of methanol exchanged by dry deposition is inversely proportional to the ecosystem capacity to store methanol, the latest depending directly on Kh (Laffineur et al., 2012, Eq. 2). Consequently, methanol fluxes exchanged by deposition/outgazing are inversely proportional to Kh, and can thus be expressed as an exponential function of -1/T.

$$Kh = K_1 e^{K_2/T} \quad \text{(Eq. 1)}$$

$$Flux = \frac{([MeOH]_{in}-[MeOH]_{out})}{R_a} = f([MeOH]_{in}) = f\left(\frac{C_{MeOH,dissolved}}{Capacity}\right) = f\left(\frac{C_{MeOH,dissolved}}{Kh * f(Moisture)}\right) \Rightarrow Flux \sim \frac{1}{Kh} = \frac{1}{K_1 e^{K_2/T}} = \frac{1}{K_1} e^{-K_2/T} \quad \text{(Eq. 2)}$$

Future outcomes

Quantify the surface temperature under the presence of plants (with a radiative model) to estimate soil exchanges and deduce plant exchanges

About ...

Experimental set-up:

Ecosystem-scale:

- **Site: Lonzée Terrestrial Observatory (ICOS candidate site, Belgium)**
- **Soil type: silt loamy**
- **Flux meas: DEC-MS (+ PTR-MS for BVOC mixing ratio)**
- **Campaigns: 5 months on maize (incl. 2 weeks on bare soil: B1) and 3 weeks on bare soil (B2). Both campaigns followed winter wheat culture.**

Chambers experiments :

- **Controlled conditions (T, PPFD,...), maize of Prosil variety studied at 3 distinct growing stages (young, mature, senescent), soil covered to remove any possible soil methanol emission. More details in the poster of Mozaffar et al. presented at this GRC.**

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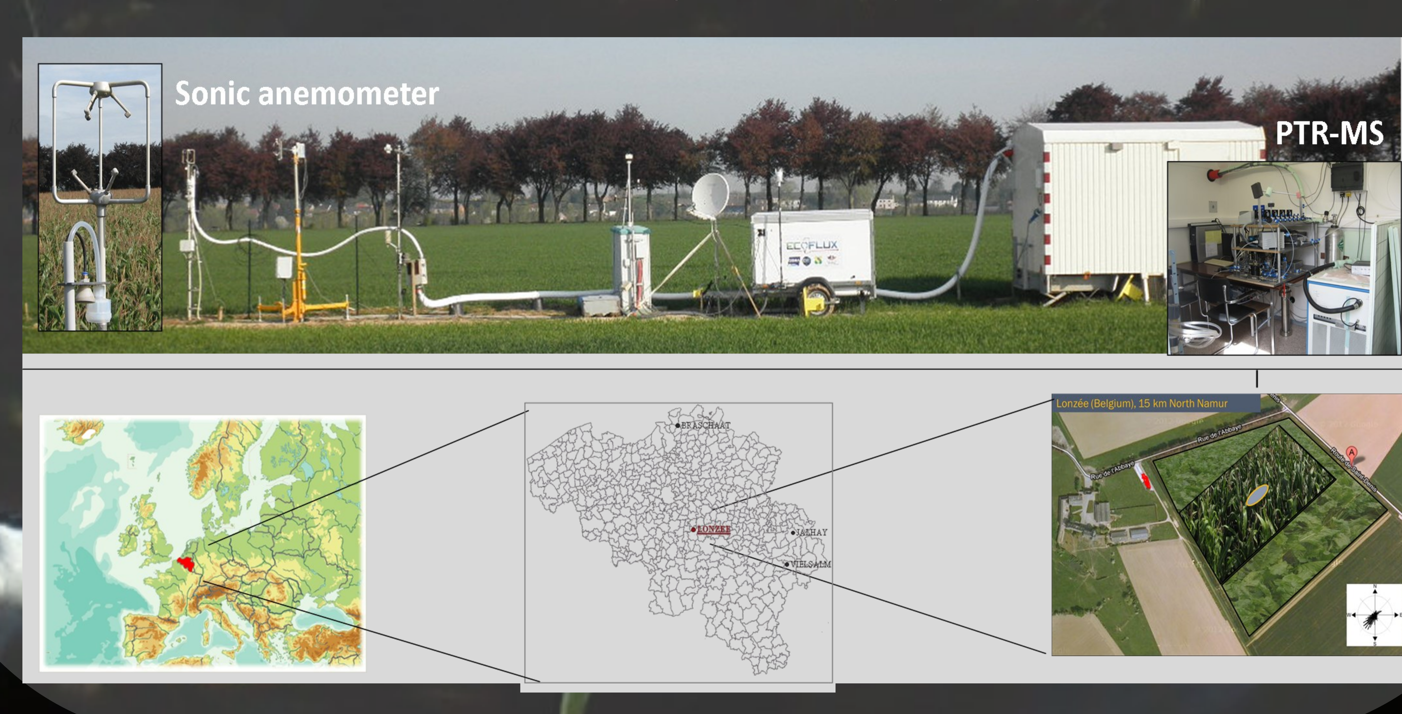

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