Biotic, abiotic and management controls on methanol fluxes above a temperate mountain grassland

Lukas Hörtnagl[1], Ines Bamberger[2], Martin Graus[2], Taina Ruuskanen[2], Ralf Schnitzhofer[2,3], Markus Müller[2,3], Armin Hansel[2], and Georg Wohlfahrt[1]

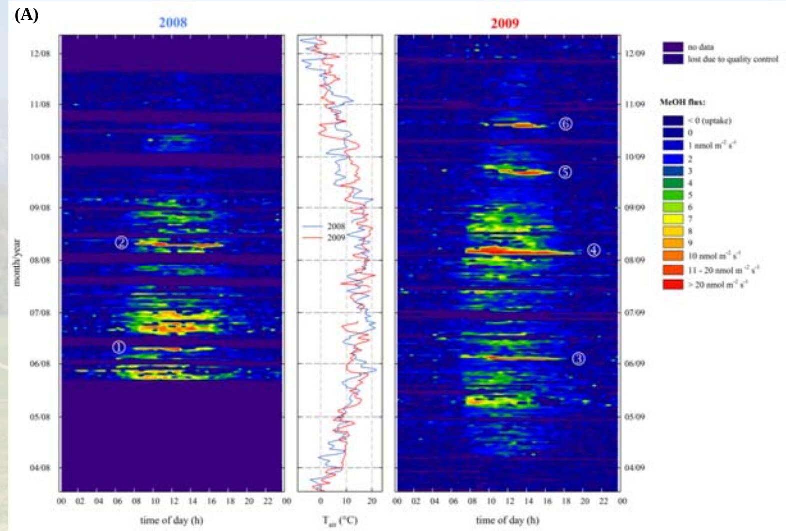
[1] University of Innsbruck, Institute of Ecology, Innsbruck, Austria (lukas.hoertnagl@uibk.ac.at) | [2] University of Innsbruck, Institute of Ion Physics and Applied Physics, Innsbruck, Austria | [3] currently at: IONICON ANALYTIK, Innsbruck, Austria

BACKGROUND Methanol is the second most abundant organic gas in the atmosphere after methane and represents a significant global source of tropospheric carbon monoxide and formaldehyde and is thought to play a minor but non negligible role in tropospheric chemistry through reducing concentrations of the hydroxyl radical.

MeOH is thought to be released mainly as a by-product of pectin demethylation during leaf growth in green plants (Fall and Benson, 1996), resulting in significant seasonal variations in methanol emissions. In accordance with these findings, MacDonald and Fall (1993) reported high emission rates for young leaves. Methanol emissions are temperature and light dependent, further the stomatal opening plays an important role in observed emission patterns. Stomata can constrain the emission of more soluble compounds like methanol over a longer time period than the emission of less water soluble volatiles, resulting in a direct effect of stomatal conductance on the efflux rate of methanol.

It was previously hypothesised that (i) stomatal conductance and plant growth play a key role in the emission of methanol, (ii) methanol fluxes increase with air temperature, and (iii) during cutting (leaf wounding) events and during drying high amounts of methanol are emitted into the atmosphere.

METHODS Methanol fluxes were measured above a managed, temperate mountain grassland in Stubai Valley (Tyrol, Austria) during two growing seasons (2008 and 2009). Half-hourly flux values were calculated by means of the disjunct eddy covariance method using 3-dimensional wind-data of a sonic anemometer and mixing ratios of methanol measured with a proton-transfer-reaction-mass-spectrometer (PTR-MS). The surface conductance to water vapour was derived from measured evapotranspiration by inverting the Penman-Monteith combination equation (Wohlfahrt et al., 2009) for dry canopy conditions and used as a proxy for canopy−scale stomatal conductance.



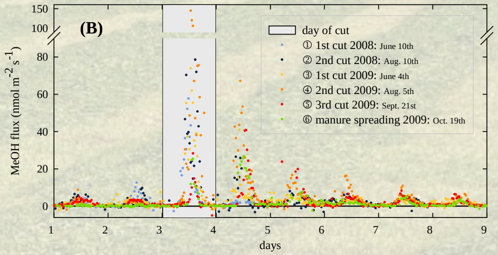


Figure 1 (A) MeOH fluxes during the measurement campaign in 2008 and 2009, T_{air} is shown as daily average temperature. **(B)** MeOH emissions before, during and after management events, colored points represent half-hourly fluxes.

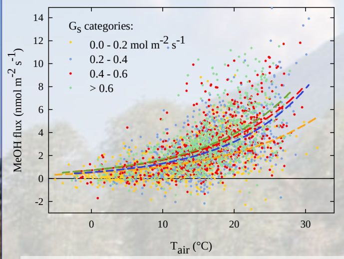


Figure 2 MeOH flux as a function of air temperature (T_{air}), colors illustrate different classes of ecosystem surface conductance (G_s).

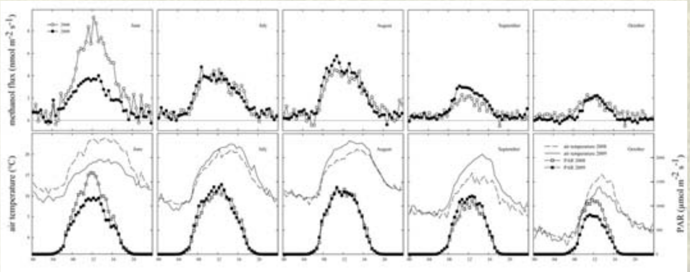


Figure 3 Average diurnal cycles of MeOH fluxes, air temperature (T_{air}) and PAR in 2008 and 2009.

RESULTS & CONCLUSION Fig. 1 (A) shows methanol (MeOH) fluxes measured during the measurement campaigns in 2008 and 2009, where positive numbers describe fluxes from the canopy to the atmosphere. Strongest emissions were observed directly after cut events, where MeOH is thought to be emitted as a leaf wound component.

In addition, during warm periods with daily average temperatures around 20°C, MeOH emissions increased significantly (e.g. end of June 2008). One explanation is the temperature dependence the of gas/liquid-phase distribution coefficient H (Henry's law constant), which determines the amount of MeOH that diffuses from the liquid- into the gas-phase within the plant cells. Higher temperatures lead to higher H values and therefore to an increased release of MeOH. Further, during cell wall expansion in growing plant cells MeOH is produced by the temperature dependent enzyme pectin methylesterase.

MeOH emissions are depicted in detail in Fig. 1 (B), with a maximum value of 144.5 nmol m^{-2} s^{-1} during the 2nd cut in 2009. All other cuts showed lower emissions with a maximum around 80 nmol m^{-2} s^{-1}, similar to numbers reported by Davison et al. (2008) for a meadow in Switzerland. Manure spreading in October was only partly measured in 2008, but resulted in strong emissions in 2009 (up to 26.7 nmol m^{-2} s^{-1}).

The findings shown in Fig. 1 (A) and (B) underline the major impact of management controls on the MeOH budget of a temperate grassland.

Fig. 2 shows MeOH emissions as a function of T_{air} in different categories of surface conductance (G_s), management effects have been exluded from the data. The flux is restricted by low G_s values (0-0.2), in which case the stomata are nearly closed. These findings are in accordance with Niinemets et Reichstein (2004), who described the influcence of stomatal openess on components with high water solubility like MeOH.

Average diurnal cycles for both years are shown in Fig. 3. Methanol fluxes exhibited a clear diurnal cycle with close−to−zero fluxes during nighttime and emissions, up to 9.2 nmol m^{-2} s^{-1}, which followed the diurnal course of incident photosynthetically active radiation (PAR) and air temperature (T_{air}) during daytime.

References:
Davison, B., Brunner, A., Ammann, C., Spirig, C., Jocher, M., Neftel, A., et al. (2008). Cut induced VOC emissions from agricultural grasslands. *Plant Biol*, *10*, 101055/s-2007-965043. | Fall, R. and Benson, A. A. (1996): Leaf methanol – the simplest natural product from plants, Trends Plant Sci., 1, 296–301. | MacDonald, R., & Fall, R. (1993). Detection of substantial emissions of methanol from plants to the atmosphere. *Atmospheric Environment*, *27*, 1709-1713. |
Niinemets, U., Loreto, F., & Reichstein, M. (2004). Physiological and physicochemical controls on foliar volatile organic compound emissions. *Trends in Plant Science*, *9*(4), 180-186.| Wohlfahrt, G., Haslwanter, A., Hörtnagl, L., Jasoni, R. L., Fenstermaker, L. F., Arnone III, J. a., et al. (2009). On the consequences of the energy imbalance for calculating surface conductance to water vapour. *Agricultural and Forest Meteorology*, *149*(9), 1556-1559. doi: 10.1016/j.agrformet.2009.03.015.

visit us: www.biomet.co.at

Der Wissenschaftsfonds.