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

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

[1] Institute of Ecology, University of Innsbruck, Austria [2] Institute of Ion Physics and Applied Physics, University of Innsbruck, Austria [*] current address: Division of Atmospheric Sciences , University of Helsinki, Finland
[**] current address: IRCELYON, Institute on Catalysis and Environmental Research, University of Lyon, France [***] current address: Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, CO 80307, USA

universität innsbruck

BACKGROUND AND OBJECTIVES

Methanol (MeOH) 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 appear to be temperature and light dependent, further 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.

Based on leaf-level studies we hypothesized that (i) air temperature would represent the major abiotic driver of methanol emissions and (ii) g_s and plant growth would constitute the major biotic controls on the emission of methanol.

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.

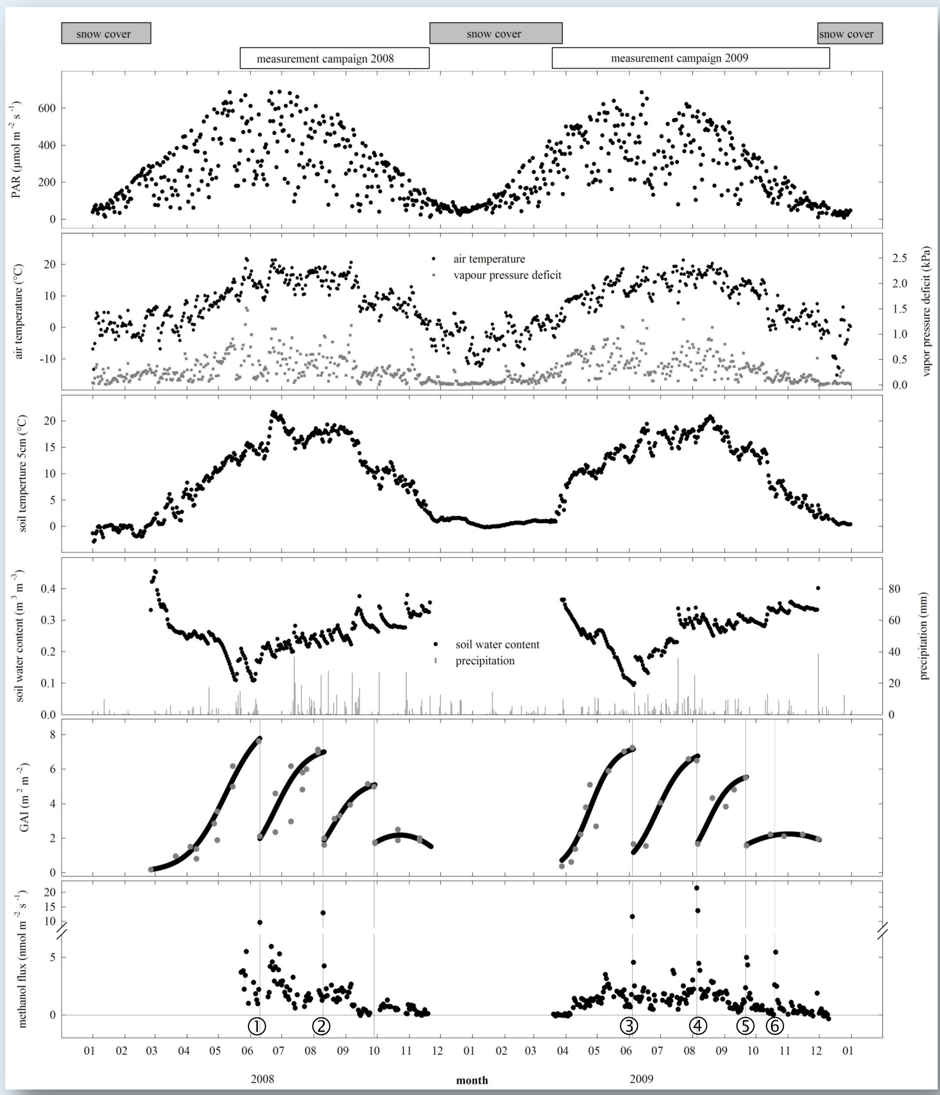


Figure 1 Daily averages of photosynthetically active radiation (PAR), air temperature, vapour pressure deficit, soil temperature and water content at 0.05 m soil depth, precipitation, green plant area index (GAI) and measured methanol flux over the whole measurement campaign during 2008 and 2009. Vertical lines show management dates. Circled numbers at the bottom of the last panel refer to management events that are also shown in Figure 2 and 3.

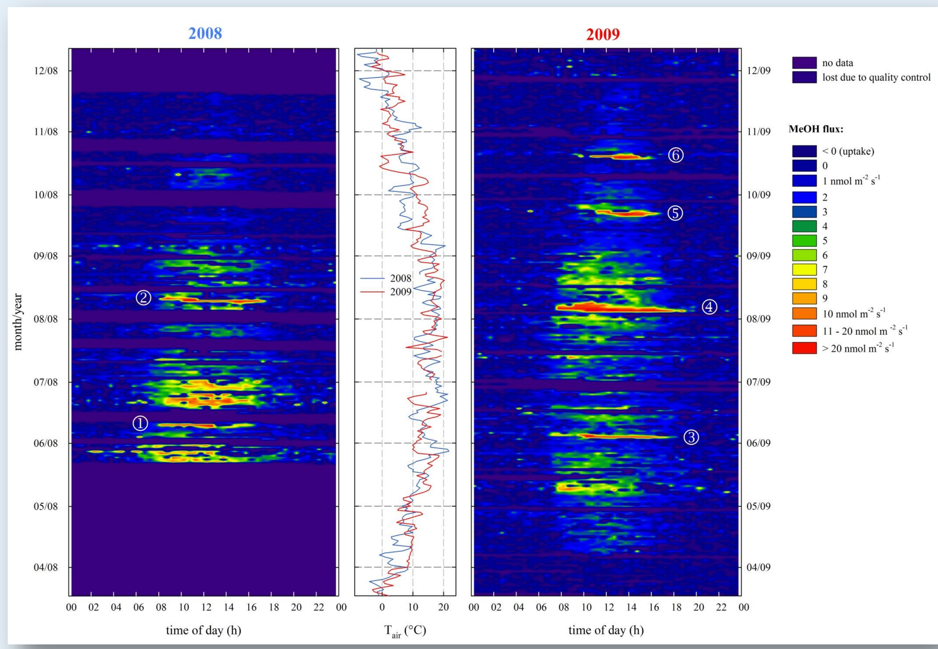


Figure 2 Methanol fluxes during the measurement campaigns in 2008 and 2009, T_{air} is shown as daily average temperature.

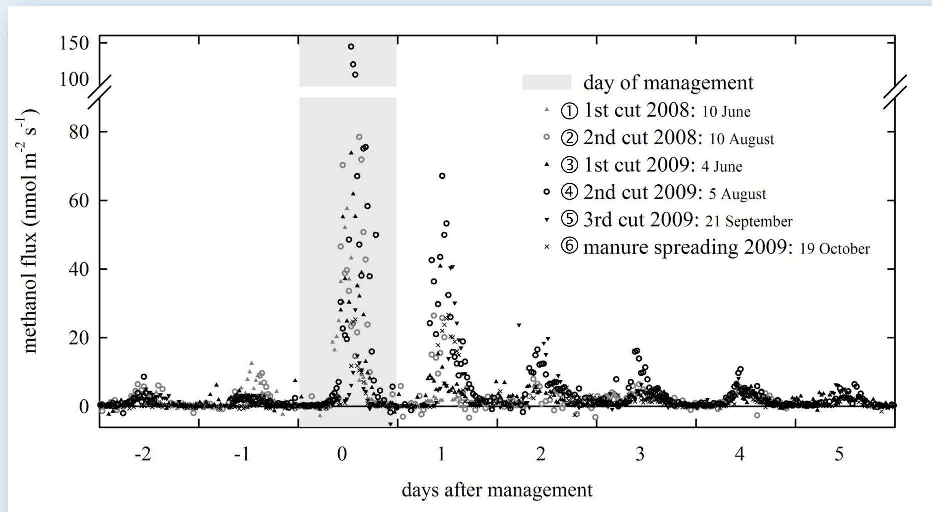


Figure 3 Methanol emissions before, during and after management events, points represent half-hourly fluxes.

RESULTS & CONCLUSION

Fig. 1 and 2 show 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 methanol is thought to be emitted as a leaf wound component.

In addition, during warm periods with daily average temperatures around 20°C, methanol 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 methanol 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 methanol. Further, during cell wall expansion in growing plant cells methanol is produced by the temperature dependent enzyme pectin methylesterase.

Methanol emissions during management events are depicted in detail in Fig. 3, 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.

To our knowledge this study is the first to report elevated methanol emissions after the field-scale application of organic fertilizer. The spreading of organic manure in October 2009 resulted in strong emissions of methanol on the day of fertilization and the following days, with peak emissions of the same order of magnitude like observed during the 3rd cut in 2009. The observed peaks of methanol efflux were probably due to increased microbial activity during the decomposition of organic matter brought in by fertilization, which can be the cause for the release of substantial amounts of VOCs at the soil-litter interface (Ramirez et al., 2010) and may have been fueled by increased nutrient availability and, during this specific fertilization event, rising air temperatures. Fresh manure has been reported to contain large amounts of alcohols, mainly methanol and ethanol (Sun et al., 2008; Ngwabie et al., 2008). Although the mature manure used for fertilization in Neustift was stored for several weeks prior to application, there might still have been considerable amounts of alcohols in the liquid parts of the manure from within the manure heap. Therefore, the spreading of the fertilizer and the accompanying expansion of its surface area in combination with relatively high air temperatures may have lead to increased volatilization of methanol to the atmosphere. However, as soil VOC production has not received much attention in past studies, little is known about the emission of microbially-produced VOCs and their emission patterns among different soil and litter types (Leff and Fierer, 2008).

The findings shown in Fig. 1, 2 and 3 underline the major impact of management events on the methanol budget of a temperate grassland.

Fig. 4 shows methanol emissions as a function of T_{air} in different categories of surface conductance (g_{surf}), management effects have been exluded from the data. The flux is restricted by low g_{surf} 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 infuence of stomatal openess on compounds with high water solubility like methanol.

Average diurnal cycles for both years are shown in Fig. 5. 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.

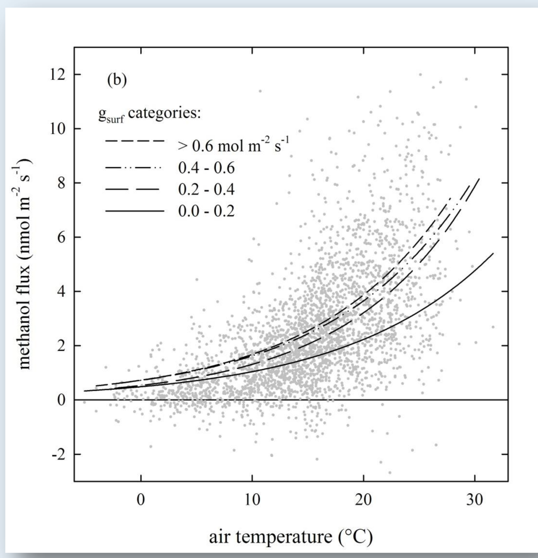


Figure 4 Methanol flux as a function of air temperature (T_{air}) in different classes of ecosystem surface conductance (g_{surf}). Management events were excluded.

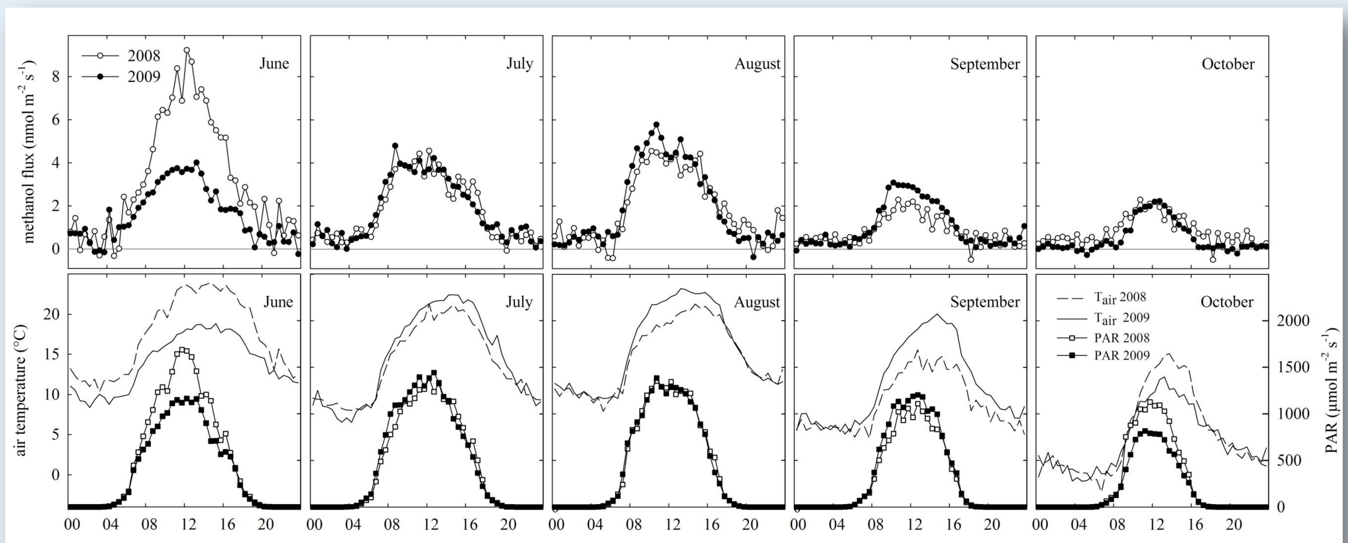
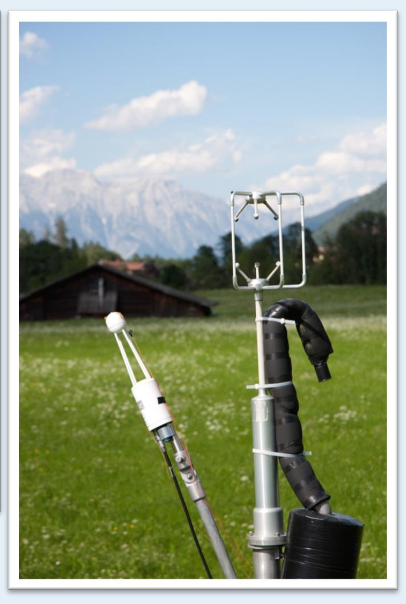


Figure 5 Average diurnal cycles of methanol fluxes, air temperature and photosynthetically active radiation (PAR) in June, July, August, September and October 2008 and 2009. The calculation of T_{air} and PAR is based on half-hourly values when the methanol flux was measured. Management events were excluded from the calculation.



ACKNOWLEDGEMENTS

This study was financially supported by the Austrian National Science Fund under contract P19849-B16, the Tyrolean Science Fund under contract Uni-404/486. Family Hofer (Neustift, Austria) is acknowledged for granting us access to the study site. Additional support was obtained by the Translational-Research-Programm (L518-N20) of the Austrian National Science Fund and the Industry-Academia Partnerships and Pathways (IAPP; 218065) funded by the European Commission.

Fall, R., and A. A. Benson (1996), Leaf methanol - the simplest natural product from plants, Trends in Plant Science, 1(9), 296-301, doi:10.1016/S1360-1385(96)88175-0.
Leff, J. W., and N. Fierer (2008), Volatile organic compound (VOC) emissions from soil and litter samples, Soil Biology and Biochemistry, 40(7), 1629-1636, doi:10.1016/j.soilbio.2008.01.018.
MacDonald, R. C., and R. Fall (1993), Detection of substantial emissions of methanol from plants to the atmosphere, Atmospheric Environment. Part A. General Topics, 27(11), 1709-1713, doi:10.1016/0960-1686(93)90233-O.
Ngwabie, N. M., G. W. Schade, T. G. Custer, S. Linke, and T. Hinz (2008), Abundances and flux estimates of volatile organic compounds from a dairy cowshed in germany, Journal of Environment Quality, 37(2), 565, doi:10.2134/jeq2006.0417.
Niinemets, Ü., F. Loreto, and M. Reichstein (2004), Physiological and physicochemical controls on foliar volatile organic compound emissions., Trends in plant science, 9(4), 180-6, doi:10.1016/j.tplants.2004.02.006.
Ramirez, K. S., C. L. Lauber, and N. Fierer (2010), Microbial consumption and production of volatile organic compounds at the soil-litter interface, Biogeochemistry, 99(1-3), 97-107, doi:10.1007/s10533-009-9393-x.
Sun, H., S. L. Trabue, K. Scoggin, W. A. Jackson, Y. Pan, Y. Zhao, I. L. Malkina, J. A. Koziel, and F. M. Mitloehner (2008), Alcohol, volatile fatty acid, phenol, and methane emissions from dairy cows and fresh manure, Journal of Environment Quality, 37(2), 615, doi:10.2134/jeq2007.0357.

BIOMETinnsbruck
www.biomet.co.at

Der Wissenschaftsfonds.