

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

Lukas Hörtnagl,<sup>1</sup> Ines Bamberger,<sup>2</sup> Martin Graus,<sup>2,3,4</sup> Taina M. Ruuskanen,<sup>2,5</sup>  
Ralf Schnitzhofer,<sup>2</sup> Markus Müller,<sup>2,6</sup> Armin Hansel,<sup>2</sup> and Georg Wohlfahrt<sup>1</sup>

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[1] Methanol (CH<sub>3</sub>OH) fluxes were quantified above a managed temperate mountain grassland in the Stubai Valley (Tyrol, Austria) during the growing seasons 2008 and 2009. Half-hourly methanol fluxes were calculated by means of the virtual disjunct eddy covariance (vDEC) method using three-dimensional wind data from a sonic anemometer and methanol volume mixing ratios measured with a proton transfer reaction mass spectrometer (PTR-MS). During (undisturbed) mature and growing phases, methanol fluxes exhibited a clear diurnal cycle with close-to-zero fluxes during nighttime and emissions, up to 10 nmol m<sup>-2</sup> s<sup>-1</sup>, which followed the diurnal course of radiation and air temperature. Management events were found to represent the largest perturbations of methanol exchange at the studied grassland ecosystem: Peak emissions of 144.5 nmol m<sup>-2</sup> s<sup>-1</sup> were found during/after cutting of the meadow, reflecting the wounding of the plant material and subsequent depletion of the leaf internal aqueous methanol pools. After the application of organic fertilizer, elevated methanol emissions of up to 26.7 nmol m<sup>-2</sup> s<sup>-1</sup> were observed, likely reflecting enhanced microbial activity associated with the applied manure. Simple and multiple linear regression analyses revealed air temperature and radiation as the dominant abiotic controls, jointly explaining 47% and 70% of the variability in half-hourly and daily methanol fluxes. In contrast to published leaf-level laboratory studies, the surface conductance and the daily change in the amount of green plant area, used as ecosystem-scale proxies for stomatal conductance and growth, respectively, were found to exert only minor biotic controls on methanol exchange.

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### 1. Introduction

[2] Volatile organic compounds (VOCs) have received increased attention in recent years due to their role in atmospheric chemistry [Chameides *et al.*, 1988]. The emission of VOCs from plants to the atmosphere constitutes a significant source of reactive nonmethane hydrocarbons [Cojocariu *et al.*, 2005] and therefore strongly affects the physical/chemical properties of the atmosphere and thus climate [Arey *et al.*, 1991; Bermejo *et al.*, 2003]. In the presence of NO<sub>x</sub> (NO, NO<sub>2</sub>) and sunlight, VOCs react to

form tropospheric ozone [Atkinson, 2000], which is a greenhouse gas and represents a risk to plants and human health [Bernard *et al.*, 2001]. VOCs react with the hydroxyl radical (OH) and thus decrease its concentration which in turn affects the atmospheric lifetime and hence the concentration of greenhouse gases such as methane. Finally, VOCs directly and indirectly affect the radiative balance of the Earth-atmosphere system through contributing to the formation and growth of primary and secondary organic aerosols [Kulmala *et al.*, 2004; Ramanathan *et al.*, 2001]. Changes in the emission and uptake of VOCs from/to the earth's surface thus have the potential to modify climate [Kanakidou *et al.*, 2005].

[3] Methanol (CH<sub>3</sub>OH) is the second most abundant VOC in the troposphere after methane [Custer and Schade, 2007; Jacob *et al.*, 2005] and represents nearly 20% of total VOC emissions [Guenther *et al.*, 1995], with typical concentrations in the range of 1–10 ppbv in the continental boundary layer [Singh *et al.*, 1995; Heikes *et al.*, 2002]. Methanol is known to play a crucial role in atmospheric chemistry [Folberth *et al.*, 2006; Folkens and Chatfield, 2000; Lary and Shallcross, 2000; Singh *et al.*, 1995; Sommariva *et al.*, 2005]. It is a

<sup>1</sup>Institute of Ecology, University of Innsbruck, Innsbruck, Austria.

<sup>2</sup>Institute of Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria.

<sup>3</sup>Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, Colorado, USA.

<sup>4</sup>Now at Chemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.

<sup>5</sup>Now at Division of Atmospheric Sciences, University of Helsinki, Helsinki, Finland.

<sup>6</sup>Now at IRCELYON, University of Lyon, Villeurbanne, France.

significant atmospheric source of formaldehyde [Riemer *et al.*, 1998; Palmer *et al.*, 2003] and carbon monoxide [Duncan *et al.*, 2007] and plays a minor role in the carbon cycle [Heikes *et al.*, 2002]. Compared to other volatiles, the lifetime of methanol (5–12 days) is relatively long [Galbally and Kirstine, 2002; Heikes *et al.*, 2002; Tie *et al.*, 2003; Jacob *et al.*, 2005], and can play a significant role in controlling tropospheric oxidants in the upper troposphere [Tie *et al.*, 2003].

[4] Sources of methanol are thought to be primarily biogenic (40–80% [Millet *et al.*, 2008; Heikes *et al.*, 2002; Jacob *et al.*, 2005]) and numerous studies have reported green plant and soil sources of methanol [Brunner *et al.*, 2007; Cojocariu *et al.*, 2004; Custer and Schade, 2007; de Gouw *et al.*, 2000; Fukui and Doskey, 1998; Karl *et al.*, 2001a, 2001b, 2002, 2003, 2005; Kirstine *et al.*, 1998; Schade and Goldstein, 2001; Spirig *et al.*, 2005; Warneke *et al.*, 1999, 2002; Rinne *et al.*, 2005; Schade and Custer, 2004; Baker *et al.*, 2001]. Estimates of the global terrestrial plant source of methanol ranging from 77 to 312 Tg yr<sup>-1</sup> are still highly uncertain [Jacob *et al.*, 2005; Millet *et al.*, 2008].

[5] Plants are thought to release methanol mainly as a by-product of pectin demethylation during leaf growth [Fall and Benson, 1996; Galbally and Kirstine, 2002; Hüve *et al.*, 2007], resulting in significant seasonal variations in atmospheric methanol concentrations [Tie *et al.*, 2003]. In accordance with these findings, MacDonald and Fall [1993] reported high emission rates for young growing leaves as opposed to mature ones. Note that while the substrate, pectin, is the same, this process is different from the recently reported emission of methane (CH<sub>4</sub>) under oxic environmental conditions after pectin irradiation by UV, where ester methyl groups of pectin can serve as a precursor of CH<sub>4</sub> [Keppler *et al.*, 2008].

[6] Methanol emissions are temperature and light dependent; in addition stomatal opening plays an important role in explaining observed emission patterns [Folkers *et al.*, 2008; Hüve *et al.*, 2007; Custer and Schade, 2007; Brunner *et al.*, 2007; Karl *et al.*, 2005; Schade and Goldstein, 2001]. The sensitivity of different VOCs to changes in stomatal conductance ( $g_s$ ) depends on the equilibrium gas/liquid-phase distribution coefficient  $H$  (Henry's law constant, Pa m<sup>3</sup> mol<sup>-1</sup>) which is compound specific and temperature dependent. Compounds with high water solubility like methanol have a low  $H$  value; therefore, large increases in aqueous-phase concentrations are needed to support an increase in gas-phase concentrations [Niinemets and Reichstein, 2003a, 2003b]. Accordingly, stomata can constrain the emission of more soluble compounds like methanol over a longer time period than the emission of less soluble volatiles, resulting in a direct effect of  $g_s$  on the efflux rate of methanol [Nemecek-Marshall *et al.*, 1995].

[7] Sinks of methanol are highly uncertain as well and are estimated to be in the range of 107 to 284 Tg yr<sup>-1</sup> [Jacob *et al.*, 2005], with the main sink being the gas-phase oxidation by OH [Schade *et al.*, 2008], which takes place on a timescale of approximately 10 days [Millet *et al.*, 2008]. Minor contributions are from the uptake of methanol by the ocean [Sinha *et al.*, 2007; Mao *et al.*, 2006] for which recent studies estimate a 10 to 15 Tg yr<sup>-1</sup> sink [Singh *et al.*, 2004; Jacob *et al.*, 2005] and wet and dry deposition to land [Karl *et al.*, 2004, 2005; Jacob *et al.*, 2005; Talbot *et al.*,

2005; Mao *et al.*, 2006], which may only be observable at night as methanol emissions are regulated by  $g_s$  [Schade *et al.*, 2008]. The processes responsible for the uptake of methanol in plant canopies are still unclear, but generally trace gas uptake in soils is microbially mediated when methanol diffuses to active methylophilic microorganism sites in the soil, a process which in turn is affected by physical parameters such as soil texture and water filled pore space [e.g., Smith *et al.*, 2003; Yonemura *et al.*, 2000]. Methylophilic bacteria can also be found on leaf surfaces [Fall and Benson, 1996] and may contribute to observed methanol deposition fluxes.

[8] Globally, grasslands cover around 40% of the ice-free terrestrial surface [Ramankutty and Foley, 1999]. In the Alps, grassland farming (grazing by domestic ungulates and cutting for hay production) is the dominant agricultural practice consuming >85% of the available agricultural land in 75% of the municipalities [Tappeiner *et al.*, 2008]. In contrast to many forest ecosystems, whose VOC fluxes are dominated by terpenoids [Rinne *et al.*, 2007], methanol is the major VOC emitted from grasslands not only after cutting when large amounts of various VOCs escape to the atmosphere from the severed plant material [Davison *et al.*, 2008; Ruuskanen *et al.*, 2010], but also during undisturbed conditions [Fukui and Doskey, 1998; de Gouw *et al.*, 2000; Karl *et al.*, 2001a, 2001b; Warneke *et al.*, 2002; Karl *et al.*, 2005; Brunner *et al.*, 2007; Bamberger *et al.*, 2010].

[9] The uncertainties in global sources and sinks of methanol [Millet *et al.*, 2008] are in apparent contradiction to the well-established understanding of the processes and pathways involved in the production of methanol in and its emission from leaves [Fall and Benson, 1996] which reflects difficulties in transferring leaf-level laboratory studies to field conditions and the ecosystem level [Niinemets *et al.*, 2010]. The objective of the present paper is thus to test whether the controls on methanol fluxes reported at leaf level and often under controlled environmental conditions are applicable under in situ conditions at ecosystem scale. To this end we quantified the diurnal, seasonal and interannual variability of methanol exchange and analyzed the data with regard to the major biotic and abiotic controls. Based on the above mentioned leaf-level studies we hypothesized that (1) air temperature would represent the major abiotic driver of methanol emissions and (2)  $g_s$  and plant growth would constitute the key biotic controls on the emission of methanol. As previous studies over grassland [e.g., Karl *et al.*, 2001a, 2001b] have shown emissions of various compounds to be elevated immediately after cutting we further hypothesized that (3) during cutting (leaf wounding) events and subsequent drying high amounts of methanol are emitted into the atmosphere. We selected the study site Neustift, a temperate mountain grassland in Austria, because it is cut three times per year for hay production and has been described extensively in terms of the effects of cutting on the net ecosystem CO<sub>2</sub> and energy exchange [Hammerle *et al.*, 2008; Wohlfahrt *et al.*, 2008].

## 2. Methods

### 2.1. Site Description

[10] The study site is located at an intensively managed meadow in the middle of the flat valley bottom at an ele-

vation of 970 m above sea level (asl) near the village of Neustift (47°07'N, 11°19'E) in the Stubai Valley (Austria). The fetch is homogeneous up to 300 m to the north-northeast and 900 m to the south-southwest of the instrument tower, parallel to the valley's orientation and the dominant daytime and nighttime wind directions, respectively. During the night wind velocities are usually low and the atmosphere shows stable stratification. This resulted in a larger footprint than during daytime, where conditions were typically unstable and wind velocities were higher [Bamberger *et al.*, 2010].

[11] The climate in Stubai Valley is humid continental with alpine influences characterized by an average annual temperature of 6.5°C and an average annual precipitation of 852 mm. The vegetation of the meadow consists mainly of only a few dominant graminoids (*Dactylis glomerata*, *Festuca pratensis*, *Phleum pratensis*, *Trisetum flavescens*) and forbs (*Ranunculus acris*, *Taraxacum officinale*, *Trifolium repens*, *Trifolium pratense*, *Carum carvi*), while coniferous forest is the predominant vegetation type on the slopes of the surrounding mountains. The meadow is cut and harvested three times a year, with cuts taking place at the beginning of June and August and at the end of September. Fertilization takes place once per year, typically at the end of October by manure spreading.

[12] Measurements were conducted from 22 May until 20 November 2008 (182 days), and continued the following year starting on 19 March 2009, some days before snowmelt, until 11 December 2009 (267 days).

## 2.2. Eddy Covariance Measurements

[13] The net ecosystem methanol exchange was measured using the virtual disjunct eddy covariance (vDEC) [Karl *et al.*, 2002] method that is based on the eddy covariance method [Baldocchi *et al.*, 1988]. The three wind components and the speed of sound were measured with a three-dimensional sonic anemometer (R3IA, Gill Instruments, Lymington, United Kingdom) 2.5 m above ground, while methanol volume mixing ratios were simultaneously detected by a PTR-MS at  $m/z$  33. The sample inlet was 0.1 m below the anemometer. Sample air went through a particulate filter (1–2  $\mu\text{m}$ , PTFE), was drawn through a 16 m (2008)/12 m (2009) PFA Teflon tube with 0.004 m inner diameter and was finally analyzed for VOC concentrations by the PTR-MS. To minimize interactions between tube walls and sample air, the inlet line was heated to 40°C (2008)/35°C (2009). The flow rate was held constant at 8  $\text{sl min}^{-1}$  (standard liter per minute; air volume normalized to standard temperature and pressure conditions: 273 K, 1013 hPa). The 20 Hz sonic anemometer data were stored to a hard drive of a personal computer using the EddyMeas software (O. Kolle, Max Planck Institute for Biogeochemistry, Jena, Germany).

## 2.3. PTR-MS Setup

[14] For the measurement of selected VOCs a high-sensitivity PTR-MS was deployed in a container next to the field site during the measurement campaigns. The PTR-MS method is described in detail by Hansel *et al.* [1995] and Lindinger *et al.* [1998] and was used to analyze ambient air for a number of VOCs. In 2008, 13 species of VOCs were measured sequentially, resulting in a repetition rate of 2.82 s until 10 July, after which it was changed to 3.00 s (15 species) until 6 November 2008 and

after that to 1.80 s (8 species) until 20 November. In 2009 the repetition rate was 2.25 s until 6 April (12 species) and then 2.35 s until 11 December (13 species). The dwell time for methanol was 0.5 s/0.2 s during 2008/2009. In addition to the air sampling, a pump continuously flushed 500 ml of ambient air through a home-built catalytic converter (350°C) to produce VOC-free zero air, which was switched into the PTR-MS during the last 5 min of every half-hour period to determine the instrumental background (zero calibration). Sensitivities of the PTR-MS were calibrated once a week in 2008 and every 50 h in 2009 by adding a multicomponent gas standard containing VOCs in  $\text{N}_2$  (Apel Riemer Inc., USA) to VOC-free air at ambient humidity. An automated routine calibrated the PTR-MS with the flow of the gas standard adjusted to 1 standard cubic centimeters per minute (sccm), 2.5 sccm, 5 sccm and 7.5 sccm, respectively, and diluted with 500 sccm scrubbed ambient air. The known calibration gas mixture was analyzed by the PTR-MS and sensitivities were determined from linear regression of the known VOC volume mixing ratios and the respective signal intensities [see Bamberger *et al.*, 2010]. Typical calibration factors for methanol were 12 normalized counts per second (ncps)  $\text{ppbv}^{-1}$ . A typical value for the limit of detection for methanol, calculated with each calibration, was 0.5 ppbv (for 1 s integration time).

[15] The PTR-MS was operated at a drift tube pressure of 2.15 mbar/2.3 mbar and a drift voltage of 550 V/600V during 2008/2009. Data were stored in 30 min files and processed to VOC volume mixing ratios in ppbv using a homemade program based on MATLAB 7.4.0 (R2007a, The MathWorks, Inc.). Detailed information regarding setup, calibration and operation of the instrument was presented by Bamberger *et al.* [2010].

## 2.4. Flux Calculations

[16] Due to the zero calibration, half-hourly flux calculations are based on measurements over the first 25 min of each 30 min period. Methanol fluxes were calculated as the covariance between the turbulent departures of the vertical wind speed and the methanol volume mixing ratios using the postprocessing software EdiRe (University of Edinburgh). Means and turbulent departures were calculated by Reynolds (block) averaging.

[17] Because of the sequential measurement of VOCs by the PTR-MS the concentration time series of a specific compound is disjunct and its time resolution lower than that of the 20 Hz wind data. Fluxes were therefore calculated by means of the vDEC method [Karl *et al.*, 2002] by using a subsample of the horizontal wind data as given by the sampling rate of the PTR-MS. As shown by Hörtnagl *et al.* [2010] the vDEC method does not result in a systematic bias, but causes the random flux uncertainty to increase as compared to 20 Hz sampling. The random methanol flux uncertainty, based on the methods of Hollinger and Richardson [2005], has been presented previously by Bamberger *et al.* [2010].

[18] A three axis coordinate rotation was performed by aligning the coordinate system's vector basis with the mean wind streamlines [Kaimal and Finnigan, 1994]. The tubing induced time delay of the VOC signals was determined by optimizing the correlation coefficient with the vertical wind

velocity [McMillen, 1988] within a time window of  $\pm 50$  s. For methanol the determination of the time delay worked well and the frequency distribution of the lag times showed a peak around 1.5 s, which is slightly longer than the expected time delay based on tube length, diameter and flow rate. A second lag window of  $\pm 3$  s around the peak of the distribution was defined. If the inferred lag time was outside this time window, it was set to the peak value of the frequency distribution (i.e., 1.5 s). As shown by *Bamberger et al.* [2010] the raw methanol fluxes were then corrected for high-pass (block averaging) and low-pass (lateral sensor separation, dynamic frequency response, scalar and vector path averaging, frequency response mismatch and the attenuation of concentration fluctuations down the sampling tube) filtering according to *Moore* [1986], *Massman* [2000] and *Aubinet et al.* [1999]. Frequency-response corrections were based on a site-specific model cospectrum described by *Wohlfahrt et al.* [2005]. Instrumentation, data treatment and quality control of CO<sub>2</sub>, sensible and latent heat fluxes have been described by *Wohlfahrt et al.* [2008] and *Hammerle et al.* [2008]. The surface conductance to water vapor ( $g_{\text{surf}}$ ) was calculated after *Wohlfahrt et al.* [2009] and is used as a proxy for the canopy-integrated stomatal conductance in the following.

## 2.5. Quality Control

[19] Half-hourly methanol fluxes were subjected to several quality control tests. Data were excluded from further analysis if (1) the third rotation angle exceeded 10° [McMillen, 1988], (2) the stationarity test for methanol fluxes exceeded 60% [*Foken and Wichura*, 1996], (3) the deviation of the integral similarity characteristics was larger than 60% [*Foken and Wichura*, 1996], (4) the maximum of the footprint function [*Hsieh et al.*, 2000] was outside the boundaries of the meadow, (5) the measured background signal of methanol was higher than its ambient concentration (averaged over half an hour) and (6) the background drift was greater than the sum of the standard deviations of the two adjacent background concentration measurements within an hour. If the difference between a specific data point and the averaged signal of a certain half hour was higher than 20 times the theoretical standard deviation (noise) of the signal, the data point was defined as an outlier. Half hours with more than five outliers were flagged and not used for further analysis, except for during and 1 day after cutting events, when large fluctuations in methanol concentrations were found to be physically realistic. The flux detection limit was calculated according to *Karl et al.* [2002] on a half-hourly basis and used as a postprocessing quality control criterion, i.e., half-hourly fluxes were rejected if below the detection limit. All fluxes that passed the above mentioned quality criterion exceeded the flux detection limit which was typically below  $0.1 \text{ nmol m}^{-2} \text{ s}^{-1}$ . Over the course of the two measurement campaigns 17757 half-hourly fluxes for methanol were recorded, of which 13880 (78%) passed all quality tests and were used in the subsequent analysis.

## 2.6. Ancillary Data

[20] Meteorological measurements were collected continuously by a data logger (CR10X, Campbell Scientific, Logan, Utah) and included total and diffuse photosynthetically active radiation (PAR) (BF3H, Delta-T, Cambridge,

United Kingdom), air temperature ( $T_{\text{air}}$ ) and humidity at 2 m height measured by the means of a combined temperature/humidity sensor (RFT-2, UMS, Munich, Germany), soil temperature ( $T_{\text{soil}}$ ) at 0.05 m depth (TCAV thermocouple, Campbell Scientific, Logan, Utah), volumetric soil water content (ML2x, Delta-T Devices, Cambridge, United Kingdom) and precipitation (52202, R. M. Young, Traverse City, Michigan).

[21] The green plant area index (GAI) was assessed (1) in a destructive fashion by clipping of square plots of  $0.09 \text{ m}^2$  (3–5 replicates) and subsequent plant area determination (Li-3100, Li-Cor, Lincoln, Nebraska) and (2) from measurements of canopy height which was related to destructively measured GAI [*Wohlfahrt et al.*, 2008]. Continuous time series of the GAI were derived by fitting appropriate empirical functions, separately for each growing phase, to measured data. The daily change in GAI, referred to as dGAI, is the difference between subsequent daily values and used as a surrogate for growth. For a more detailed list of all auxiliary parameters measured at this site see *Hammerle et al.* [2008] and *Wohlfahrt et al.* [2008].

## 2.7. Statistical Analyses

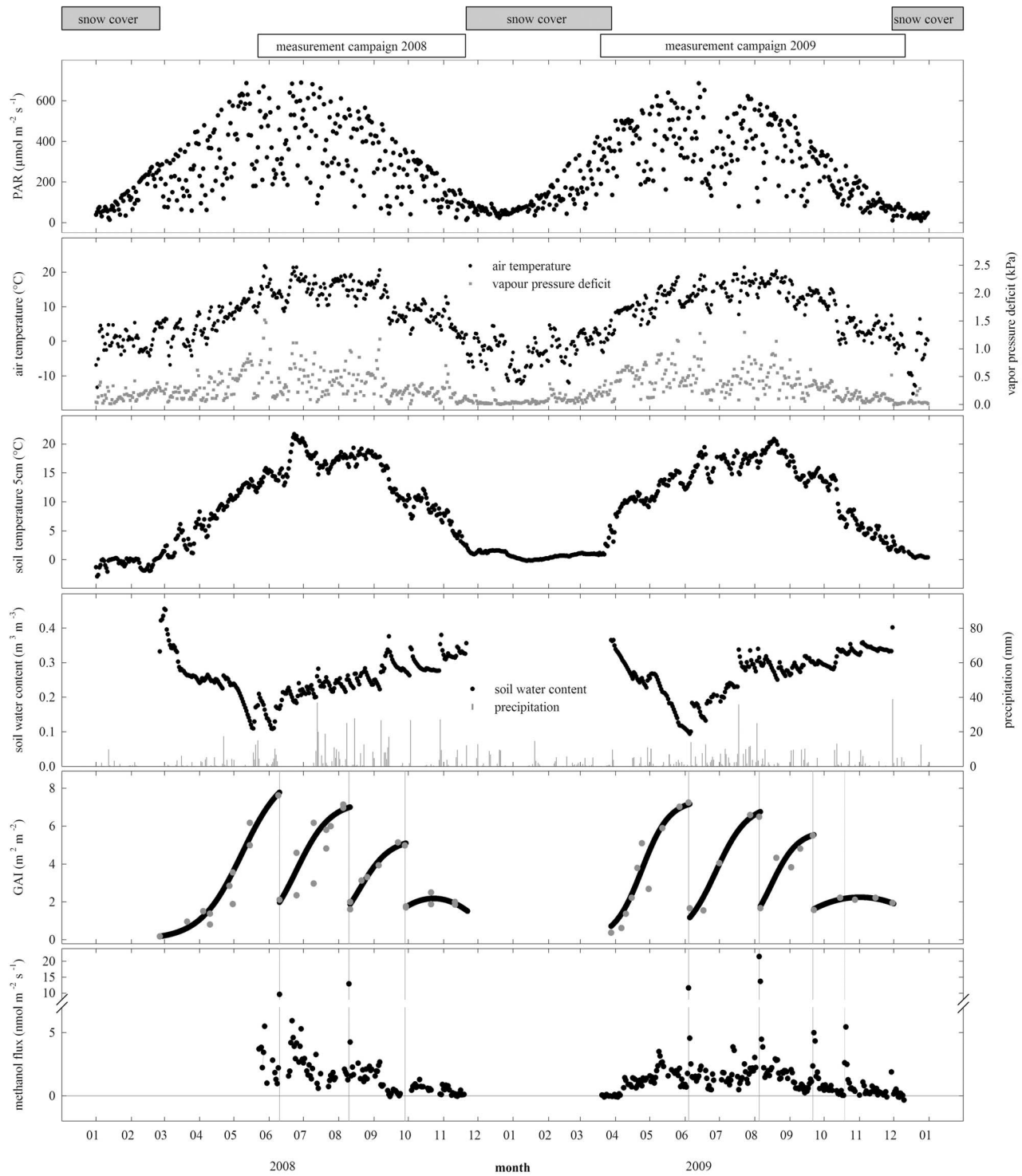
[22] Statistical analyses were performed using Statistica 9 (StatSoft, Inc.) and SigmaPlot 11 (Systat Software, Inc.). The partial correlation reported in the present study is a measure of the correlation between two variables that remains after controlling for the effects of one or more other predictor variables. The tolerance of a variable as given in Table 2 is defined as 1 minus the squared multiple correlation of this variable with all other independent variables in the regression equation and is a measure of how redundant the contribution of a variable is as compared to the contribution of the other independent variables. The higher the tolerance of a variable, the more unique is its contribution to the regression equation.

[23] For the regression analyses in Table 2 some independent variables ( $g_s$ ,  $T_{\text{soil}}$ ,  $T_{\text{air}}$ , PAR) were linearized using the equation  $y = x^n$  [*Lozán*, 1992]. In order to linearize data for the analysis shown in Figure 5 (i.e., the relationship between air temperature and methanol flux), the natural logarithm of the observed methanol flux was calculated, and data were then fitted using the equation  $\ln(F_{\text{methanol}}) = k T_{\text{air}} + d$ .

## 3. Results

### 3.1. Environmental Conditions

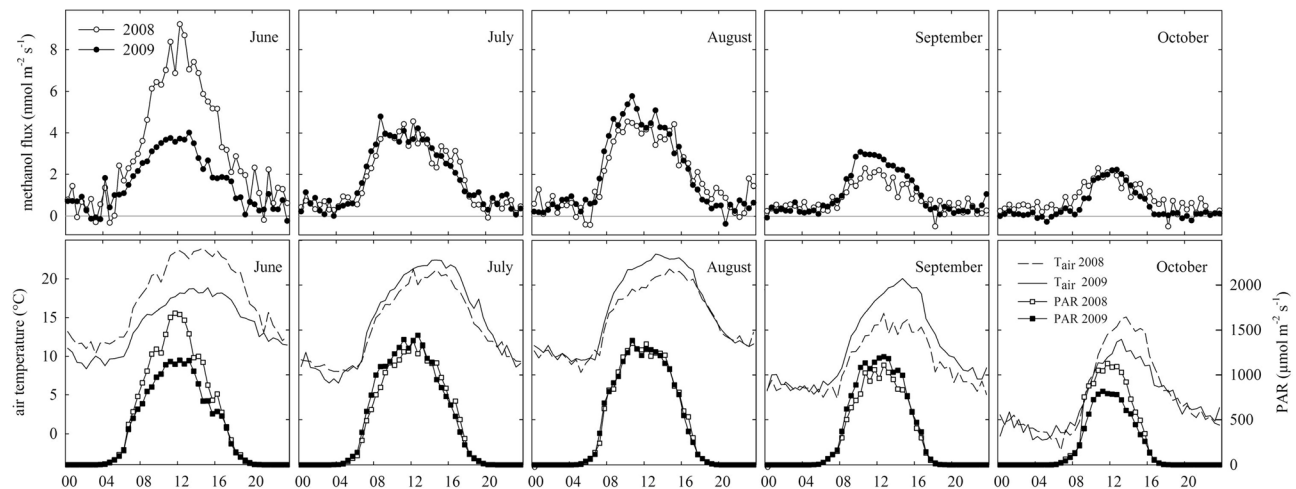
[24] With annual averages of 7.1°C and 6.8°C in 2008 and 2009, respectively,  $T_{\text{air}}$  was close to the 2001–2007 average of 6.7°C. Total precipitation was 648 mm yr<sup>-1</sup> in 2008 and 638 mm yr<sup>-1</sup> in 2009, well below the 2001–2007 average of 765 mm yr<sup>-1</sup>. Over the course of the measurement campaigns, precipitation was registered on 77 and 124 days in 2008 and 2009, respectively, with a total precipitation of 458 and 498 mm (Figure 1). Monthly  $T_{\text{air}}$  was very similar to the long-term trend, with the exception of March 2009 being cooler and April and November 2009 being warmer than the average. Differences between the two measurement years were much more evident for rainfall. June 2008 was exceptionally dry and showed only one third of the rainfall compared to the long-term average, while the amount of precipitation recorded in June 2009 was 50% above the



**Figure 1.** Daily averages of photosynthetically active radiation (PAR), air temperature, vapor 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.

average (Figure 1). Rainfall in September and October 2008 as well as in November 2009 was higher by 30%, while March to May and August 2009 received only half of the average rainfall. PAR was very similar in both years with

maximum daily sums of  $59 \text{ mol m}^{-2} \text{ d}^{-1}$ . A notable difference was a strong decrease of PAR at the end of June 2009 that showed maximum daily sums of around  $20 \text{ mol m}^{-2} \text{ d}^{-1}$ , whereas values were around  $50 \text{ mol m}^{-2} \text{ d}^{-1}$  in June 2008



**Figure 2.** Average diurnal cycles of methanol fluxes, air temperature ( $T_{\text{air}}$ ) and photosynthetically active radiation (PAR) in June, July, August, September and October 2008 and 2009. The calculation of  $T_{\text{air}}$  and PAR is based on half-hourly values when the methanol flux was measured. Management events were excluded from the calculation.

(Figure 1). Daily average  $T_{\text{soil}}$  were around  $0^{\circ}\text{C}$  during snow cover and increased rapidly by up to  $3^{\circ}\text{C d}^{-1}$  right after snowmelt in 2009 (Figure 1), while the increase was less steep and occurred about one month earlier in 2008. The drying phase of the soil before the first cut was similar in both years.

[25] The maximum values of GAI decreased from the first to the third cut in both years. GAI was close to zero right after snowmelt, increased to up to  $7.8 \text{ m}^{-2} \text{ m}^{-2}$  before cutting and was reduced to less than  $2.0 \text{ m}^{-2} \text{ m}^{-2}$  due to harvesting (Figure 1). After the third cut, GAI first increased and later decreased.

[26] The months from June to October were captured in full in both years and monthly diurnal cycles of  $T_{\text{air}}$  and PAR are compared in Figure 2. June 2008 was considerably warmer than 2009, with mean  $T_{\text{air}}$  of up to  $23.9^{\circ}\text{C}$  as compared to  $18.8^{\circ}\text{C}$  in 2008, while also mean PAR was significantly higher.

### 3.2. Seasonal and Interannual Variability of Methanol Fluxes

[27] Methanol emissions were close to zero as long as snow covered the ground and for about one week thereafter (spring 2009; Figure 1). The earliest distinct methanol emissions after snowmelt were measured on 8 April 2009 with a daily

average of  $0.6 \text{ nmol m}^{-2} \text{ s}^{-1}$ . Afterwards, emissions continued to increase as the weather became warmer. In absence of management actions highest fluxes were recorded during warm periods with daily average temperatures  $>20^{\circ}\text{C}$ , when average methanol emissions reached up to  $5.9 \text{ nmol m}^{-2} \text{ s}^{-1}$  (Figure 1). The grass cut increased the daily average fluxes of methanol to values ranging from  $9.6$  to  $21.5 \text{ nmol m}^{-2} \text{ s}^{-1}$  (Figure 1). These emissions decreased rapidly on the days following the cut, reaching precut values of around  $2 \text{ nmol m}^{-2} \text{ s}^{-1}$  after about 3 days (Figure 1). Another emission peak was found during manure spreading on 20 October 2009 ( $5.4 \text{ nmol m}^{-2} \text{ s}^{-1}$ ; Figure 1).

[28] The influence of management activities on half-hourly emissions of methanol is shown in detail in Figure 3 for both years, while corresponding numbers are given in Table 1. On cutting days, maximum fluxes between  $40.7$  and  $144.5 \text{ nmol m}^{-2} \text{ s}^{-1}$  were measured. Emissions were far lower 1 day later, with maximum values ranging from  $2.8 \text{ nmol m}^{-2} \text{ s}^{-1}$  in June 2008, a day with a relatively low maximum  $T_{\text{air}}$  of  $18.8^{\circ}\text{C}$ , to  $67.1 \text{ nmol m}^{-2} \text{ s}^{-1}$  in August 2009. This was similar on the days thereafter, with methanol emissions further decreasing before reaching precut peak values of about  $5 \text{ nmol m}^{-2} \text{ s}^{-1}$  by the fourth day after the cut (Figure 3).

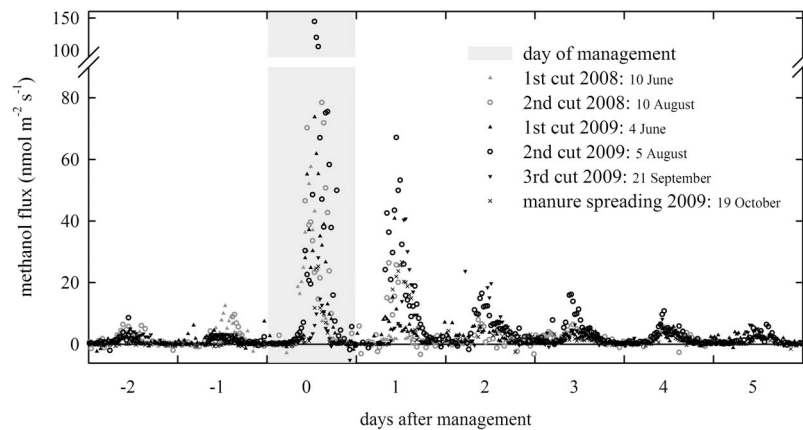
**Table 1.** Maximum Methanol Fluxes Before, During and After Management Events<sup>a</sup>

Days After Management	First Cut June 2008	Second Cut August 2008	First Cut June 2009	Second Cut August 2009	Third Cut September 2009	Fertilization October 2009
-2	4.1 (17.6)	6.4 (19.4)	3.9 (16.6)	8.6 (17.0)	5.0 (23.7)	1.2 (4.3)
-1	12.5 (23.4)	9.6 (17.4)	7.5 (18.6)	2.4 (14.2)	3.3 (21.5)	1.1 (3.8)
0	57.6 (24.5)	78.4 <sup>b</sup> (24.6)	73.8 (18.6)	144.5 <sup>b</sup> (22.2)	28.1 <sup>b</sup> (21.9)	25.3 (4.9)
1	3.8 <sup>c</sup> (18.6)	26.4 <sup>b</sup> (26.5)	40.9 (21.3)	67.1 <sup>b</sup> (25.4)	40.7 <sup>b</sup> (22.0)	26.7 (9.9)
2	–	7.9 (23.9)	6.9 (20.4)	16.5 (26.4)	23.7 <sup>b</sup> (21.9)	7.5 (14.1)
3	–	6.4 (16.9)	5.2 (17.5)	16.2 (24.2)	6.4 (20.8)	3.4 (12.9)
4	–	6.6 (23.3)	5.8 (19.9)	10.8 (21.9)	8.2 (19.8)	5.1 (10.6)
5	–	–	3.9 (19.3)	6.4 (20.9)	6.3 (20.8)	4.1 (9.7)

<sup>a</sup>Flux rates are reported in  $\text{nmol m}^{-2} \text{ s}^{-1}$ . Numbers in parentheses give the maximum air temperature in  $^{\circ}\text{C}$  for the respective day.

<sup>b</sup>Grass left on field for drying.

<sup>c</sup>Day not fully captured by measurements.



**Figure 3.** Half-hourly methanol fluxes before, during and after different management events during the measurement campaigns.

[29] The effect of fertilization could be captured in October 2009, when the spreading of manure resulted in peak emissions of  $25.3 \text{ nmol m}^{-2} \text{ s}^{-1}$  on the day of the spreading and even higher emissions of up to  $26.7 \text{ nmol m}^{-2} \text{ s}^{-1}$  one day later (Figure 3). Those numbers are nearly nine times higher than observed emissions during the days before the manure was applied, when peak values of around  $3 \text{ nmol m}^{-2} \text{ s}^{-1}$  were found (data not shown). However, the 2 days before manure spreading, as shown in Figure 3 and Table 1, were characterized by cold weather with maximum  $T_{\text{air}}$  of  $5^{\circ}\text{C}$  and showed the lowest methanol emissions in October. The immediate influence of fertilization on methanol emissions can be seen in form of elevated peak emissions for 4 days after the spreading (Figure 3).

[30] Average diurnal cycles of methanol fluxes not related to management actions are shown for both years in Figure 2. Methanol fluxes exhibited a clear diurnal cycle with close-to-zero fluxes during nighttime and emissions which followed the diurnal course of incident PAR and  $T_{\text{air}}$  during daytime (Figure 2).  $T_{\text{air}}$  corresponded well with the methanol flux on a monthly basis, especially when comparing the 2 years. June 2008 was the warmest month during the measurement campaigns and showed the highest average methanol emissions with up to  $9.2 \text{ nmol m}^{-2} \text{ s}^{-1}$  as compared to  $4.0 \text{ nmol m}^{-2} \text{ s}^{-1}$  in June 2009 when  $T_{\text{air}}$  was considerably lower (Figure 2). A similar pattern can be seen in August and September 2009, where air temperatures were warmer and methanol emissions higher than the year before, and to a lesser extent in July. However, in October 2009, when the growing season was coming to an end, warmer conditions did not result in higher methanol emissions (Figure 2).

[31] Between June and October, methanol emissions resulted in the meadow losing a total of  $191 \text{ mg C m}^{-2}$  over 103 days in 2008 and  $255 \text{ mg C m}^{-2}$  over 134 days in 2009, the average daily loss ( $1.9 \text{ mg C m}^{-2} \text{ d}^{-1}$ ) being exactly the same in both years.

### 3.3. Controls on Methanol Exchange

[32] In order to explore the controls on methanol exchange we conducted simple and multiple linear regression analyses based on the half-hourly and daily average data (Table 2).

[33] Simple linear regression resulted in equally high positive correlations with the latent heat flux,  $T_{\text{air}}$  and PAR, while negative correlations were found for the net ecosystem  $\text{CO}_2$  exchange (NEE), soil water content at 0.05 m soil depth (SWC) and the fraction of diffuse radiation ( $f_{\text{dif}}$ ). All regressors were highly significant at the significance level  $p < 0.001$  (Table 2). When using daily averages of the same variables, correlations increased for the latent heat flux,  $T_{\text{air}}$  and PAR. On a daily timescale the vapor pressure deficit (VPD),  $T_{\text{soil}}$  in 5 cm depth and dGAI became important factors in describing the methanol exchange (Table 2). However, the largest difference was found for the methanol volume mixing ratio (VMR), which was positively correlated with the methanol flux and doubled its influence on a diurnal timescale. To a lesser extent, this was also the case for SWC, the negative correlation of which increased considerably. The longer timescale resulted in close-to-zero correlations for NEE and sensible heat, which were the only nonsignificant regressors (Table 2).

[34] The multiple linear regression analysis confirmed the dominating influence of  $T_{\text{air}}$  and PAR on both timescales. When the methanol concentration was not factored in and based on half-hourly values,  $T_{\text{air}}$  and PAR resulted in similarly high partial correlations. When compared to the simple linear regression, the partial correlations of VPD changed in sign and became negative (Table 2). The analysis resulted in  $g_{\text{surf}}$  having the highest tolerance value, underlining its unique contribution to the chosen set of variables, followed by SWC. On the half-hourly timescale all regressors were highly significant.

[35] Using daily averages,  $T_{\text{air}}$  and PAR remained the most important drivers for methanol exchange and were also the only highly significant variables. Along with these two variables, only  $f_{\text{dif}}$  resulted in a significance of  $p < 0.05$  and a high partial correlation, the latter being positive as opposed to the negative correlation found in the simple linear regression analysis. Generally, tolerance values hardly changed on the daily timescale as compared to the half-hourly values (Table 2).

[36] In a second step, the methanol VMR was included in the multiple linear regression equation. Compared to the analysis without methanol VMR factored in and using half-hourly values, the influence of  $T_{\text{air}}$  decreased considerably

**Table 2.** Regression Analysis of the Methanol Flux<sup>a</sup>

	Simple Linear Regression						Multiple Linear Regression					
	Half-Hourly			Daily Average			Half-Hourly			Daily Average		
	N	r	p	N	r	p	Partial Correlation	Tolerance	p	Partial Correlation	Tolerance	p
NEE	5503	-0.44	***	228	-0.08	ns	–	–	–	–	–	–
Latent heat flux	5503	0.63	***	219	0.71	***	–	–	–	–	–	–
Sensible heat flux	5503	0.32	***	235	-0.01	ns	–	–	–	–	–	–
GAI	5503	–	–	321	0.39	***	–	–	–	0.10 (0.11)	0.64 (0.64)	ns (ns)
dGAI	5503	–	–	321	0.53	***	–	–	–	0.12 (0.18)	0.51 (0.51)	ns (*)
SWC	5503	-0.36	***	321	-0.60	***	-0.12	0.69 (0.59)	*** (ns)	0.00 (0.18)	0.51 (0.46)	ns (*)
$f_{\text{dif}}^b$	5503	-0.43	***	321	-0.25	***	0.10	0.32 (0.32)	*** (***)	0.20 (0.14)	0.21 (0.21)	* (ns)
$g_{\text{surf}}^b$	3954	0.34	***	219	0.35	***	0.08	0.79 (0.75)	*** (***)	0.00 (0.15)	0.79 (0.73)	ns (ns)
VPD	5503	0.50	***	321	0.68	***	-0.25 (-0.17)	0.20 (0.19)	*** (***)	0.04 (0.06)	0.14 (0.14)	ns (ns)
$T_{\text{soil}}^b$	5503	0.45	***	321	0.72	***	-0.06 (0.00)	0.24 (0.23)	*** (ns)	0.01 (0.11)	0.12 (0.11)	ns (ns)
$T_{\text{air}}^b$	5503	0.60	***	321	0.82	***	0.32 (0.19)	0.10 (0.08)	*** (***)	0.29 (0.11)	0.07 (0.06)	*** (ns)
PAR <sup>b</sup>	5503	0.60	***	321	0.63	***	0.36 (0.39)	0.29 (0.29)	*** (***)	0.28 (0.16)	0.14 (0.13)	*** (*)
Methanol VMR	5503	0.41	***	321	0.80	***	-(0.30)	-(0.52)	-(***)	-(0.49)	-(0.28)	-(***)
							Half-Hourly			Daily Average		
Whole model $r^2$							0.52 (0.56)			0.74 (0.80)		

<sup>a</sup>Correlation coefficients of a simple linear regression analysis and partial correlations, tolerance and significance of a multiple linear regression analysis, using half-hourly and daily average values of net ecosystem CO<sub>2</sub> exchange (NEE), latent and sensible heat flux, green plant area index (GAI), change in green plant area index (dGAI), soil water content (SWC) at 0.05 m soil depth, fraction of diffuse radiation ( $f_{\text{dif}}$ ), surface conductance ( $g_{\text{surf}}$ ), vapor pressure deficit (VPD), soil temperature ( $T_{\text{soil}}$ ) at 0.05 m soil depth, air temperature ( $T_{\text{air}}$ ), photosynthetically active radiation (PAR) and methanol volume mixing ratio (VMR) as independent variables. For the multiple regression analysis 3154 half-hourly and 169 daily average data points were used, respectively. Numbers in parentheses refer to the analysis with the methanol concentration included in the multiple regression equation. Management events were excluded from the analysis. N, number of cases; r, correlation coefficient; p, significance level. One asterisk indicates  $p < 0.05$ , and three asterisks indicate  $p < 0.001$ ; ns, not significant.

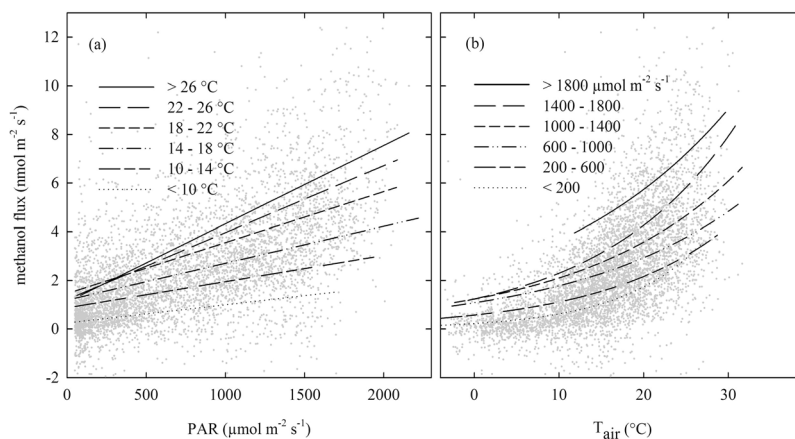
<sup>b</sup>Linearized.

(Table 2). Methanol concentration had the second highest partial correlation after PAR and its tolerance value was one of the highest observed. Except for SWC and  $T_{\text{soil}}$ , all variables were highly significant (Table 2). When methanol VMR was factored in on a daily timescale, partial correlations changed considerably. The highest influence on the measured methanol flux was found for the methanol VMR, also the only regressor that was highly significant. In comparison to the same analysis without the methanol VMR, the importance of  $T_{\text{air}}$  and PAR diminished clearly, with the former becoming statistically insignificant (Table 2). In contrast, dGAI and SWC became insignificant, while for  $f_{\text{dif}}$  the opposite was observed. Tolerance values remained similar for

all variables, with dGAI and SWC providing the least redundant contribution to the regression. However, for the methanol concentration the tolerance value on a daily timescale was clearly lower than when using half-hourly values.

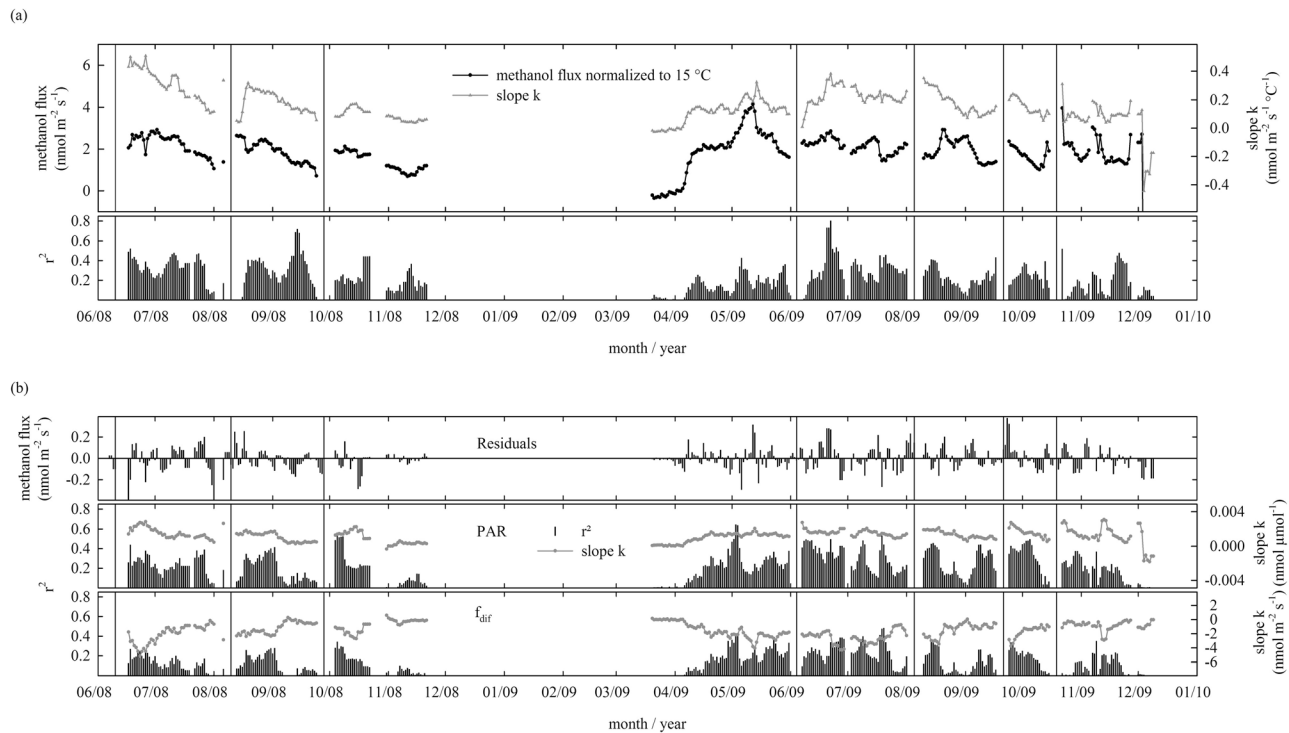
[37] The multiple linear regression analysis in Table 2 resulted in all variables combined being able to explain 52% and 74% of the observed variance of the measured methanol flux at the half-hourly and daily timescale. When methanol concentration was factored in, the corresponding numbers were somewhat higher (56% and 80%, respectively).

[38] With PAR and  $T_{\text{air}}$  identified as the main drivers for methanol emissions, Figures 4a and 4b further examine their



**Figure 4.** Methanol flux (a) as a function of photosynthetically active radiation (PAR) for different classes of air temperature ( $T_{\text{air}}$ ) and (b) as a function of  $T_{\text{air}}$  for different classes of PAR on a half-hourly time scale. Management events, wet canopy conditions and half hours with PAR below  $50 \mu\text{mol m}^{-2} \text{s}^{-1}$  were excluded from the analysis. Numbers for the regression lines are given in Table A1.





**Figure 5.** Seasonal and interannual variability in the temperature sensitivity of the methanol flux for moving time windows of 7 days, with each following data point being shifted by 1 day. (a) Methanol flux normalized to an air temperature ( $T_{\text{air}}$ ) of 15°C, the slope of a linear regression between air temperature and the log-transformed methanol flux ( $k$ ) and  $r^2$  which shows the variance of the observed methanol flux that can be explained by  $T_{\text{air}}$ . (b) The residuals show the difference between the observed and the predicted (based on  $T_{\text{air}}$ ) flux, while  $r^2$  shows to what extent the observed variance of the residuals can be explained in a linear regression by photosynthetically active radiation (PAR) or fraction of diffuse radiation ( $f_{\text{dif}}$ ), other independent variables were not significant. Vertical lines show management dates.

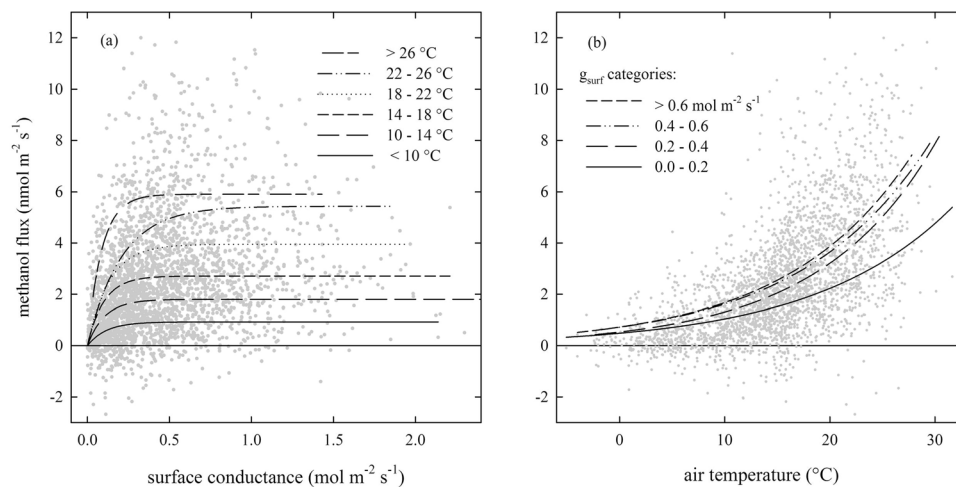
joint influence using half-hourly values. The measured methanol flux increased linearly with PAR and showed higher sensitivity to PAR as air temperatures increased (Figure 4a). Methanol emissions increased exponentially with  $T_{\text{air}}$  and at a given air temperature the measured flux was higher during periods with high PAR values (Figure 4b).

[39] Figure 5a shows the seasonal and interannual variation of the temperature sensitivity of the methanol flux for 7 day moving time windows. Throughout the measurement campaigns, the methanol flux normalized to 15°C changed continuously (Figure 5a). In 2008, maximum values were found in June and July. Efflux was minimal right after snowmelt in 2009 but increased over the following weeks until it peaked in mid-May. Generally, the methanol flux normalized to 15°C decreased toward the end of the growing season in both years, a pattern which was more pronounced in 2008 than in 2009. Figure 5a also shows the slope  $k$  of a linear regression between air temperature and the (log-transformed) methanol flux as a measure of its temperature sensitivity. In 2008, highest sensitivities were found directly after the first cut and decreased afterwards. Although the temperature sensitivity showed distinct peaks in certain 7 day segments, the general pattern was less pronounced in 2009 than in 2008. Generally, the methanol flux normalized to 15°C and the temperature sensitivity were in phase and showed a positive correlation, although

there were certain time windows throughout the measurement campaigns when this was not the case. One example is the time period directly after the second cut in August 2009, when the methanol flux normalized to 15°C and the temperature sensitivity were negatively correlated. The  $r^2$  given in Figure 5a shows the variance of the observed methanol flux that can be explained by  $T_{\text{air}}$ , which was found to be at least 25% for more than half of the 7 day periods, with a maximum of 80% in June 2009.

[40] The residuals in Figure 5b show the difference between the observed and the predicted (based on temperature) methanol flux, where positive residuals show time periods during which the flux has been underestimated. Figures 5b (middle) and 5b (bottom) show the resulting slope and  $r^2$  when the residuals are linearly related to PAR and  $f_{\text{dif}}$ . During certain time periods the slopes of PAR and  $f_{\text{dif}}$  were negatively correlated, while  $r^2$  showed a positive correlation of the two variables with the observed residuals, e.g., in June and July 2008 (Figure 5b). The median value for the explained residual variance for PAR and  $f_{\text{dif}}$  was found to be 22% and 13%, respectively, with maximum values of 65% and 48%.

[41] The methanol exchange over both growing seasons was simulated by fitting observed fluxes to (log-transformed)  $T_{\text{air}}$  in subsequent 7 day segments, resulting in varying values for sensitivity  $k$  and offset  $d$  for each segment, which were then used to simulate half-hourly fluxes



**Figure 6.** (a) The influence of surface conductance ( $g_{\text{surf}}$ ) on the observed methanol emissions in different classes of air temperature ( $T_{\text{air}}$ ). (b) Methanol flux as a function of  $T_{\text{air}}$ , lines illustrate different classes of  $g_{\text{surf}}$ . Management events, wet canopy conditions and half hours with PAR below  $50 \mu\text{mol m}^{-2} \text{s}^{-1}$  were excluded from the analysis. Numbers for the regression lines are given in Table A1.

based on measured air temperatures. The simulated cumulative carbon emission of  $0.277 \text{ g C m}^{-2}$  was slightly lower than the observed emission of  $0.290 \text{ g C m}^{-2}$ . When  $k$  and  $d$  were derived from the pooled data and therefore constant for both years, the carbon loss amounted to  $0.274 \text{ g C m}^{-2}$ , i.e., only 1% below the value calculated based on temporally varying parameters. Note that days influenced by management events were not included in these calculations.

[42] In the literature,  $T_{\text{air}}$  and  $g_{\text{s}}$  have been identified as important drivers for methanol emissions at the leaf level [e.g., Hüve *et al.*, 2007; Niinemets *et al.*, 2004; Harley *et al.*, 2007]. Figure 6a thus explores ecosystem-scale methanol emissions as a function of  $g_{\text{surf}}$  stratified according to  $T_{\text{air}}$ . The methanol flux was approximately linearly related to  $g_{\text{surf}}$  at low  $g_{\text{surf}}$  values and became independent of  $g_{\text{surf}}$  at higher values. The  $g_{\text{surf}}$  value up to which a linear relationship was observed rose with air temperature and was found at  $0.2 \text{ mol m}^{-2} \text{ s}^{-1}$  for  $T_{\text{air}} < 10^\circ\text{C}$  and at  $0.5 \text{ mol m}^{-2} \text{ s}^{-1}$  during warm periods with  $T_{\text{air}}$  between 22 and  $26^\circ\text{C}$  (Figure 6a). Figure 6b shows the methanol flux as a function of  $T_{\text{air}}$  stratified into classes of surface conductance. Except for very low  $g_{\text{surf}}$  values, the temperature response is largely independent of  $g_{\text{surf}}$ .

## 4. Discussion

### 4.1. Magnitude of Methanol Exchange

[43] Daily average fluxes depicted in Figure 1 and diurnal cycles of methanol fluxes in Figure 2 showed a general emission from the canopy into the atmosphere, which is in accordance with Brunner *et al.* [2007], who measured methanol fluxes over an intensively and extensively managed grassland in Switzerland. In the same study, maximum fluxes not related to management events reached up to  $18.4 \text{ nmol m}^{-2} \text{ s}^{-1}$  over the extensively managed field, which is similar to the  $17.9 \text{ nmol m}^{-2} \text{ s}^{-1}$  found in the present study (data not shown). Diurnal cycles of methanol as reported by Brunner *et al.* [2007] for the mature phase during August show peak emissions of  $7 \text{ nmol m}^{-2} \text{ s}^{-1}$  around noon and

confirm the findings in the present study, which showed average peak emissions of up to  $6 \text{ nmol m}^{-2} \text{ s}^{-1}$  in August 2008 (Figure 2).

[44] Brunner *et al.* [2007] calculated the cumulative methanol emissions during the mature phase of the extensive field about three weeks before cutting, which resulted in a total emission of  $6.3 \text{ mg C m}^{-2}$  over 6 days. This compares well with our findings of  $8.5$  and  $7.7 \text{ mg C m}^{-2}$  during similar time periods in July (2008 and 2009, respectively). However, the field site in Neustift still showed strong growth rates during this phase, whereas the LAI reported by Brunner *et al.* [2007] increased only slightly during the 6 day period.

[45] The highest methanol emissions over the course of the whole measurement campaign were consistently measured on the day of cutting and the days thereafter, when methanol stored inside severed plant cells escaped to the atmosphere [Niinemets *et al.*, 2004; Loreto *et al.*, 2006]. The observed maximum fluxes shown in Table 1 compare very well to numbers reported in the literature, where numerous studies reported maximum methanol fluxes in the range of  $69.4\text{--}110.9 \text{ nmol m}^{-2} \text{ s}^{-1}$  on the day of cutting [Davison *et al.*, 2008; Brunner *et al.*, 2007; Warneke *et al.*, 2002; Karl *et al.*, 2001b]. Methanol emissions were still elevated 1 day after the cut, for which the same studies reported maximum fluxes of  $6.9\text{--}44.2 \text{ nmol m}^{-2} \text{ s}^{-1}$  as compared to  $3.8\text{--}67.1 \text{ nmol m}^{-2} \text{ s}^{-1}$  in the present study (Table 1). A secondary methanol emission pulse was occasionally observed when the drying hay was turned, as occurred after the second cut in August 2009 or the third cut in September 2009, which presumably allowed residual liquid phase methanol to evaporate. Davison *et al.* [2008] reported average daytime fluxes of methanol between 07:00 and 17:00 LT for 3 days in June following the cutting of agricultural grassland. Numbers given in their study range from  $8.7$  to  $15.5 \text{ nmol m}^{-2} \text{ s}^{-1}$ , while the five cutting dates observed in the present study showed average methanol fluxes during the same time of day in the range of  $2.0\text{--}27.9 \text{ nmol m}^{-2} \text{ s}^{-1}$ .

[46] 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 as observed during the third cut in 2009 (Table 1). Due to the rapid emission response it is unlikely that the organic fertilizer had an immediate stimulating effect on canopy growth causing methanol emissions to rise because of increased pectin demethylation. Instead, 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].

#### 4.2. Drivers of Methanol Flux

[47] The highly positive (partial) correlations of the methanol VMR with the observed methanol flux (Table 2), i.e., methanol emission increased with ambient concentrations, is counterintuitive as from Fick's first law of diffusion one would expect a negative correlation, i.e., methanol emissions to increase as ambient concentrations decrease due to an increase in the diffusion gradient. We thus interpret the observed positive correlation between the methanol flux and ambient VMR to reflect increases in ambient VMR during periods of high emissions. However, it is difficult to substantiate to what extent the local methanol emissions contributed to the observed methanol VMR. For the reasons stated above, methanol VMR was not included in the discussion of the other dominant drivers.

[48] The statistical analysis (Table 2) identified  $T_{\text{air}}$  and PAR as the key drivers of methanol emissions which jointly explained 47% and 70% of the variability in half-hourly and daily average methanol fluxes, respectively. Some regressors, e.g., the sensible heat flux, were significantly related to the methanol flux at the half-hourly but not at the daily time step, which reflects their diurnal covariation with  $T_{\text{air}}$  and PAR. In contrast, SWC, which exhibits little or no variability at the subdaily time step, became more significant in the analysis of daily average data.

[49] The dominant control of temperature on methanol emission has two probable reasons: First, warm air temperatures during the growing season often constitute ideal conditions for plant growth. Pectin methylesterases (PMEs)

are cell wall enzymes that, among other functions, enable the expansion of cell walls by catalyzing the demethylation of pectin within the plant cells [Körner *et al.*, 2009; Frenkel *et al.*, 1998]. The enzymatic activity of PMEs increases with leaf temperature, resulting in higher rates of methanol production within the leaf. Second, the temperature dependent gas/liquid-phase distribution coefficient  $H$  (Henry's law constant) determines the partitioning between the liquid- and gas-phase within the leaf interior [Niinemets and Reichstein, 2003a, 2003b]. Higher temperatures lead to increased partitioning to the gas-phase and to an increased release of methanol. The temporal analysis of the temperature dependency of the methanol flux convincingly shows that both the methanol emission normalized to a reference temperature and the temperature sensitivity change seasonally and differ interannually, suggesting that emission algorithms with constant parameters may be inappropriate for simulating methanol flux variability at time scales covering one or more growing seasons [Niinemets *et al.*, 2010].

[50] Based on leaf-level laboratory experiments, Harley *et al.* [2007] concluded that there is not enough evidence for a direct effect of PAR on methanol production and emission. While any direct effect of PAR on the production and release of methanol is hard to quantify at the canopy scale where PAR is generally correlated with air temperature, this study provides several lines of evidence (Table 2 and Figures 4 and 5) that PAR may be controlling methanol emissions in addition to and independently from air temperature. Further studies at leaf level, both in the field and laboratory, are required to shed light on the possible independent role of PAR in controlling methanol emissions and the associated biochemical pathways.

[51] When methanol is produced, it has to partition to the gas phase and diffuse to the intercellular air space before being emitted through the stomata [Folkers *et al.*, 2008]. Niinemets and Reichstein [2003a] conclusively showed that the stomatal sensitivity of VOC emissions is mainly affected by the Henry's law constant. As methanol has a low  $H$  value and is highly soluble in water, its emission is directly limited by stomatal conductance. As a consequence, the regulation of water loss in plants by adjusting stomatal conductance in order to avoid dehydration [Jones, 1996] directly affects the efflux of methanol from leaves [MacDonald and Fall, 1993]. During the night, stomata are largely closed, which can lead to an accumulation of methanol in the leaf internal gaseous pool [Niinemets and Reichstein, 2003b]. In the morning the gas phase pool is rapidly emptied upon stomatal opening, leading typically to a transient emission peak [Nemecek-Marshall *et al.*, 1995]. This could not be observed in the present study where the diurnal emission pattern smoothly followed the course of the two major abiotic drivers, air temperature and PAR (Figure 2). Lacking a scale-appropriate metric of canopy ( $g_s$ ), we used the surface conductance ( $g_{\text{surf}}$ ) as a proxy, recognizing that  $g_{\text{surf}}$  includes a generally unknown contribution by soil evaporation which however is deemed negligible once the canopy is reasonably closed [Wieser *et al.*, 2008]. Contrary to our hypothesis,  $g_{\text{surf}}$  explained only a minor fraction of the variability in methanol fluxes (Table 2) and limited methanol emissions only at very low values (Figure 5). This apparent contradiction to earlier leaf-level experimental [Nemecek-Marshall *et al.*, 1995; Hüve *et al.*, 2007] and modeling [Niinemets and Reichstein,

**Table A1.** Regression Lines for Figures 4 and 6<sup>a</sup>

	Regression Lines for Figure 4a; Equation $f = k + ax$ ; Air Temperature (°C)					
	<10	10–14	14–18	18–22	22–26	>26
$r$	0.24 ***	0.33 ***	0.42 ***	0.49 ***	0.56 ***	0.48 ***
Standard error of estimate	1.05	1.40	1.64	1.95	2.03	2.61
$k$	0.24	0.87	1.18	1.45	1.21	1.10
$a$	$7.5 \times 10^{-4}$	$1 \times 10^{-3}$	$2 \times 10^{-3}$	$2 \times 10^{-3}$	$3 \times 10^{-3}$	$3 \times 10^{-3}$
	Regression Lines for Figure 4b; Equation $f = a \exp(bx)$ ; PAR ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ )					
	<200	200–600	600–1000	1000–1400	1400–1800	>1800
$r$	0.37 ***	0.44 ***	0.43 ***	0.44 ***	0.55 ***	0.37 ***
Standard error of estimate	1.51	1.34	1.59	1.97	2.01	2.87
$a$	0.22	0.57	1.07	1.23	1.23	2.30
$b$	0.10	0.07	0.05	0.05	0.06	0.05
	Regression Lines for Figure 6a; Equation $f = a[1 - \exp(-bx)]$ ; Air Temperature (°C)					
	<10	10–14	14–18	18–22	22–26	>26
$r$	0.24 ***	0.24 ***	0.10 *	0.20 ***	0.34 ***	0.20 (ns)
Standard error of estimate	0.90	1.27	1.75	2.20	2.50	3.19
$a$	0.93	1.80	2.71	3.95	5.44	5.91
$b$	8.88	9.54	9.97	7.6	4.84	11.37
	Regression Lines for Figure 6b; Equation $f = a \exp(bx)$ ; Surface Conductance ( $\text{mol m}^{-2} \text{s}^{-1}$ )					
	0–0.2	0.2–0.4	0.4–0.6	>0.6		
$r$	0.47 ***	0.57 ***	0.60 ***	0.58 ***		
Standard error of estimate	1.44	1.83	1.85	1.88		
$a$	0.49	0.54	0.72	0.73		
$b$	0.08	0.09	0.08	0.08		

<sup>a</sup>Parameters are  $r$ , correlation coefficient;  $a$ ,  $b$ , equation coefficients;  $k$ , slope; PAR, photosynthetic active radiation. One asterisk indicates significant with  $p < 0.05$ , and three asterisks indicate highly significant with  $p < 0.001$ ; ns, not significant. Significance levels are corrected for the mean of the observations (SigmaPlot 11.0, Systat Software, Inc.).

2003a, 2003b] studies may be attributed to two main causes: First, a plant canopy under field conditions does not behave like a single leaf under controlled environmental conditions in an enclosure. Rather, leaves in a plant canopy experience vertical gradients in microclimate, environmental conditions in a plant canopy are highly dynamic and may differ clearly from the conditions at screen height. As a consequence, vertical gradients in stomatal conductance are typically found in plant canopies [Sinclair *et al.*, 1976], which may act to smear out any transient methanol emissions in response to changes in stomatal conductance. For example, upon sun rise sunlit leaves in the upper canopy may be expected to open stomata, while leaves in the lower canopy still experience low light intensities with stomata largely closed. Second, the averaging time of our eddy covariance flux measurements (0.5 h) is much longer than typical half-life times of the aqueous pool ( $<500$  s [Niinemets *et al.*, 2004]), which again causes any transient emissions to be smeared out. Finally, it should be acknowledged that ecosystem-atmosphere flux measurements contain an unknown soil component (both uptake/emission reported for methanol [Karl *et al.*, 2004, 2005; Schade *et al.*, 2008]) which may act to buffer any dynamic leaf response.

[52] Methanol is produced as a by-product of the demethylation of pectin in plant cell walls by the temperature dependent enzyme pectin methyltransferase [Nemecek-Marshall *et al.*, 1995]. Hüve *et al.* [2007] compared old and young (growing) leaves and found for the latter the peak methanol emission rate to be about four times higher than in mature leaves. In the present study, no direct measurements of plant

growth were available, instead the daily change in the amount of photosynthetically active plant area, dGAI, was used as a surrogate for growth. In contrast to our hypothesis, dGAI clearly ranked behind abiotic variables such as air temperature or PAR in determining methanol fluxes. The reasons for this discrepancy to the leaf-level laboratory measurements mentioned above are unclear at present. Possibly, the temporal resolution of our GAI measurements from which dGAI is inferred is too poor to properly resolve daily changes in growth rate. The relationship between dGAI and methanol fluxes may also be obscured by an inverse correlation between GAI and dGAI—dGAI is smallest shortly before the cuts when GAI and thus the amount of methanol-emitting plant area is highest. It should though also be mentioned that we lack a clear understanding of the growth rhythms of the various plant species of this grassland [see also Brunner *et al.*, 2007], which generally follow different spatial and temporal strategies [Bahn *et al.*, 1994] and thus may exhibit contrasting growth rhythms and magnitudes. On another note, most of our laboratory knowledge is based on dicots and grasses possibly behave differently due to a different form of pectin [Galbally and Kirstine, 2002].

## 5. Summary and Conclusion

[53] Two years of methanol flux measurements above a temperate mountain grassland site in Neustift, Stubai Valley, revealed that methanol was continuously emitted by the vegetation and exhibited a large interannual variability. Management actions at the field site, i.e., cutting and the

application of organic fertilizer, were found to represent the largest perturbations of the seasonal methanol exchange at the investigated grassland ecosystem. In addition to the well-known positive relationship with temperature, a direct control of methanol emissions by PAR was proposed which merits further studies. In contrary to expectations based on leaf-level laboratory studies, surface conductance and the diurnal change in GAI, which were used as proxies for the canopy-integrated stomatal conductance and growth respectively, explained only a minor fraction of the temporal variability in methanol fluxes. We suggest this discrepancy to result from differences in spatial and temporal scale of flux as opposed to leaf-level enclosure measurements and controlled laboratory environments as opposed to real-world field conditions. In order to close the apparent gap that exists in transferring leaf-level laboratory knowledge to in situ conditions at the ecosystem scale, which hampers the development and parameterization of ecosystem models, concurrent studies on leaf/soil and ecosystem-scale methanol exchange under field conditions are advocated.

## Appendix A

[54] Table A1 gives details for the regressions shown in Figures 4 and 6.

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I. Bamberger, A. Hansel, and R. Schnitzhofer, Institute of Ion Physics and Applied Physics, University of Innsbruck, Technikerstrasse 25, A-6020 Innsbruck, Austria.

M. Gaus, Chemical Sciences Division, Earth System Research Laboratory, NOAA, 325 Broadway, Boulder, CO 80305-3337, USA.

L. Hörtnagl and G. Wohlfahrt, Institute of Ecology, University of Innsbruck, Sternwartestraße 15, A-6020 Innsbruck, Austria. (georg.wohlfahrt@uibk.ac.at)

M. Müller, IRCELYON, University of Lyon, Avenue Albert Einstein, F-69629 Villeurbanne, France.

T. M. Ruuskanen, Division of Atmospheric Sciences, University of Helsinki, Gustaf Hällströminkatu 2, FI-00014 Helsinki, Finland.