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Long term BVOC fluxes above mountain grassland

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Abstract

Grasslands comprise natural tropical savannah over managed temperate fields to tundra and cover over a quarter of the Earth's land surface. Plant growth, maintenance and decay result in volatile organic compound (VOCs) emissions to the atmosphere. Furthermore, biogenic VOCs (BVOCs) are emitted due to various environmental stresses including cutting and drying during harvesting. Fluxes of BVOCs were measured with a proton-transfer-reaction – mass-spectrometer (PTR-MS) over temperate mountain grassland in Stubai Valley (Tyrol, Austria) over one growing season (2008). VOC fluxes were calculated from the disjunct PTR-MS data using the virtual disjunct eddy covariance method and the gap filling method. The two independent methods obtained methanol fluxes following a regression line of $y=0.94x-0.06$ (correlation factor: $R^2=0.94$). Methanol showed strong daytime emissions throughout the growing season. With maximal values of 9.7 nmol m^{-2} s^{-1} the methanol fluxes from growing grassland were considerably higher at the beginning of the growing season in June compared to those measured during October (2.5 nmol m^{-2} s^{-1}). During the growth only methanol emissions were observed. The cutting and drying of the grass increased the emissions of methanol, up to 30 nmol m^{-2} s^{-2}. In addition, emissions of acetaldehyde, up to 10 nmol m^{-2} s^{-1}, and hexenal (leaf aldehyde) were detected during harvesting.

1 Introduction

Volatile organic compounds (VOCs) attain to the atmosphere from a variety of biogenic and anthropogenic sources with an estimated emission of 1300 Tg C yr^{-1} (Goldstein and Galbally, 2007). Up to 90% of those emissions are assumed to be of natural origin (Guenther et al., 1995). In the presence of VOCs the photochemical equilibrium between NO, NO_2 and ozone can be shifted out of steady-state towards the formation of tropospheric ozone (Sillman, 1999). VOCs contribute to the formation of condensable matter and secondary organic aerosols, and thus indirectly effect cloud formation

(Kulmala et al., 2004; Ramanathan et al., 2001). Moreover, secondary organic aerosols have negative effects on human health (Dockery et al., 1993). As a consequence biogenic VOCs (BVOCs) play a key role in tropospheric chemistry. However, the spatial and temporal variation of the biosphere-atmosphere exchange of organic trace gases is poorly determined as quantitative measurements are hard to obtain.

BVOCs are emitted from processes such as growth, maintenance and decay of organic material (Goldstein and Galbally, 2007). Methanol in particular is released from growing plants due to cell wall synthesis (Fall and Benson, 1996). Furthermore, VOCs are emitted as a consequence of plant stress like cutting grass (Fall et al., 1999; Karl et al., 2001) or in response to environmental stress conditions (temperature and light, ozone, water) (Loreto et al., 2006; Beauchamp et al., 2005, Sharkey and Loreto, 1993; Bertin and Staudt, 1996). The overall amount and the range of emitted VOCs depends on the plant species (Kesselmeier, 2001), meteorological factors such as light, temperature and plant physiological and physiochemical status (Niinemets et al., 2004).

Long term ecosystem-scale VOC emission measurements are needed to determine and characterize the VOC emissions from single events (cutting, stress events) as well as the continuous emissions during plant growth and its seasonal changes. Grasslands cover one quarter of the Earth's land surface (Graedel and Crutzen, 1993), but long term VOC emission studies from e.g. managed grasslands are missing. Only two VOC emission studies, which cover more than one growing season have been conducted (Kirstine et al., 1998; Fukui and Doskey, 1998). However, both of these studies were performed under controlled conditions using static chambers. Brunner et al. (2007) investigated only one growth period of grassland in between harvestings during one summer. The quantification of VOC emissions and their contribution to the global VOC budget requires measurements under environmental conditions that cover more than one growth period.

This paper identifies seasonal changes of concentrations and fluxes of different VOCs over grassland. We report VOC fluxes and concentrations from PTR-MS measurements above a temperate mountain grassland in an Austrian valley. VOC fluxes are

calculated independently with virtual disjunct eddy covariance (vDEC; Karl et al., 2002) and gap filling (Spirig et al., 2005) methods and the results are compared. The diurnal patterns of fluxes and concentrations are presented for the months of June (representing summer) and October (representing autumn) and the differences between the two months are discussed. Grass harvesting is presented as an example for a short but intensive VOC burst to the atmosphere.

2 Experimental

2.1 Site description

The experiments were performed over grassland in Stubai Valley (Austria) close to the village Neustift (47°07′ N, 11°19′ E). The intensively managed meadow is located in the middle of a flat valley bottom 970 m a.s.l. It is cut and harvested three times a year which results in three growing periods (periods between two cuts) of the grass per growing season. The thermally induced valley wind system is reflected in the wind distribution in Fig. 1. The maximum of the footprint function was calculated according to Hsieh et al. (2000) and is shown in Fig. 1 overlaid on an aerial picture of the study site. The footprint was larger during the night, when the wind velocities are usually weak and the atmosphere is stably stratified, than during unstable daytime conditions when higher wind velocities were encountered.

The climate in Stubai valley is humid continental with alpine influences. The average annual temperature (1980–2000) was 6.5 °C and the average annual rainfall was 852 mm. A more detailed description of the study site, soil, vegetation and climate is given in Hammerle et al. (2008) and Wohlfahrt et al. (2008).

2.2 Eddy covariance and meteorological instrumentation

The net ecosystem VOC exchange was measured using the disjunct eddy covariance (DEC) method that is based on the eddy covariance method (Baldocchi et al., 1988).

The three wind components were measured by a three-dimensional sonic anemometer (R3IA, Gill Instruments, Lymington, UK), VOC volume mixing ratios by a PTR-MS instrument. Sample air was sucked from the inlet, displaced 0.1 m laterally and 0.1 m below the centre of the sensor volume of the sonic anemometer mounted at 2.5 m above ground, through 16 m heated (to 40 °C) PTFA Teflon tube of 0.004 m inner diameter through a filter (1–2 µm, PTFE) to the PTR-MS at a flow rate of 8 slm. The 20 Hz sonic anemometer data was stored to a hard drive of a personal computer for post-processing using the *EdiSol* software (University of Edinburgh).

An automated weather station continuously measured incident global and photosynthetically active radiation, air and soil temperature, relative humidity, leaf wetness, rainfall, soil water content, wind speed and wind direction at the field site (Hammerle et al., 2008; Wohlfahrt et al., 2008).

2.3 PTR-MS setup and operation

Selected VOCs (Table 1) were measured by means of a high sensitivity PTR-MS. The working principle of PTR-MS is described elsewhere (Hansel et al., 1995; Lindinger et al., 1998). The PTR-MS system was deployed in a container next to the field site. The measurement setup of the PTR-MS is illustrated in Fig. 2. Additionally to the air sampling (as described above), a pump continuously flushed 500 ml of the incoming air through a home-build catalytic converter to produce VOC-free zero-air. During the last five minutes of every half hour, zero-air was lined into the PTR-MS to determine the instrumental background (zero calibration). The instrument's sensitivity was calibrated once a week using a gas standard containing 11 VOCs in N_2 (Apel Riemer Inc., USA). For that purpose the adjustable calibration gas flow (1 sccm, 2.5 sccm, 5 sccm or 7.5 sccm) was diluted with 500 sccm zero-air and the known gas mixture was analyzed by the PTR-MS. Sensitivities were determined from linear regression of the known VOC volume mixing ratios and the respective signal intensities.

Ambient air was analyzed for a number of VOCs at a repetition rate of 2.82 s until the 10 July, when it was changed to 3.00 s. The dwell-time for each single mass channel

was less than 0.5 s. A list of the recorded masses and their dwell times is given in Table 1. The PTR-MS was operated at a drift tube pressure of 2.15 mbar and a drift voltage of 550 V. The PTR-MS data was stored in half-hourly files and processed to VOC concentrations in ppbv using MATLAB 7.4.0 (R2007a, The MathWorks, Inc, USA).

3 Data analysis

3.1 VOC flux calculations

Half-hourly VOC fluxes were calculated as the covariance between the turbulent fluctuations of the vertical wind speed and the VOC mixing ratios using the post-processing software *EdiRe* (University of Edinburgh). Means and turbulent fluctuations were calculated by Reynolds (block) averaging.

Two methods which differ in the way they deal with the disjunct sampling of the VOC concentrations were employed: The virtual Disjunct Eddy Covariance (vDEC) method, presented by Karl et al. (2002), calculates the flux from a subsample of the horizontal wind data as given by the sampling rate of the PTR-MS. The gap filling method, discussed by Spirig et al. (2005), fills the missing VOC data by repeating the nearest neighbouring VOC mixing ratios to match the 20 Hz time resolution of the wind dataset. For a comparison of these two methods using high-frequency CO_2 and H_2O flux measurements see Hörtnagl et al. (2009) (submitted to Atmospheric Environment). The following processing steps are identical for both methods, except where indicated otherwise.

A three-axis coordinate rotation was performed aligning the co-ordinate system's vector basis with the mean wind streamlines (Kaimal and Finnigan, 1994). Negative fluxes represent the transport from the atmosphere towards the surface (deposition), positive ones the reverse (emission). The tube-induced time delay of the VOC signals was determined by optimizing the correlation coefficient with the vertical wind velocity (McMillen, 1988) within a ±50 s time window. As shown exemplarily in Fig. 3,

this worked generally well for methanol (*m/z* 33) and the water cluster measured at the mass to charge ratio *m/z* 37 (not shown). For the other masses, for which the time delay determination from the cross-correlation was not consistently successful, the methanol time delay was used instead. If no suitable time delay could be identified for a given half-hourly period, it was set to the value of a neighbouring measurement. As shown in Fig. 3 the cross correlation was much noisier for the vDEC as opposed to the gap filling method, which is in accordance with the findings of Hörtnagl et al. (2009). Frequency response corrections were applied to the raw VOC fluxes accounting 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 following Moore (1986), Massman (2000) and Aubinet et al. (2000). Additional low-pass filtering occurs for the fluxes calculated with the gap filling method, which was corrected according to Hörtnagl et al. (2009) – the lower covariance of the gap filling method in Fig. 3 is indicative of this flux loss as cospectral corrections are applied during a later processing step. Frequency-response corrections were based on a site-specific model co-spectrum described by Wohlfahrt et al. (2005), as discussed in the next section.

3.2 Frequency response of the flux measurements

Higher frequencies of the methanol flux are dampened compared to the sensible heat flux (Fig. 4). The flux loss results mainly from the attenuation of the concentration fluctuations in the sampling tube (Massman, 1991) in conjunction with the slower time response of the PTR-MS as opposed to the sonic anemometer, and in case of the gap filling method additional low-pass filtering due to the data treatment. Figure 4 also depicts the cospectral reference model (see Wohlfahrt et al., 2005 for further details) and the simulated (i.e. attenuated) cospectrum for the methanol flux (calculated with the gap-filling method). Both the reference model and the attenuated reference model correspond reasonably well with the sensible heat (which experiences relatively little

low-pass filtering) and the methanol flux cospectra, respectively. This confirms the approach of correcting for imperfections in the frequency response of our flux measurement system – all fluxes presented below were corrected accordingly.

3.3 Quality control

Half-hourly fluxes were quality controlled by removal of time periods with (1) ambient concentrations of VOCs which are (averaged over half an hour) below the measured background concentration (concentrations are below the limit of detection for the specific VOC), (2) a significant background drift within half an hour, (3) the third rotation angle exceeding ±10° (McMillen, 1988), (4) the stationarity test for the various VOC fluxes exceeding 60% (Foken and Wichura, 1996), (5) the deviation of the integral similarity characteristics larger than 60% (Foken and Wichura, 1996), and (6) the maximum of the footprint function (Hsieh et al., 2000) is outside of the boundaries of the meadow (cf. Novick et al., 2004).

A measured point was considered an outlier if the difference to the averaged signal during the half hour was higher than 10 times the theoretical standard deviation (noise) of the signal. Outliers of the VOC measurements were replaced by the averaged VOC concentration during the respective half-hour period. Half hours like this were used for flux calculation as long as all other quality criteria were fulfilled.

3.4 Random methanol flux uncertainty

The random uncertainty of the half-hourly vDEC methanol flux measurements was determined based on measurements under similar environmental conditions during adjacent days as suggested by Hollinger and Richardson (2005). As shown in Fig. 5 the random methanol flux uncertainty was larger during daytime as compared to night-time, in contrast to CO_2 fluxes measured at that site (Haslwanter et al., 2009). While slopes of linear regressions through night-time data are similar for CO_2 and methanol (0.19 and 0.22, respectively), the slope of a linear regression through the daytime

methanol flux uncertainty is almost four times that of CO_2 (0.31 vs. 0.08). We interpret this finding that during night-time, the random flux uncertainty is determined to a large degree by the variability of the exchange processes, which are often non-stationary and intermittent, and thus similar for methanol and CO_2. During daytime, when the turbulent exchange is steadier, the disjunct sampling of the methanol values causes a larger random variability (Hörtnagl et al., 2009) as compared to the CO_2 fluxes which are acquired at 20 Hz.

4 Results and discussion

4.1 Comparison of the VOC fluxes calculated by virtual disjunct eddy covariance and gap filling method

Compared to the vDEC method, the gap filling method introduces an additional flux dampening. Hörtnagl et al. (2009) simulated a disjunct data set from a 20 Hz series of H_2O and CO_2 data and also identified an additional low pass filtering for the gap filling method compared to the vDEC method. After the correction of the VOC fluxes which were calculated with the gap filling method using the empirical correction function introduced by Hörtnagl et al. (2009) both methods showed comparable results (Fig. 6). A comparison of the time series of VOC fluxes calculated with the vDEC method and the gap filling method over a period of one week (18.06.2008–24.06.2008) gives a correlation factor of R^2=0.94 with a slope of 0.96 and an offset of −0.06 for the regression line. Although both methods give the same methanol fluxes the vDEC method required less corrections and was therefore considered to be more reliable.

4.2 VOC emissions from growing and cut grass

The VOC emissions from growing grassland were studied for the second growing period starting at 15 June 2008 (5 d after the first cutting) up to the 9 August 2008 (1 d

before the second cutting). During this period the average air temperature was 16.0 °C and the total rainfall was 85 mm. Methanol was the only measured VOC that was emitted from the undisturbed growing grassland. The average emissions of methanol from the growing grassland were 2.5 nmol m^{-2} s^{-1} and the average methanol concentration was 5.2 ppbv. The methanol fluxes we observed during the growing period were in the same range like the methanol fluxes detected by Brunner et al. (2007) over intensively managed grassland in central Switzerland.

During this growing period no significant emissions of other VOCs were ascertained. Nevertheless there were periods where fluxes of other compounds than methanol could be detected, for example during the second cutting of the meadow on 10 August 2008. Figure 7 depicts the fluxes of CO_2, H_2O, three different VOCs (methanol (*m/z* 33), acetaldehyde (*m/z* 45), hexenal (*m/z* 99)) as well as the air temperature and global radiation before and after the cutting. The edges of the meadow, which were inaccessible with a tractor, were already cut on 9 August. The deposition/emission pattern of the CO_2 fluxes was distorted during the harvest. The latent heat flux shows a clear diurnal pattern. Emission fluxes of methanol, acetaldehyde and *m/z* 99 were detected. The latter compound is expected to be hexenal, which is emitted as a result of leaf wounding after cutting (Fall et al., 1999). For the first two compounds the fluxes were highest during the cut on 10 August (for methanol up to 30 nmol m^{-2} s^{-1}, for acetaldehyde to 10 nmol m^{-2} s^{-1}). High emissions (>20 nmol m^{-2} s^{-1} for methanol and >7 nmol m^{-2} s^{-1} for acetaldehyde) were still visible during the drying and turning of the hay on the next day. The hexenal was predominantly present during the cut on 9 and 10 August and only to a smaller extent during drying. Fluxes of methanol, acetaldehyde, and the leaf wounding compounds were also detected during the grass-cut of a study site in Switzerland (Davison et al., 2008). Note that due to a peculiar weather situation (foehn wind), winds were blowing across the valley or out of the valley for much of the time between noon 11 and the morning of the 13 August, in contrast to the usual wind patterns at the site (Fig. 1). The grassland fields in these wind directions had not been cut yet and therefore measured VOC emissions were much lower and the net CO_2 flux

was dominated by uptake during these times.

4.3 Seasonality of diurnal VOC patterns

The seasonality of diurnal VOC fluxes and ambient concentrations was compared for a summer and a fall month. Table 2 shows the number of half hours which contributed to the statistics of the calculated flux diurnal patterns. For both months and both VOCs shown in Table 2 and Fig. 8 we have sufficient number of quality controlled data points in each half hour of the day to produce the meaningful compound plots for the visualization of diurnal patterns.

Figure 8 shows the median diurnal patterns with the corresponding 75% and 25% percentiles for methanol (*m/z* 33) (upper left and right panel), the sum of all monoterpenes (*m/z* 137) (lower left and right panel) for the months June and October 2008. In June no distinct diurnal cycle for the methanol concentrations (7–9 ppbv) was visible. This was caused by extensive sources, the long lifetime of methanol, and the efficient mixing during the daytimes. However, the fluxes of methanol showed a distinct diurnal cycle with maximum values around noon and fluxes close to zero during the night. This diurnal pattern strongly follows the diurnal pattern of the global radiation (compare to Fig. 9 upper left panel). Methanol is leaking from the stomata and thus methanol emissions depend, among other factors, on stomatal conductance (Niinemets et al., 2004) which largely follows the diurnal course of radiation (Wohlfahrt et al., 2009). Therefore in the early morning the methanol fluxes started to increase until they reached a maximum level of 9.7 nmol m^{-2} s^{-1} at 12:30 CET; afterwards they decreased slowly and reached zero level in the late evening. As methanol is, *inter alia*, produced during plant growth (Fall and Benson, 1996), the meadow is not a spot source but methanol emissions are a global phenomenon (Jacob et al., 2005).

In October the concentration behavior was different: Due to the lower radiation (compare Fig. 9 upper right panel) the mixing during daytime was less efficient. The methanol concentrations were weaker and slowly increased from below 0.7 ppbv during the night to 2.9 ppbv in the late afternoon before they decreased again. The methanol

fluxes still showed a distinct diurnal pattern. The rise started, compared to June, later in the morning, reached its maximal value, 2.5 nmol m^{-2} s^{-1}, around 11:30 CET and dropped to zero at 16:30 CET. The general diurnal pattern for methanol fluxes in October was, as in June, very similar to the diurnal pattern of the global radiation (Fig. 9 upper and lower right panel). A possible reason for the weaker fluxes in October compared to June could be, apart from the reduced radiation, the lower temperature in October (Harley et al., 2007; compare Fig. 9 upper left and upper right panels).

The diurnal patterns of fluxes and volume mixing ratios of monoterpenes (*m/z* 137) showed different characteristics as compared to methanol (Fig. 8 left and right lower panel). No significant monoterpene fluxes from the grassland were detected. The clear diurnal cycles in the concentrations, with minima around 200 pptv during noon and maxima between 400 pptv in October and 600 pptv in June during the night (Fig. 8 lower left and right panel), were therefore driven by the transport of monoterpenes by the thermally induced valley wind system and the vertical mixing. The valley bottom is covered with grassland, but the vegetation on the mountain slopes is composed mainly of coniferous tree species such as norway spruce. Coniferous forest is known to emit monoterpenes (Janson, 1993; Hakola et al., 2006; Grabmer et al., 2006; Rinne et al., 2007). Unlike the methanol emissions above the meadow, the monoterpene emissions from the trees are temperature but less light dependent (Niinemets et al., 2004). The emitted monoterpenes mix down to the valley bottom with the decreasing boundary layer in the late evening and during night. Therefore the highest monoterpene concentrations are reached during the night.

5 Summary and conclusions

Disjunct eddy covariance flux measurements were accomplished at a intensively managed temperate mountain grassland during the growing season 2008. The application of the virtual disjunct eddy covariance method and the gap filling method for the VOC flux calculations provided very similar results. However, the virtual disjunct eddy covari-

ance method requires less corrections for VOC flux calculations of disjunct data and is therefore easier to use and more reliable. The comparison of the flux diurnal cycles for June 2008 and October 2008 identified a significant difference in the emission maxima for the two months. The diurnal pattern of methanol for the two months changed in a similar way compared to the global radiation, seemingly driven by the reduction in irradiation, temperature and possibly plant growth. Methanol was emitted at during the harvesting and growth of the grassland. During the cutting, additional to the methanol fluxes, fluxes of hexenal were detected. Acetaldehyde and methanol showed not only fluxes during the cutting but also during the drying of the grass.

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Table 1. List of the measured masses/compounds with the integration times and the timeframe in which they were measured.

mass *m/z*	possible compounds	integration time	timeframe
32		0.1 s	full growing season
37		0.1 s	10.07.2008–06.11.2008
33	methanol	0.5 s	full growing season
45	acetaldehyde	0.2 s	full growing season
59		0.2 s	full growing season
99	(E)-2-, (Z)-3-hexenal	0.2 s	full growing season
81	monoterpene (frag.), (E)-2-, (Z)-3-hexenal (frag.)	0.2 s	full growing season
57		0.2 s	full growing season
137	monoterpenes	0.2 s	full growing season
143		0.1 s	23.05.2008–06.11.2008
101		0.1 s	23.05.2008–06.11.2008
83		0.1 s	23.05.2008–06.11.2008
85		0.1 s	23.05.2008–06.11.2008
87		0.1 s	23.05.2008–06.11.2008
69		0.1 s	23.05.2008–06.11.2008

Table 2. List of the remaining half hours for the calculation of the flux diurnal cycles in June and October after applying the quality control on *m/z* 33 and *m/z* 137 (partitioned to night-time and daytime).

		Flux values for calculation of diurnal cycle			
		Daytime half hours between 06:00–18:00 CET		Night-time half hours between 18:00–06:00 CET	
Month	*m/z*	min	max	min	max
Jun	33	31	44	25	37
	137	19	32	28	36
Oct	33	19	34	21	33
	137	22	33	25	37

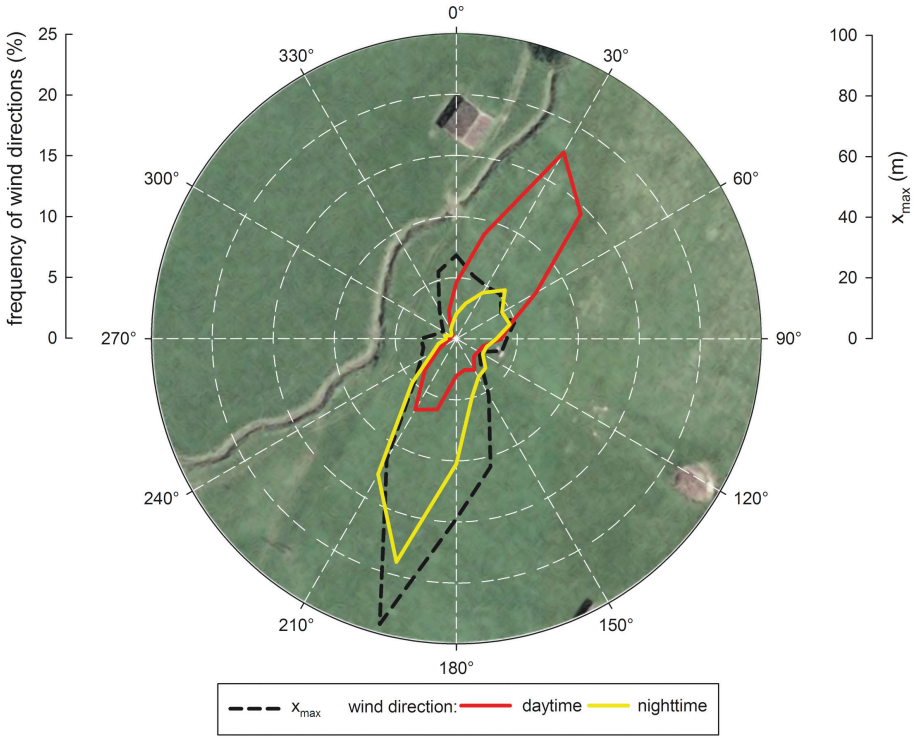

Fig. 1. Polar plot of the maximum of the footprint function x_{max} (dashed black line) and the frequency the wind direction during daytime (red line) and night-time (yellow line) overlaid on an aerial picture (*TIRIS*, http://tiris.tirol.gv.at/) of the study site.

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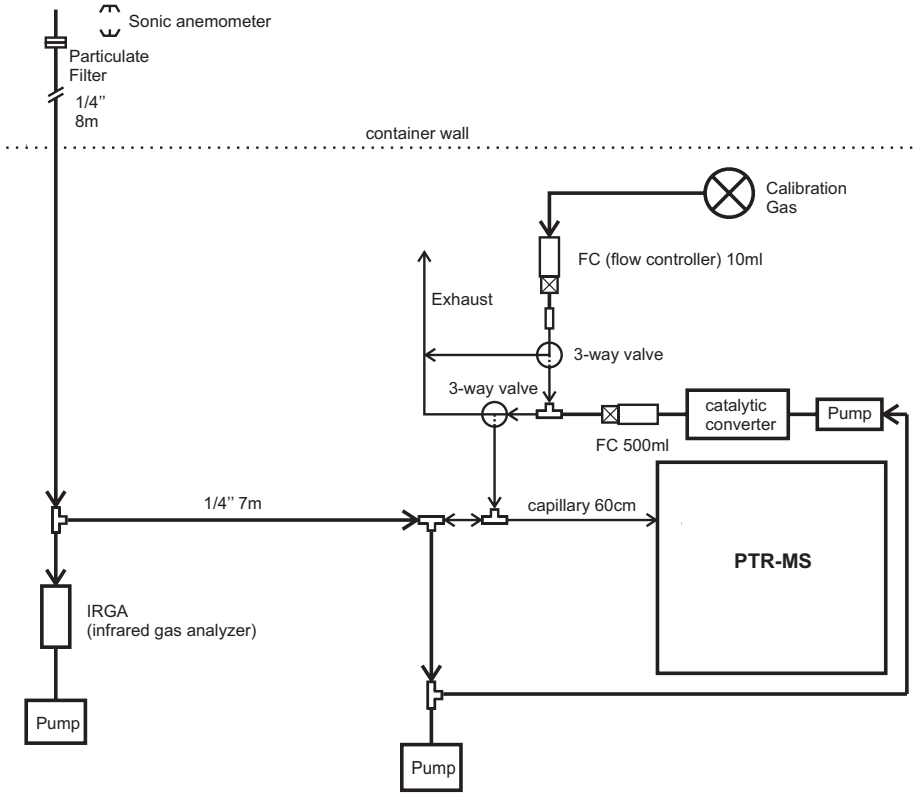

Fig. 2. Schematical drawing of the PTR-MS inlet system and setup.

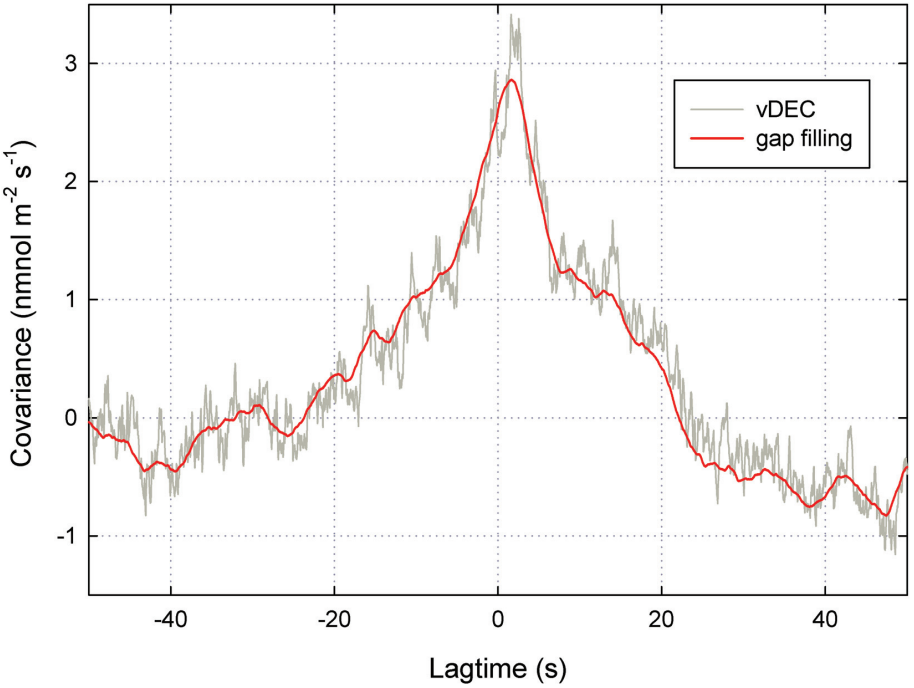

Fig. 3. Example (9 September 2008 10:45 CET) for the time delay between the methanol time series and the vertical wind velocity. Maximum covariances, i.e. lag times were 1.60 s for the vDEC method and 1.65 s for the gap filling method.

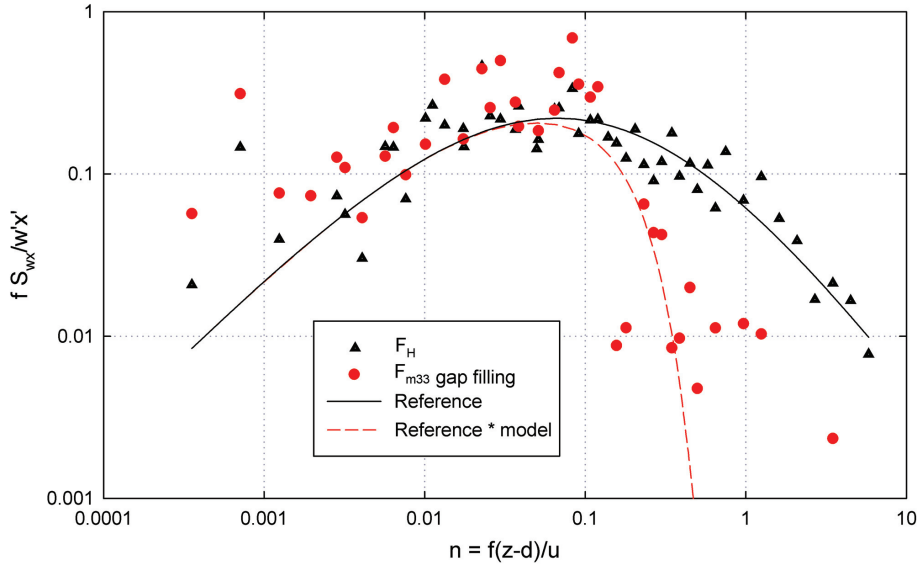

Fig. 4. Comparison of the cospectra for the sensible heat (black triangles) and methanol flux (red points; gap filling method) together with the cospectral reference model (Wohlfahrt et al., 2005; black line) and the reference model attenuated by a series of transfer functions which account for high- and low-pass filtering of the methanol flux (red dashed line).

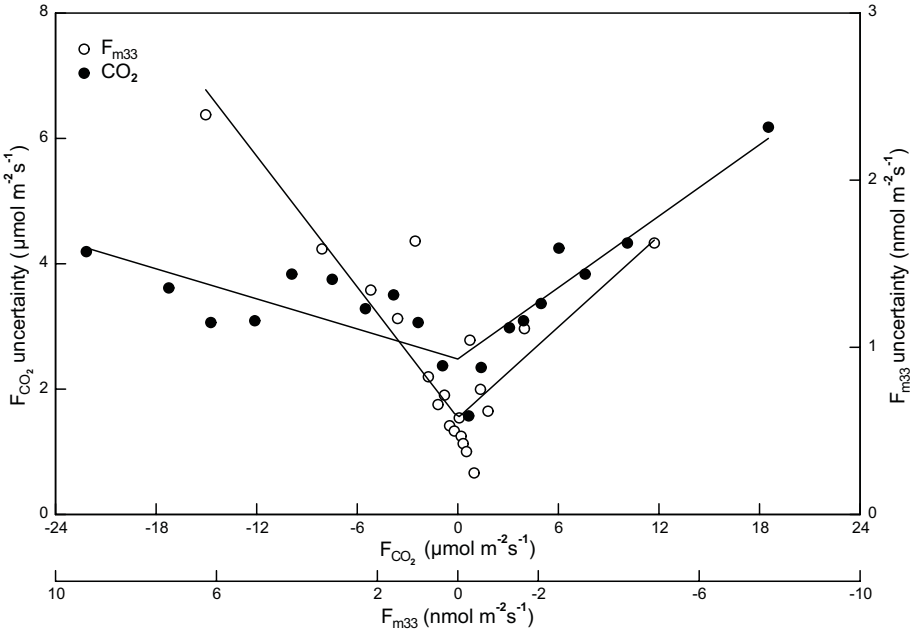

Fig. 5. Random uncertainty of methanol flux (vDEC method) and CO_2 flux (from Haslwanter et al., 2009) derived according to Hollinger and Richardson (2005). Data have been binned into classes of equal size. A double-linear relationship with a common y-intercept was fit to the methanol flux data: $y=0.31x+0.58$ (daytime, $R^2=0.83$), $y=-0.22x+0.58$ (night-time, $R^2=0.71$). Note that the x-axis for methanol fluxes was flipped in order to match CO_2 fluxes which are opposite in sign.

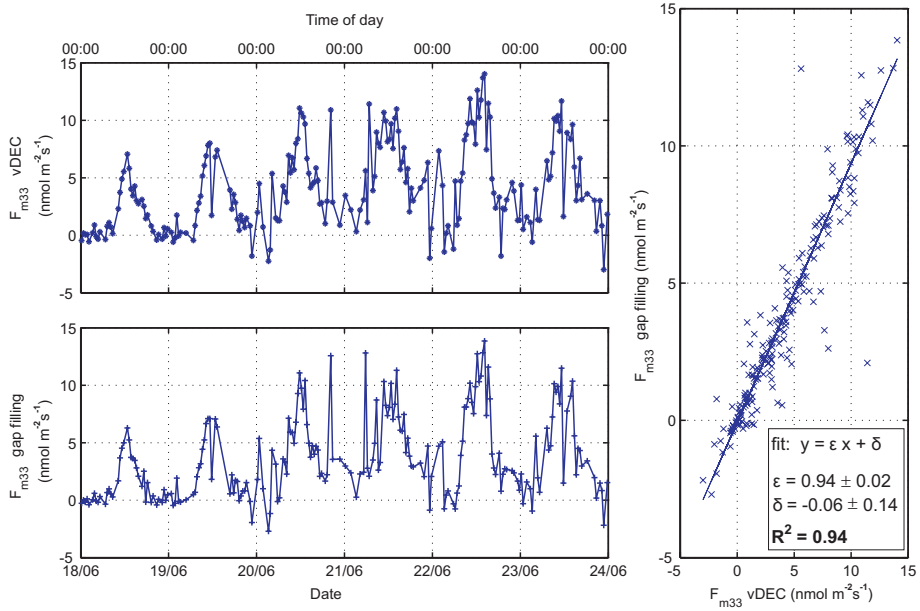

Fig. 6. Methanol fluxes calculated with the vDEC (upper left panel) and the gap filling (lower left panel) method and the scatter plot between both including the regression line. Both fluxes agree with a correlation coefficient of R^2=0.94.

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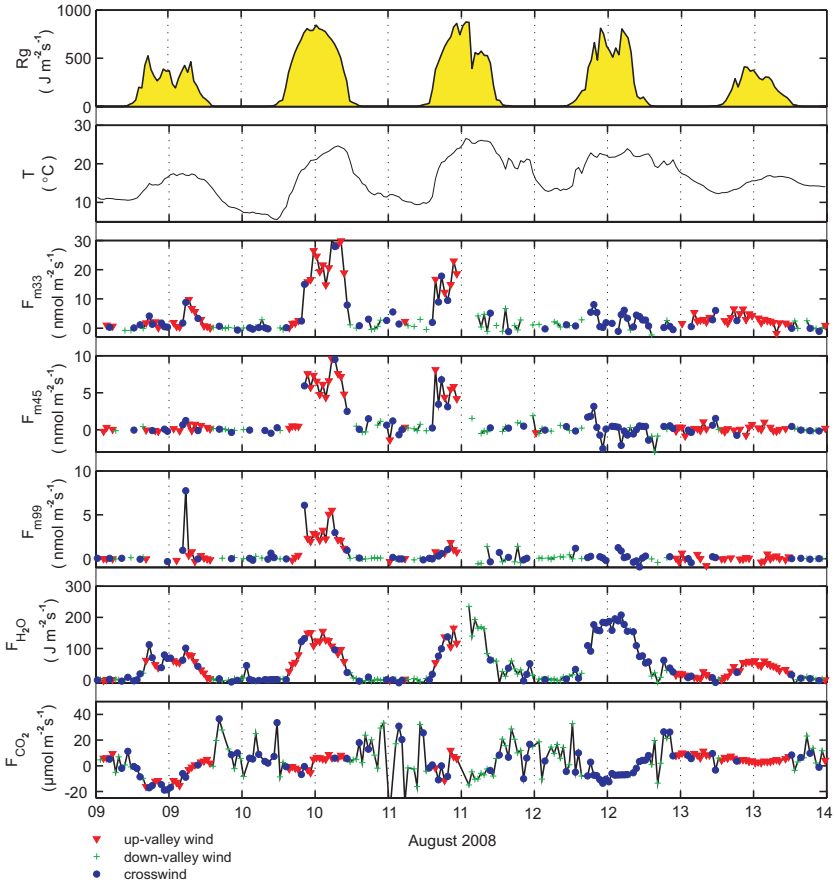

Fig. 7. From the upper panels to the lower: Time series of the global radiation (Rg), temperature, methanol flux, acetaldehyde flux, flux *m/z* 99, latent heat flux and CO_2 flux during the second hay harvest on the 10 August 2008.

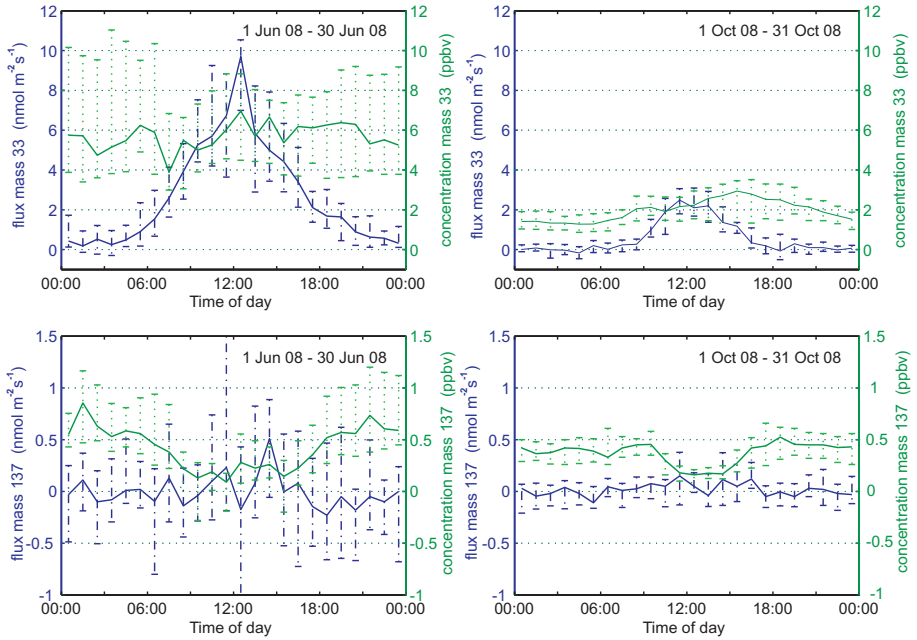

Fig. 8. Median diurnal cycles of methanol (upper panels) and monoterpene (lower panels) concentrations (green lines) and fluxes (blue lines) including the 25% and 75% percentiles for the months June and October 2008.

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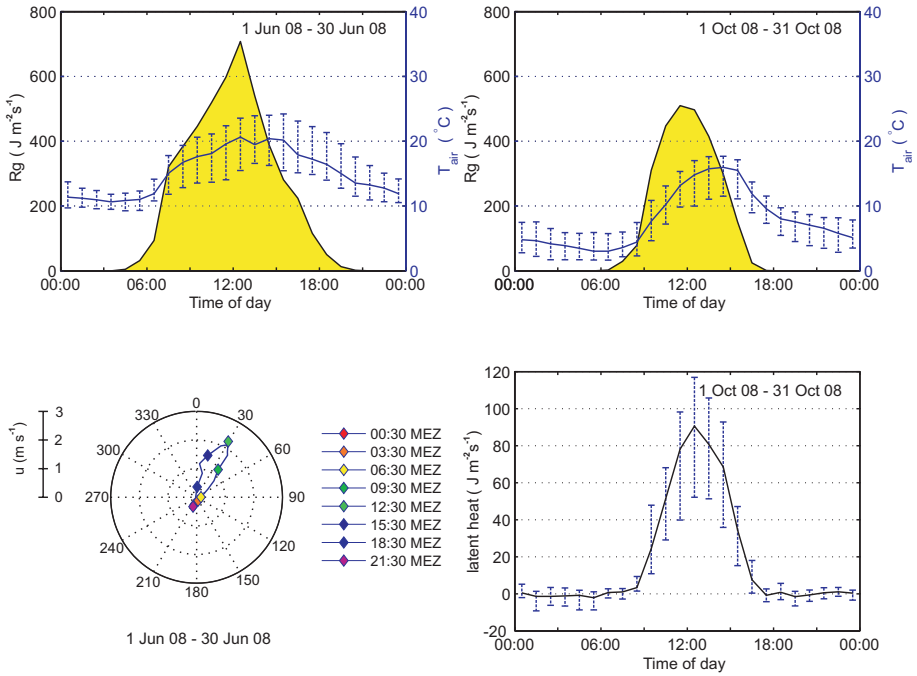

Fig. 9. Upper panels: median diurnal cycles of the temperature including the 25% and 75% percentiles overlaid on the diurnal cycle of the global radiation for the months June and October 2008. Lower left and right panel: polar plot of the median diurnal cycle of the horizontal wind speed in June 2008 and diurnal cycle of the latent heat flux for October 2008.