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Deposition fluxes of terpenes over grassland

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[1] Eddy covariance flux measurements were carried out for two subsequent vegetation periods above a temperate mountain grassland in an alpine valley using a proton-transfer-reaction-mass spectrometer (PTR-MS) and a PTR time-of-flight-mass spectrometer (PTR-TOF). In 2008 and during the first half of the vegetation period 2009 the volume mixing ratios (VMRs) for the sum of monoterpenes (MTs) were typically well below 1 ppbv and neither MT emission nor deposition was observed. After a hailstorm in July 2009 an order of magnitude higher amount of terpenes was transported to the site from nearby coniferous forests causing elevated VMRs. As a consequence, deposition fluxes of terpenes to the grassland, which continued over a time period of several weeks without significant reemission, were observed. For days without precipitation the deposition occurred at velocities close to the aerodynamic limit. In addition to monoterpene uptake, deposition fluxes of the sum of sesquiterpenes (SQTs) and the sum of oxygenated terpenes (OTs) were detected. Considering an entire growing season for the grassland (i.e., 1 April to 1 November 2009), the cumulative carbon deposition of monoterpenes reached 276 mg C m^{-2}. This is comparable to the net carbon emission of methanol (329 mg C m^{-2}), which is the dominant nonmethane volatile organic compound (VOC) emitted from this site, during the same time period. It is suggested that deposition of monoterpenes to terrestrial ecosystems could play a more significant role in the reactive carbon budget than previously assumed.

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1. Introduction

[2] VOCs are involved in the production of tropospheric ozone [*Atkinson*, 2000] and the formation of secondary organic aerosols [*Hallquist et al.*, 2009]. Biogenic VOCs (BVOCs) contribute up to 90 percent to the global emissions of VOCs [*Guenther et al.*, 1995]. Uncertainties in both, emission and deposition models of BVOCs affect the accuracy regarding the estimation of global VOC budgets, climate modeling, and the reactive carbon budget and call for detailed studies of the VOC exchange between the biosphere and the atmosphere.

[3] Historically, studies have sought to quantify the dominant compounds emitted from different ecosystems, e.g., terpenes from forested sites [*Rinne et al.*, 2007; *Spirig et al.*, 2005] and methanol from grassland [*Bamberger et al.*, 2010; *Brunner et al.*, 2007; *Kirstine et al.*, 1998]. Terpene emissions by trees are known to be controlled by light (formation by enzymatic reactions), and/or temperature (release from storage pools) depending on the tree species [*Niinemets et al.*, 2004]. Furthermore, environmental stress, like the damage of coniferous tree needles (e.g., by strong wind, hail, insects, etc.), triggers the release of terpenes to the atmosphere [*Loreto et al.*, 2000]. Light and temperature-driven algorithms [*Guenther et al.*, 1993] are used to predict terpene emissions from vegetation in ecosystem models [*Baldocchi et al.*, 1999; *Potter et al.*, 2001]. Although temperature- and light-dependent emissions of terpenes from the biosphere are relatively well explored (compared to other VOCs) there are still controversies how reliable these algorithms are, as well as how to predict emissions in response to stress [*Grote and Niinemets*, 2008]. Because of a limited amount of data, stress induced emissions in response to extreme environmental conditions or physical damage of trees are not yet included in ecosystem-scale emission models [*Arneth and Niinemets*, 2010].

[4] Compared to plant emissions, the knowledge about uptake of VOCs to the vegetation is very limited. Deposition can either take place via precipitation (wet deposition) or by transport to the ground by air motions (dry deposition) [*Wesely*

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and Hicks, 2000]. Models to estimate dry deposition are parameterized using concentration measurements and deposition velocities which are calculated from resistance models that are based on meteorological conditions and surface properties [*Hicks et al.*, 1987]. The performance of these models for less explored compounds (e.g., BVOCs) is weak, especially over complex terrain [*Wesely and Hicks*, 2000], and it is thus uncertain to which extent deposition processes play a role under field conditions for individual compounds. According to Fick's law of diffusion, the VOC exchange between biosphere and atmosphere should be bidirectional depending on the concentration gradient between ambient air and the leaf interior. For some oxygenated species like acetaldehyde, which exhibit a compensation point, i.e., an ambient volume mixing ratio (VMR) at which emission turns to deposition [*Kesselmeier*, 2001], bidirectional fluxes are well established [*Jardine et al.*, 2008]. In a laboratory experiment also deposition of nonoxygenated VOCs (terpenes) to plants was observed [*Noe et al.*, 2008]. An experiment with birch seedlings growing intermixed with *Rhododendron tomentosum* gave strong evidence for the possibility of the absorbance and re-release of biogenic terpenes to neighboring plants [*Himanen et al.*, 2010]. In general, BVOC exchange is known to be compound specific [*Kesselmeier and Staudt*, 1999]. It is therefore likely that ecosystems not emitting certain compounds may nevertheless act as sinks for these species. Possibly, the relatively larger uncertainty in biospheric sinks as opposed to sources of VOCs may be responsible for acknowledged shortcomings in atmospheric VOC budgets [*Goldstein and Galbally*, 2007].

[5] The objective of the present paper is to raise the awareness in the scientific community about the larger than expected role of biospheric VOC sinks through the process of dry deposition to ecosystems that are either emitting or not emitting these compounds. To this end we report eddy covariance monoterpene (MT), sesquiterpene (SQT) and oxygenated terpene (OT) deposition flux measurements to a mountain grassland in Austria that were conducted during a "natural experiment," that is a sudden increase in ambient terpene volume mixing ratios in the aftermath of a hailstorm that caused large terpene emissions from surrounding wounded coniferous trees.

2. Experimental

2.1. Study Site

[6] The study site is located at an elevation of 970 m above sea level in the middle of a flat valley bottom close to the village of Neustift, Tyrol, Austria (47°07′N, 11°19′E). The vegetation at the intensively managed grassland site consists of a few graminoid (20–40%) and forb (60–80%) plant species. At the valley slopes coniferous forest, in particular Norway spruce (*Picea abies*), is the dominant type of vegetation. The thermally induced valley wind system at the site and the management of the grassland are described by *Bamberger et al.* [2010]. *Wohlfahrt et al.* [2008] characterize in detail the vegetation, soil and climate of the study site. The meadow was cut three times each year, during 2009 on 4 June, on 5 August and on 21 September (in 2008 on 10 June, on 10 August and on 29 September). In autumn (19 October 2009 and end of October 2008) the grassland was fertilized with organic manure. Eddy covariance fluxes using a PTR-MS and a PTR-TOF were measured covering a hailstorm event on the 16 July 2009 allowing for the investigation of the subsequent increase of terpenoid concentrations and the deposition of these compounds to the measurement site. The overall rainfall in the time period after the hailstorm (16 July until 1 August 2009) was 46 mm, the average air temperature was 16.0°C and growth of the vegetation increased the green area index (determined according to the study by *Wohlfahrt et al.* [2001]) from 5.6 $m^2\ m^{-2}$ to 6.6 $m^2\ m^{-2}$. Vegetation periods (April-October) 2008 and 2009 were warmer and drier as compared to the long-term average (11.3°C and 620 mm). However, considering the period since 2001 (when measurements at this site began), temperatures were only slightly warmer (13.5°C, 2009) and colder (12.6°C, 2008) as compared to the 2001–2009 average of 13.0°C and rainfall was only slightly below the 2001–2009 average of 488 mm (444 mm and 433 mm in 2008 and in 2009, respectively).

2.2. Instrumentation

[7] A sonic anemometer (R3IA, Gill Instruments, Lymington, U.K.) was used to measure the 3D wind components and the speed of sound at 20 Hz using a PC running the EddyMeas software (O. Kolle, MPI Jena, Germany). Volume mixing ratios of different VOCs were quantified using a conventional PTR-MS and a PTR-TOF simultaneously each running on a separate PC. The internal clocks of all three PCs were synchronized using the network time protocol (NTP, Meinberg, Germany). The sample air was taken from the inlet (2.4 m above ground 0.1 m below the center of the sonic anemometer) and guided to the inlets of both instruments through a single 12 m Teflon® tube (inner diameter 3.9 mm) at a constant flow rate of 9 SLPM (standard liter per minute) in a setup similar to Figure 2 of *Bamberger et al.* [2010]. To avoid condensation, the inlet line was heated to 35°C. During 2009 both PTR instruments were operated at E/N ratios of 130 Td with 2.3 mbar and 600 V drift tube pressure/voltage; the drift tube temperatures were stabilized to 50°C. Settings for the PTR-MS (2.15 mbar and 550 V) and the inlet line temperature (40°C) differed slightly during 2008. The working principle of the PTR-MS is explained by *Hansel et al.* [1995] and *Lindinger et al.* [1998]. A detailed description and characterization of the PTR-TOF are given by *Graus et al.* [2010]. To determine the instrumental backgrounds (zero calibration), a home-built catalytic converter (housing is stainless steel; catalyst is EnviCat®VOC 5538, Süd-Chemie AG, Germany) heated to 350°C was continuously flushed with 0.5 SLPM of ambient air. Zero calibrations for the PTR-MS were performed during the last 5 min of every half hour period, for the PTR-TOF every 7 h for 25 min. The sensitivities of the instruments were determined by a standard addition of a multicomponent gas standard (Apel Riemer Inc., United States) to VOC-free air from the catalytic converter to create concentration levels in the low ppbv range. An automated routine calibrated the PTR-MS every 50 h using four different concentration steps (1 ppbv, 2.5 ppbv, 5 ppbv and 7.5 ppbv) during 2009, typical calibration factors achieved for methanol (m/z 33, CH_4OH^+) and α-pinene (m/z 137, $C_{10}H_{16}$-H^+), were 12 ncps $ppbv^{-1}$ and 5 ncps $ppbv^{-1}$, respectively. In 2008 the instrument was calibrated once per week using the same concentration steps. For the PTR-TOF, sensitivity calibrations were performed two to three times a week using the same gas standard and

dilution procedure. A detailed description of the instrument operation, including mass scale calibration and data post processing, is given by *Müller et al.* [2010]. Typical sensitivities for the compounds analyzed by the PTR-TOF were 10.5 ncps ppbv^{-1} for α-pinene which was used to calibrate the sum of monoterpenes (m/z 137.133, $C_{10}H_{16}$-H^+), for the sum of sesquiterpenes 10.2 ncps ppbv^{-1} and for the sum of oxygenated monoterpenes 28.1 ncps ppbv^{-1}. OTs (m/z 153.1278, $C_{10}OH_{16}$-H^+) or SQTs (m/z 205.1945, $C_{15}H_{24}$-H^+) were not included in the gas standard, therefore the sensitivity of OTs was estimated using the sensitivity of hexanone (the heaviest oxygenated compound in the standard with reliable calibration values), the sensitivity of SQTs was calculated using average fragmentation patterns (60% ± 30% remained on the parent ion) for six different sesquiterpenes (farnesene, α-humulene, (−)-isolongifolene, (−)-longifolene, (−)-α-cedrene and *trans*-caryophylene) and the sensitivity of 1, 3, 5 triisopropylbenzene.

[8] The PTR-TOF was set to an extraction rate of 33.3 kHz and to a mass range up to m/z 315. Coaddition of 3333 extractions to individual full mass spectra results in 10 Hz VOC data. The PTR-MS measured 12 preselected mass channels, including m/z 33 (methanol) and m/z 137 (sum of monoterpenes), with a dwell time of 0.2 s or less and a repetition rate of 2.3 s during 2009. In 2008 the dwell time for methanol was set to 0.5 s and the repetition rates were slightly longer (up to 3.0 s).

2.3. Flux Calculation and Quality Control

[9] Fluxes from the PTR-TOF data were calculated using the eddy covariance method [*Baldocchi et al.*, 1988], from the PTR-MS data using the virtual disjunct eddy covariance (vDEC) method [*Karl et al.*, 2002], based on the covariance between fluctuating parts of the vertical wind speed and VOC concentrations. For the PTR-MS, the covariance between VOC concentrations and vertical wind speed was calculated by down sampling the 20 Hz wind data to the repeat rate of the PTR-MS (2.3–3 s), i.e., wind velocities were used only for those times when VOC concentrations were available. For the PTR-TOF, the wind data were down sampled to the 10 Hz VOC time series. A detailed description of the flux calculation procedures is given by *Bamberger et al.* [2010] in case of the PTR-MS data, and by *Ruuskanen et al.* [2011], in case of the PTR-TOF data, and is thus not reiterated here. In Appendix A we present complementary information regarding the flux calculation and quality control methodology pertaining to this particular study: examples for the lag time determination using the maximum cross-correlation method (Figure A1), a cospectral analysis (Figure A2), and estimates of the random flux uncertainty (Figure A3). While positive fluxes represent a net transport of VOCs from the ecosystem to the atmosphere (emission), negative fluxes indicate a net transport to the surface (deposition).

[10] Half-hourly PTR-MS flux data were quality controlled in an automated fashion by removing time periods with the third rotation angle exceeding ±10° [*McMillen*, 1988], the flux stationarity test or the deviation of the integral similarity characteristics exceeding 60% [*Foken and Wichura*, 1996], the maximum of the footprint function [*Hsieh et al.*, 2000] outside the site boundaries [*Novick et al.*, 2004]. Further 30 min flux periods with a background signal (averaged over 30 min) higher than the ambient VOC concentrations, a significant background drift and/or VOC sensitivities below 1 ncps ppbv^{-1} were rejected [*Bamberger et al.*, 2010]. For PTR-TOF fluxes the half-hourly periods had to pass the above mentioned footprint and stationarity tests and in addition a visual rating of the covariance peaks following *Ruuskanen et al.* [2011] exemplified in Appendix A (Figure A1). For the calculation of cumulative fluxes and 24 h averages data gaps which did not exceed 2 h were filled with linearly interpolated values.

[11] A comparison of daytime 12 hourly average MT fluxes calculated with the eddy covariance method using the PTR-TOF data and the vDEC method using the PTR-MS data shows good correspondence (slope of 1.08 ± 0.07; y intercept of −0.19 ± 0.18, $R^2 = 0.85$; Figure B1), similar to a comparison of both methods presented by *Müller et al.* [2010] for half-hourly methanol fluxes.

2.4. Calculation of Deposition Velocities

[12] The concept of dry deposition is discussed extensively in several review articles, one of the most recent by *Wesely and Hicks* [2000]. Briefly, the deposition velocity v_d of a compound i is defined by concentration C^i and flux F^i of the selected compound according to

$$v_d^i = -\frac{F^i}{C^i}. \tag{1}$$

For gases it can be expressed as a series of three resistances R_a, R_b^i and R_c^i:

$$v_d^i = \frac{1}{R_a + R_b^i + R_c^i}. \tag{2}$$

R_a, the aerodynamic resistance, is dependent on aerodynamic conditions and independent of the compound i. $\mathrm{R_b^i}$, the quasi-laminar boundary layer resistance, changes with the diffusivity of the compound and is responsible for the transfer through a thin air layer around the surface. The third resistance R_c^i, surface or canopy resistance, is the sum of several resistances in series (e.g., stomatal and mesophyll resistance) and in parallel (e.g., stomatal and cuticular resistance) and includes stomatal and nonstomatal components (e.g., to vegetation and soil surfaces), responsible for the transfer to the vegetation. While there are well established models to calculate R_a and R_b^i [*Hicks et al.*, 1987], it is considerably more difficult to find an appropriate expression for R_c^i.

[13] An upper limit for the deposition velocity $v_{d,\max}^i$ can be estimated from

$$v_{d,\max}^i = \frac{1}{R_a + R_b^i} \tag{3}$$

The aerodynamic resistance and the quasi-laminar boundary layer resistance for deriving this quantity were calculated according to *Monteith and Unsworth* [1990].

3. Results and Discussion

3.1. Deposition Fluxes of Monoterpenes

[14] Figure 1 shows 24 h average flux and volume mixing ratio values for MTs (m/z 137) measured by the PTR-MS

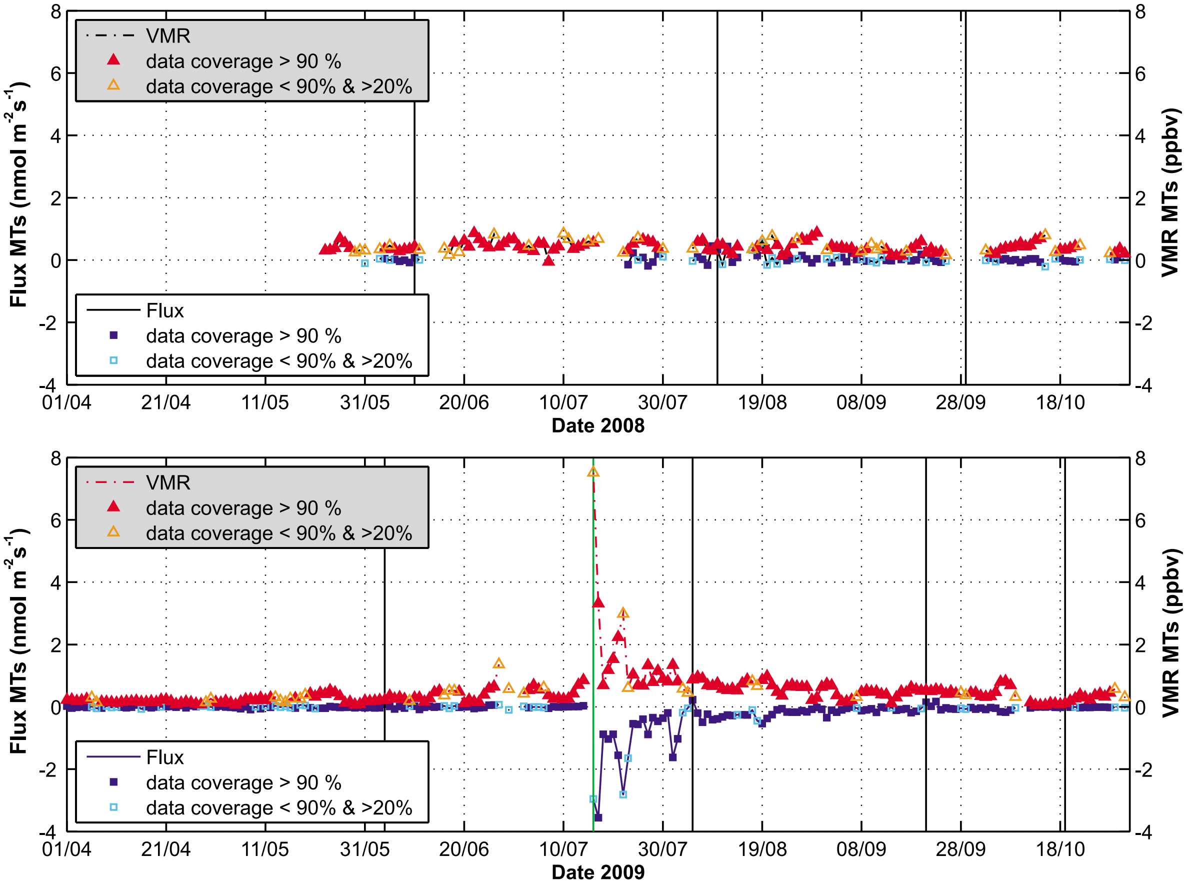

Figure 1. Time series of 24 h average fluxes and volume mixing ratios of the sum of monoterpenes (m/z 137) measured with the proton-transfer-reaction-mass spectrometer (PTR-MS) for (top) 2008 and (bottom) 2009. Solid dark blue squares (flux) and red triangles (volume mixing ratios (VMR)) represent 90% data coverage, while open light blue squares (flux) and orange triangles (VMR) represent 20–90% data coverage. Percent data coverage stands for the percentage of the total half-hourly periods per day which contributed to the 24 h averaging process after applying the quality control. The vertical lines represent dates of cutting (10 June 2008, 10 August 2008 and 29 September 2008, 4 June 2009, 5 August 2009, 21 September 2009) and fertilization (19 October 2009), and the green vertical line represents the date of the hailstorm.

above the investigated grassland during 2008 and 2009. During typical (growing) conditions the grassland was neither a source nor a significant sink for monoterpenes and the corresponding MT VMRs were well below 1 ppbv during most days. However, on days when exceptionally high VMRs of MTs were observed in the air, the grassland acted as a sink for monoterpenes. Starting on 16 July 2009 the volume mixing ratios of MTs were strongly enhanced (up to 7.5 ppbv) compared to the months before. *Loreto et al.* [2000] showed that wounding of the storage pools in pine needles triggers large emissions of monoterpenes. The observed high VMRs were most likely a consequence of a hailstorm in the late afternoon of the 16 July which may have damaged needles, small twigs, and branches of the conifers on the mountain slopes in the surrounding area. High monoterpene levels after severe hailstorms were also observed over a ponderosa pine forest at Manitou Forest Observatory, Colorado (unpublished results from the BEACHON ROCS campaign, 2010). We thus propose that for our study site in Stubai valley the wounded conifers may have acted as a source and released significant amounts of monoterpenes to the atmosphere, which would explain the elevated terpene VMRs after the hailstorm. Significant MT deposition fluxes on the order of 3.55 nmol m^{-2} s^{-1} averaged over 24 h indicate that the grassland acted as a net sink for monoterpenes during this period. VMRs and deposition fluxes remained elevated compared to undisturbed conditions (both 2008 and 2009) for several weeks. Further evidence for the key role of the enhanced ambient MT VMRs in changing MT flux direction from near-neutral to deposition is presented in Figure 2, which shows bin-averaged diurnal courses of MT VMRs, MT fluxes along with the combined aerodynamic/quasi-laminar boundary layer and surface conductance for 2 week periods before and after the hailstorm. While the combined aerodynamic/quasi-laminar boundary layer and surface conductance did not differ significantly before and after the hailstorm, MT VMRs were clearly enhanced after the hailstorm and, in particular during daytime, correlated with

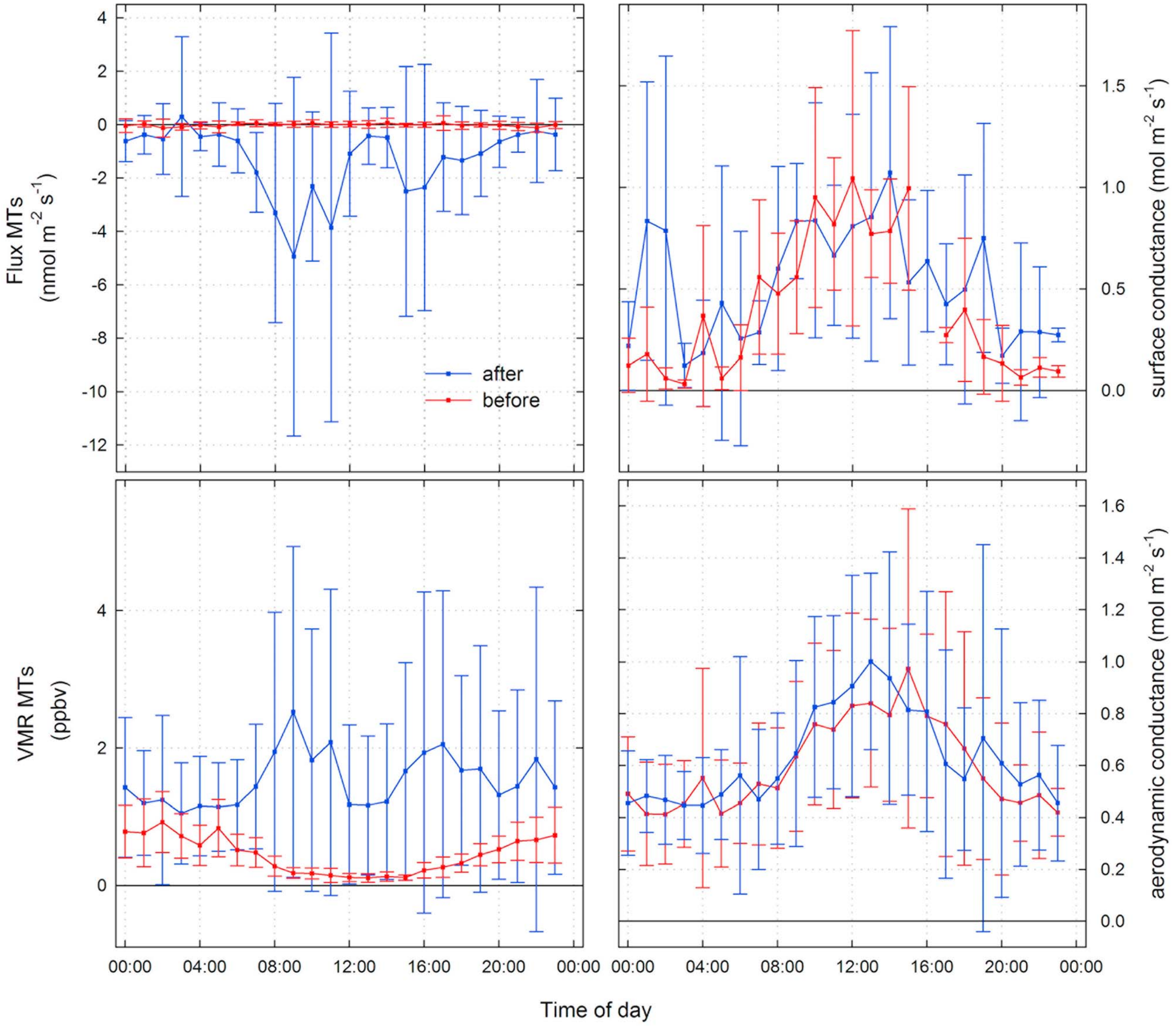

Figure 2. Mean diurnal cycles of (top left) PTR-MS monoterpene fluxes, (bottom left) PTR-MS volume mixing ratios, (top right) surface conductance, and (bottom right) combined aerodynamic/quasi-laminar boundary layer conductance with corresponding standard deviations for 2 week periods before (red symbols and lines) and after the hailstorm (blue symbols and lines).

corresponding MT deposition fluxes. Note that, as shown in Figure A3, random MT flux uncertainties are comparable for deposition and emission fluxes.

[15] To our knowledge, this is the first time that significant monoterpene deposition fluxes have been demonstrated under field conditions. *Noe et al.* [2008] demonstrated the capacity of nonemitting species to take up monoterpenes (in that case limonene) at the leaf level in a laboratory experiment. The uptake rates for limonene (per unit leaf area) measured during this laboratory experiment ranged from 0.9 nmol m^{-2} s^{-1} up to 6 nmol m^{-2} s^{-1}, depending on the measured plant species. On the basis of a ground area basis the maximum uptake rates quantified for the sum of monoterpenes over the grassland in Stubai valley were around −22 nmol m^{-2} s^{-1} (the minus indicates net uptake instead of emission). Considering the green area index for the grassland, which increased from 5.6 m^2 m^{-2} to 6.6 m^2 m^{-2} during the period of interest, the measured peak deposition values ranged between 3.3 nmol m^{-2} s^{-1} and 3.9 nmol m^{-2} s^{-1} on a green area basis, which compares well with the range of values reported by *Noe et al.* [2008]. *Himanen et al.* [2010] found further evidence for an uptake and rerelease of terpenes by nonemitting plants that grow intermixed with emitting species in a natural environment. Further work is required to quantify the contribution of various sinks, e.g., stomatal uptake, chemical losses or scavenging to the soil, to the deposition of monoterpenes observed in this study.

[16] The scatterplot between 12 h daytime averages of VMRs and deposition fluxes for 2009 (Figure 3) exhibits

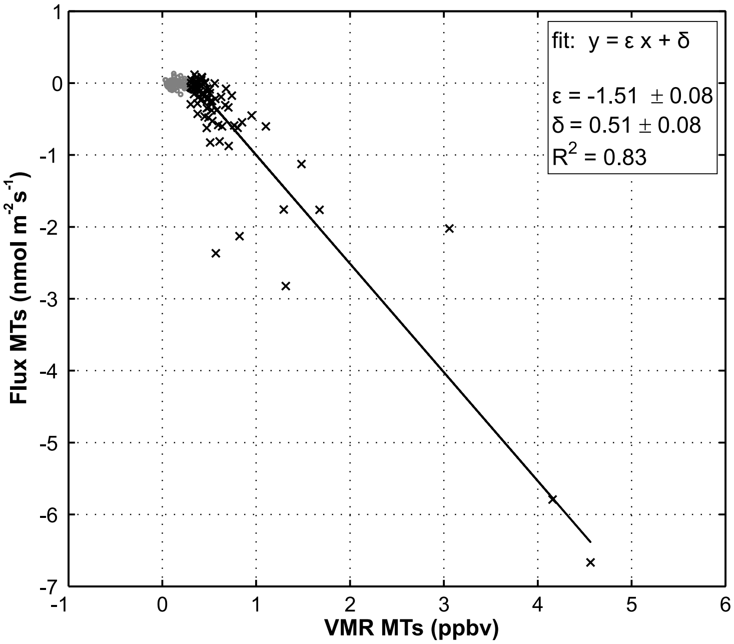

Figure 3. Scatterplot between 12 h daytime average values (06:00–18:00 Central European Time; exclusive of cutting dates) of fluxes and volume mixing ratios of monoterpenes including a fitting line valid for sufficiently high VMRs. A weighted linear least squares fit was chosen because of the heteroscedasticity of the data. Points at low VMRs (<0.30 ppbv) are shown in the figure (gray circles) but not included in the fit. If 12 h averages of VMRs exceed 0.30 ppbv (black cross), the deposition fluxes follow a regression line of $y = -1.51x + 0.51$ ($R^2 = 0.83$).

a strong correlation (R^2 = 0.83) for VMRs which exceed 0.30 ppbv (averaged over daytime hours: 06:00–18:00 LT (Central European Time)). For low VMRs (Figure 3, gray circles) fluxes scatter around zero. For sufficiently high VMRs, however, deposition fluxes of monoterpenes follow a regression line with a slope of −1.51 and an y intercept of 0.51 (gray circles, were excluded from the regression analysis). Because of the heteroscedasticity of the data a weighted linear least square fit was applied for regression analysis. The result suggests that the exposure of grassland to high VMRs of terpenes results in a corresponding uptake. Although grassland does not emit monoterpenes during undisturbed conditions, it shows a concentration (similar to a compensation point) where an uptake of monoterpenes initiates. The causes for the nonzero y intercept of the linear regression are unknown at present.

[17] It is well-known that some oxygenated compounds, e.g., acetaldehyde, exhibit a compensation point and can be emitted by or deposited to vegetation depending on ambient concentrations [*Kesselmeier*, 2001]. Terpene compounds, so far, have only been linked to emission fluxes [*Kesselmeier and Staudt*, 1999]. Forests emit large quantities of monoterpenes. For example average daytime monoterpene emissions of 2.2 nmol m^{-2} s^{-1} were reported for a mixed deciduous forest [*Spirig et al.*, 2005]. During warm days, *Grabmer et al.* [2004] reported monoterpene emission fluxes up to 2.5 nmol m^{-2} s^{-1} over a Norway Spruce forest using the relaxed eddy covariance method. Over Scots pine forest average daily emissions of 0.90 nmol m^{-2} s^{-1} were recorded for monoterpenes [*Rinne et al.*, 2007].

3.2. Deposition Velocities

[18] Figure 4 shows the time series of half-hourly monoterpene fluxes and VMRs (Figure 4, top), measured deposition velocities ($v_{d,\mathrm{MTs}}$) (equation (1)) compared to maximal deposition velocities $v_{d,\max}$ (calculated according to equation (3)) (Figure 4, middle), and horizontal wind speeds including directions and air temperature (Figure 4, bottom). The temporal behavior of monoterpene VMRs and fluxes (Figure 4, top) can be explained by precipitation, air temperatures and wind directions (Figure 4, bottom).

[19] The observed deposition velocities (Figure 4, middle) were surprisingly high with values close to the aerodynamic limit. Deposition velocities above the aerodynamic limit were rarely observed, but if, they occurred typically during wet conditions. Given the large random variability of MT flux measurements (Figure A3) and the systematic uncertainty of models used to simulate the combined aerodynamic and quasi-boundary layer conductance [*Liu et al.*, 2007], we conclude that MT deposition velocities were larger than previously assumed, which is corroborated by the study of *Karl et al.* [2010] for oxygenated VOCs. Since we observed deposition maxima during daytime, when the boundary layer is well mixed, it is unlikely that horizontal advection may have violated the assumptions of the eddy covariance method.

[20] After a cold, rainy period on 17 and 18 July 2009 VMRs and deposition fluxes of MTs were approaching almost zero. During the following days temperatures were rising slowly and monoterpene VMRs and deposition fluxes

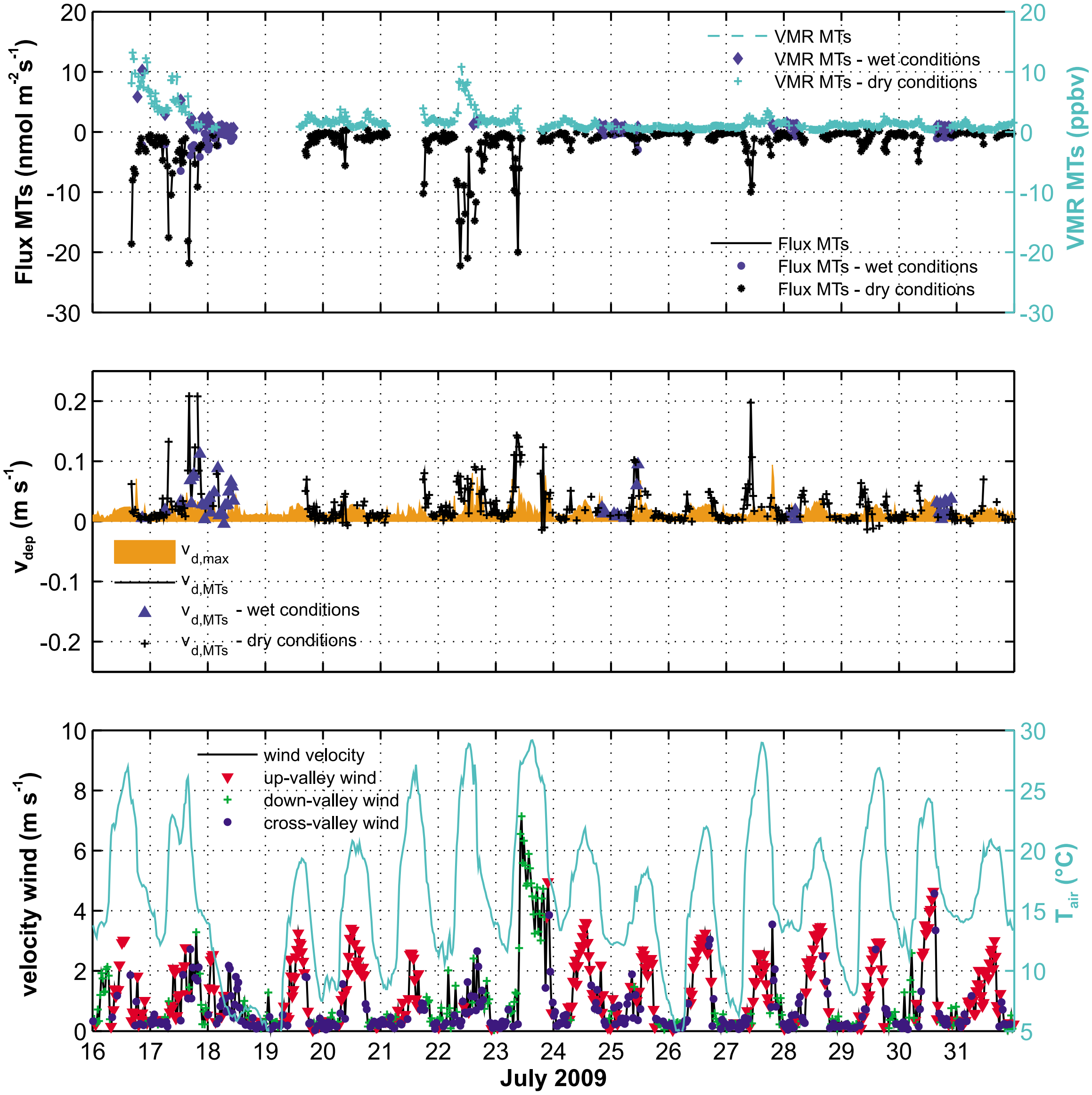

Figure 4. Time series of monoterpene fluxes measured by a PTR time-of-flight-mass spectrometer (PTR-TOF) between 16 and 31 July 2009, measured deposition velocities ($v_{d\text{,MTs}}$, calculated according to equation (1) using VMRs and fluxes measured by the PTR-TOF), ranges for the aerodynamic limit (orange shaded area $v_{d\text{,max}}$ that was calculated according to equation (3)), horizontal wind speeds according to valley wind directions and air temperature. Violet symbols for fluxes and calculated deposition velocities indicate times with precipitation.

were showing elevated daily peak values (up to 22 nmol m^{-2} s^{-1}). Note that during 22 and 23 July there was a Föhn situation and the wind deviated from the usual thermally driven valley wind system (up valley during daytime, down valley during nighttimes). Unlike the normal up and down valley wind pattern on 22 July the wind blew across the valley and transported terpene rich air directly from the valley slopes to the station, on 23 July the Föhn was fully developed and transported air from the forested top of the valley. The coincidence of direct transport from the source with high emission source strength (warm temperatures) lead to the observed daytime maxima.

3.3. Deposition of Other Terpenoids

[21] The PTR-TOF allowed also for the quantification of the sum of sesquiterpenes (m/z 205.1945, $C_{15}H_{24}$-H^+) and the sum of oxygenated terpenes (m/z 153.1278, $C_{10}OH_{16}$-H^+). Figure 5 indicates that the corresponding fluxes showed a similar pattern compared to the deposition fluxes of monoterpenes. Sesquiterpene and oxygenated terpene fluxes correlated well with the flux of the MTs (i.e., $R^2 = 0.80$ for SQTs; $R^2 = 0.87$ for OTs). The resulting coefficients of the linear regression are listed in Table 1. The magnitude of the deposition of SQT and OT fluxes and VMR was a factor 50 smaller than that of MT. We hypothesize that these compounds were

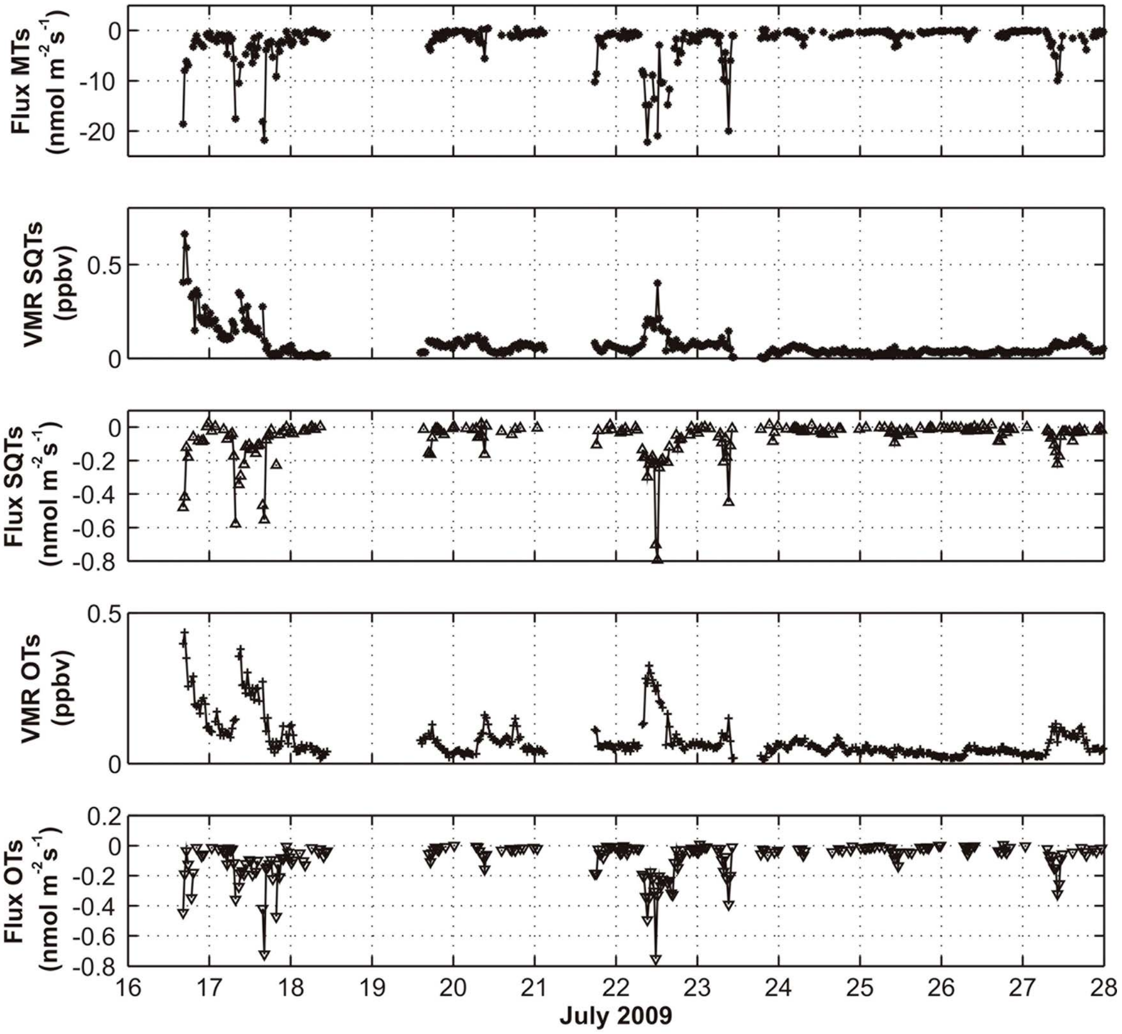

Figure 5. Time series of VMRs of sesquiterpenes ($C_{15}H_{24}$-H^+) and oxygenated terpenes ($C_{10}OH_{16}$-H^+) and fluxes of monoterpenes ($C_{10}H_{16}$-H^+), sesquiterpenes and oxygenated terpenes measured by the PTR-TOF from 16 to 28 July 2009.

coemitted with monoterpenes from nearby conifers and that the grassland acted as a sink for all terpenoids.

[22] We did not observe deposition or emission fluxes of oxidation products from monoterpenes or sesquiterpenes (e.g., pinonaldehyde, m/z 169.122). The VMRs of the oxidation products, however, were two orders of magnitude lower compared to the ones of monoterpenes. We therefore assume that if corresponding fluxes existed they were too small to be detected. Further we did not observe any significant emission or deposition fluxes of acetaldehyde or acetone (data not shown) which could in case indicate a substantial chemical loss of terpenes across our measurement height.

3.4. Cumulative Carbon Fluxes

[23] Figure 6 shows the time course of the cumulative carbon fluxes for monoterpenes, methanol and CO_2 between April and November 2009. Methanol was chosen because it exhibits the highest season-long organic carbon emission flux [*Bamberger et al.*, 2010; *Hörtnagl et al.*, 2011]; CO_2 was chosen because it represents the largest carbon flux to and from this grassland ecosystem [*Wohlfahrt et al.*, 2008]. Methanol emissions started at the beginning of April after snowmelt and continued until November 2009. Cumulative carbon fluxes of monoterpenes showed no emissions and only small (<8.40 mg C m^{-2}) deposition until the 15 July

Table 1. Correlation Coefficient R^2, Slope *m*, Offset *k*, and Number of Regression Points *n* for the Linear Regression Between Fluxes of Monoterpenes (m/z 137.133, $C_{10}H_{16}$-H^+) and Sesquiterpenes (m/z 205.1945, $C_{15}H_{24}$-H^+) and MTs and Oxygenated Terpenoids (m/z 153.1278, $C_{10}OH_{16}$-H^+)[a]

Compound	R^2_{MTs}	*m*	Δm	*k*	Δk	*n*
SQTs	0.8037	0.0230	0.0017	0.0017	0.0096	180
OTs	0.8656	0.0228	0.0013	−0.0100	0.0069	201

[a] Δm and Δk represent the 95 percent confidence bounds for m and *k*, respectively.

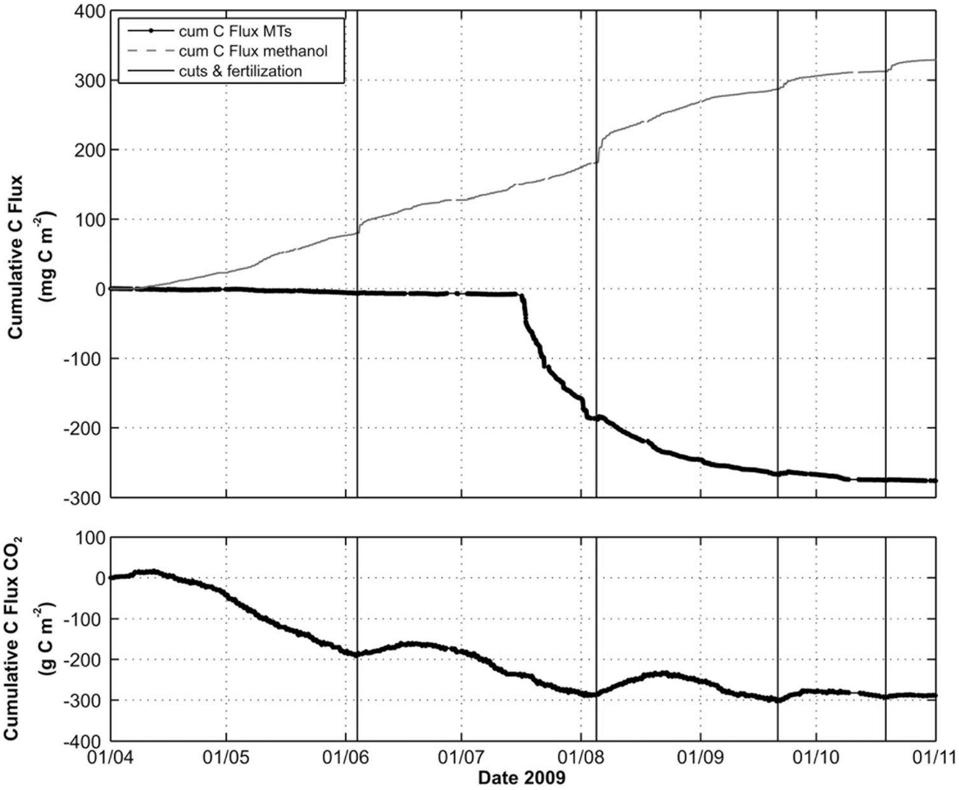

Figure 6. Cumulative carbon fluxes of monoterpenes, methanol, and CO_2 calculated from the PTR-MS and infrared gas analyzer data (gaps shorter or equal to 2 h were filled with interpolated values) for the time period from 1 April until 1 November 2009. The vertical lines represent the dates of cutting (4 June 2009, 5 August 2009, and 21 September 2009) and fertilization (19 October 2009).

2009 when the onset of the high monoterpene uptake (16 July) was most likely triggered by the above mentioned hailstorm which damaged needles and twigs of the nearby coniferous forest and elevated the valley VMRs by an order of magnitude. Starting from that point of time cumulative monoterpene deposition fluxes increased significantly and flattened out only slowly before they reached a constant level in October 2009. During periods of cutting and fertilization the methanol curve exhibited abrupt increases because of bursts of emissions from damaged vegetation; CO_2 fluxes showed a reversal from uptake to emission and back to uptake which is characteristic for vegetation recovery after cutting [*Wohlfahrt et al.*, 2008].

[24] From April to November 2009, the total amount of carbon deposited to this grassland in form of monoterpenes was 276 mg C m^{-2}. This is comparable to the net carbon emissions of methanol (329 mg C m^{-2}, including cutting and fertilization) during the same time period. The net CO_2 carbon uptake over this meadow within the mentioned period of time was 289 g C m^{-2}. Assuming that during the periods between January and April and November until December no notable uptake or emission of monoterpenes took place the measured monoterpene deposition of 0.28 g C m^{-2} yr^{-1} is remarkably high when compared to global terpene emission estimates from forested areas. For example, emission estimates for monoterpenes for different temperate forest environments range between 0.42 g C m^{-2} yr^{-1} and 0.92 g C m^{-2} yr^{-1} [*Guenther et al.*, 1995]. *Naik et al.* [2004] reported average emissions of 1.66 g C m^{-2} yr^{-1} for temperate evergreen conifer forest and 0.73 g C m^{-2} yr^{-1} for temperate deciduous forest.

[25] *Goldstein and Galbally* [2007] proposed that large fractions of the emitted BVOCs are removed from the atmosphere by the production of SOA. Our results, however, suggest that gas phase deposition processes could play a more significant role than heretofore supposed.

4. Summary and Conclusions

[26] Over a time period of two subsequent years fluxes of the sum of monoterpenes were measured above a grassland in an alpine valley using a PTR-MS. Fluxes were evaluated by means of the disjunct eddy covariance method. Within the frame of a four month campaign during the second year a PTR-TOF was additionally deployed at the field site to study complete mass spectra at 10 Hz time resolution for sesquiterpene and oxygenated terpenoid fluxes.

[27] VMR measurements suggest that coniferous trees can emit monoterpenes in large quantities in response to 'natural' stress conditions (e.g., after a hailstorm) and that, on a local scale, volume mixing ratios can be as large as several ppbv in the atmosphere. As a consequence of the enhanced volume mixing ratios in the air significant deposition of monoterpenes to grassland was observed. Deposition of sesquiterpenes and oxygenated terpenes to the grassland site was

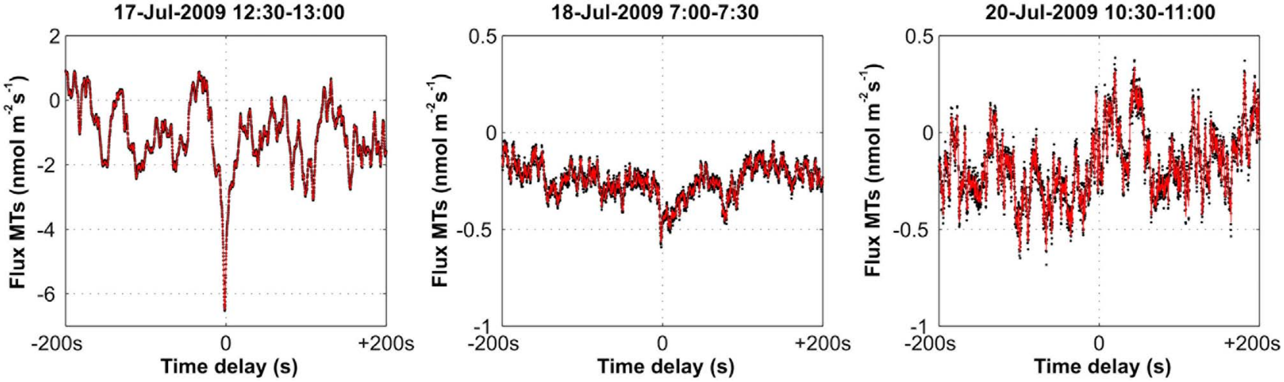

Figure A1. Example for covariance peaks which were rated as (left) class 1, (middle) class 2 and (right) class 3. The black dots represent the measurement points, and the red line is a smoothed line after the application of a moving average filter.

highly correlated with the observed monoterpene fluxes. During dry daytime conditions the observed deposition velocities were, with values close to the aerodynamic limit calculated from dry deposition theory, remarkably high. The uptake of terpenes by grassland lasted for several weeks without observed reemission. Cumulative carbon deposition fluxes of monoterpenes over grassland can reach the same range as net carbon emissions of methanol, the dominant BVOC emitted by grasslands. Moreover, the carbon uptake of monoterpenes by the grassland reached values which are in the same order of magnitude as carbon emissions of monoterpenes by forested areas used in global emission estimates.

[28] Our measurements suggest that deposition processes of monoterpenes could play a more significant role in the reactive carbon budget than previously assumed. The broader implications of this study are that bidirectional VOC exchange may occur for many, if not all, compounds. In the light of our study it may thus be worthwhile to change the terminology from the commonly used VOC emissions to VOC exchange. Finally, our findings should be incorporated into models which simulate the exchange of VOC across the ecosystem-atmosphere boundary.

Appendix A: Cross-Correlation Analysis, Cospectra, and Random Flux Uncertainty

[29] The time shift between the vertical wind velocity and the monoterpene time series (due to the residence time in the tubing, diverging computer clocks, etc.) was determined by searching for the maximum/minimum cross correlation in a given time window. For the PTR-TOF data this approach was further used to apply a quality rating following *Ruuskanen et al.* [2011]: Fluxes with a clearly visible covariance maximum or minimum were rated class 1; fluxes with a recognizable but uncertain (in peak position) maximum or minimum were rated class 2 (recognizable peak); all other half-hourly periods were rated class 3 and excluded from the analysis. Examples for these three quality classes are shown in Figure A1.

[30] A cospectral analysis of an exemplary half-hourly period (Figure A2) shows that MT cospectra measured with the PTR-MS and PTR-TOF exhibit similar cospectral density at low and intermediate frequencies as compared to sensible heat cospectra and correspond reasonably well with the site-specific cospectral reference model [*Wohlfahrt et al.*, 2005]. Note that the PTR-MS and PTR-TOF MT cospectra are characterized by a lower Nyquist frequency as compared to the sensible heat cospectra, which are acquired by the sonic anemometer at 20 Hz, due repetition rates of 2.3–3 s and 0.1 s, respectively. Because of the disjunct sampling with the PTR-MS MT cospectra are in addition noisier [*Hörtnagl et al.*, 2010]. Figure A2 also shows a simulated reference cospectrum that has been attenuated by a series of transfer functions accounting for both low- and high-pass filtering of MT fluxes [*Bamberger et al.*, 2010]. PTR-TOF cospectra nicely overlap with the attenuated model cospectrum at higher frequencies, confirming the approach of accounting for frequency loss [*Bamberger et al.*, 2010]. More than 50% of the MT fluxes were corrected with frequency response correction factors of 1.06 or less, 90% with 1.12 or less.

[31] The random MT flux uncertainty was calculated based on measurements under similar environmental conditions during adjacent days a suggested by *Hollinger and Richardson* [2005] using two years of PTR-MS and two months of PTR-TOF data. Similar environmental conditions were defined as differences in environmental conditions at the same time of day between two adjacent days of less than: 100 μmol m^{-2} s^{-1} incident photosynthetically active radiation, 2°C air temperature, 1°C soil temperature, 10% relative humidity, 1 m s^{-1} horizontal wind speed, 0.1 ppbv ambient MT mixing ratios. As shown in Figure A3 PTR-MS flux uncertainties were similar in magnitude for deposition and emission fluxes. As discussed by *Hörtnagl et al.* [2010], disjunct sampling causes an increase in the random flux uncertainty, which can be seen for MT deposition fluxes in the comparison to the fluxes calculated from the 10 Hz PTR-TOF data.

Appendix B: Comparison of Monoterpene Fluxes

[32] Figure B1 shows a comparison between the 12 h daytime monoterpene fluxes calculated from PTR-MS data and the corresponding fluxes calculated from the PTR-TOF data. It can be seen that the PTR-TOF fluxes tend to be higher compared to the PTR-MS fluxes but show the same pattern. A

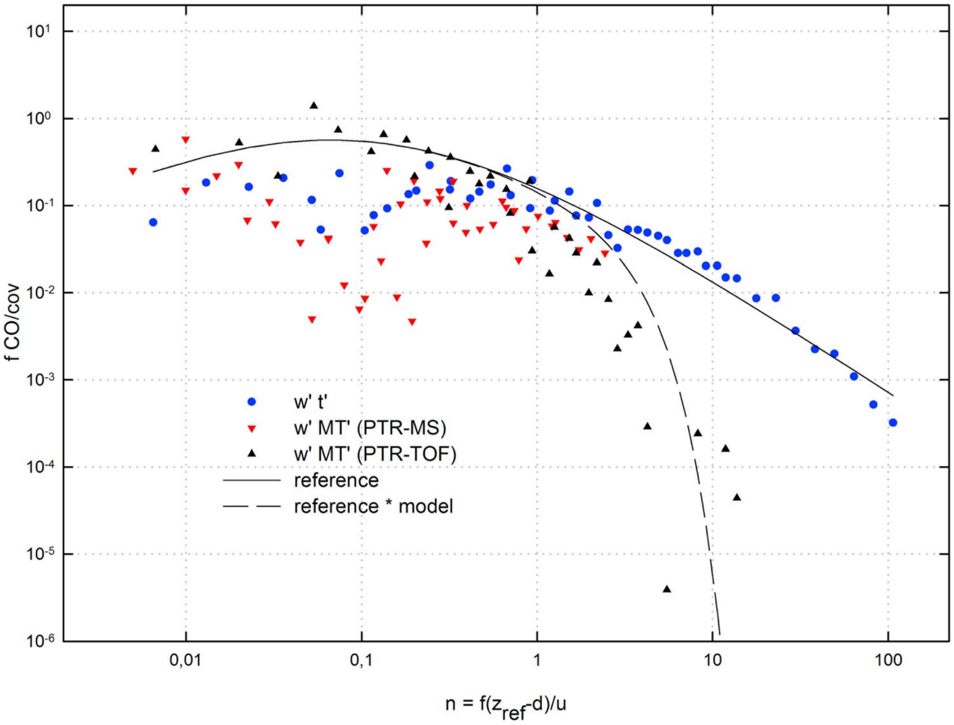

Figure A2. Comparison of exemplary cospectra for the sensible heat (blue dots) and MT (red triangles for the PTR-MS and black triangles for the PTR-TOF) flux together with the cospectral reference model (solid line) [*Wohlfahrt et al.*, 2005] and the reference model attenuated by a series of transfer functions which account for low- and high-pass filtering of the MT flux (dashed line). Cospectra have been obtained on 22 July 2009 09:00–09:30 under the following conditions: average horizontal wind speed, 0.2 m s^{-1}; Monin-Obukov stability parameter, −0.1. Note the lower Nyquist frequency for the PTR-MS and PTR-TOF MT cospectra due repetition rates of 2.3–3 s and 10 Hz compared to the 20 Hz of the sonic anemometer.

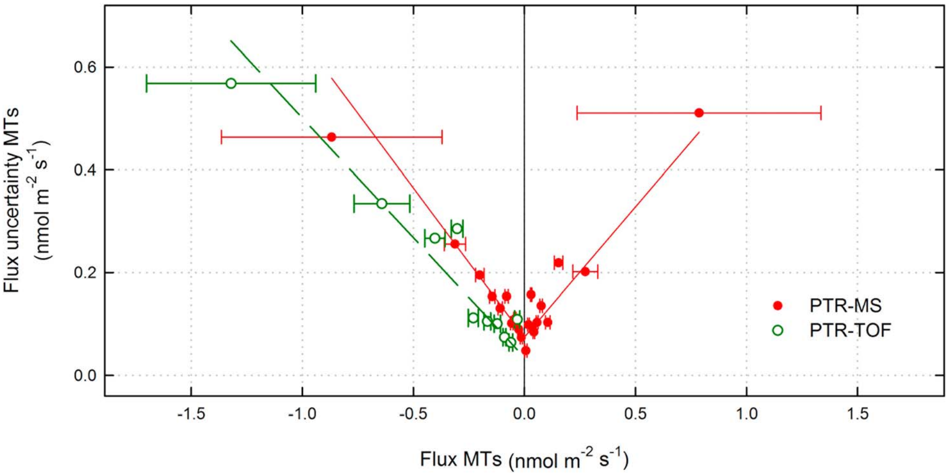

Figure A3. Random MT flux uncertainty for PTR-MS (solid red circles) and PTR-TOF (open green circles) measurements determined according to the method of *Hollinger and Richardson* [2005]. Data have been binned into classes of equal size; error bars represent ±1 standard deviation. A double-linear relationship with a common y intercept was fit to the PTR-MS data: $y = 0.51x + 0.07$ (emission), $y = -0.58x + 0.07$ (deposition), $R^2 = 0.92$. For the PTR-TOF data not enough emission fluxes were captured so that flux uncertainties have been calculated only for deposition fluxes ($y = -0.46x + 0.04$, $R^2 = 0.93$).

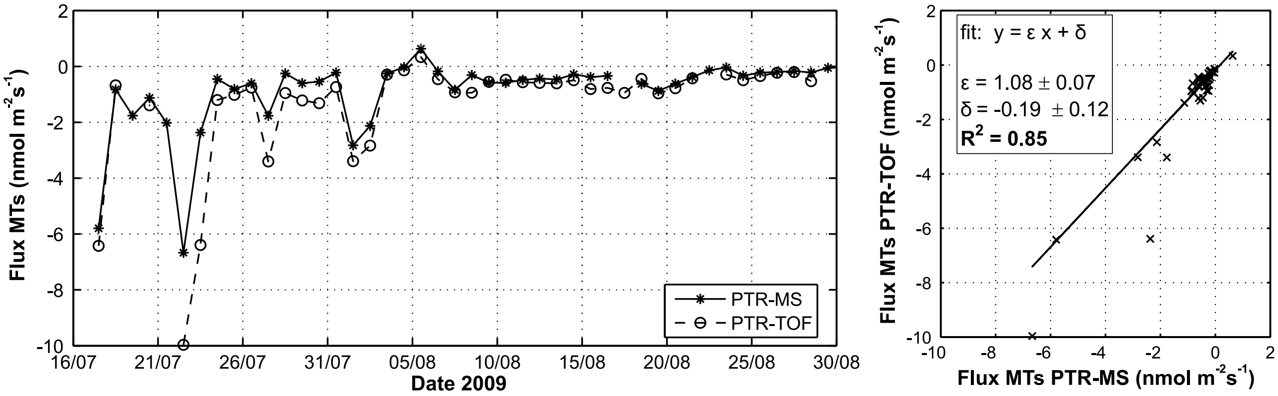

Figure B1. (left) Comparison of the time series of 12 h average fluxes measured with the PTR-MS and the PTR-TOF instrument and (right) the scatterplot including a regression line of $y = 1.08x - 0.19$ ($R^2 = 0.85$) received by a weighted linear least square fit.

weighted linear regression model with a slope of 1.08 and an offset of −0.19 leads to an R^2 of 0.85. Possible reasons for the deviation are slightly different data windows for the calculation of half-hourly fluxes (25 min for PTR-MS and 30 min for the PTR-TOF) and a general higher random variability of the vDEC fluxes compared to the fluxes calculated from a 10 Hz time series (see above).

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