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Winter greenhouse gas emissions (CO_2, CH_4 and N_2O) from a sub-alpine grassland

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Abstract

Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) fluxes were measured during the winter 2010/2011 at a sub-alpine managed grassland in Switzerland using concentration gradients within the snowpack (CO_2, CH_4, N_2O) and the eddy covariance method (CO_2). Measured snow densities were used to calculate the respective greenhouse gas (GHG) fluxes. Mean winter fluxes based on the gradient method were $0.74 \pm 0.53\,\mu mol\,m^{-2}\,s^{-1}$ for CO_2, $-0.14 \pm 0.09\,nmol\,m^{-2}\,s^{-1}$ for CH_4 and $0.23 \pm 0.23\,nmol\,m^{-2}\,s^{-1}$ for N_2O, respectively. While CO_2 and CH_4 fluxes decreased with progressing winter season N_2O fluxes did not follow a seasonal pattern. Key variables driving the fluxes of CO_2 and CH_4 were soil surface temperatures and snow-water equivalent. N_2O fluxes were only poorly explained by any of the measured factors in the soil and snow. Spatial variability across the valley floor was smallest for CO_2 and largest for N_2O. During the winter season 2010/2011 (November–April) greenhouse gas fluxes accumulated to 631–670 g CO_2 m^{-2}, -0.04 g CH_4 m^{-2} and 0.13 g N_2O m^{-2}. Total greenhouse gas emissions from the grassland were between 669–709 g CO_2 eq. m^{-2}, with N_2O contributing 5 % to the overall budget and CH_4 reducing the budget by less than 1 %. In comparison with the CO_2 fluxes measured by eddy covariance, the gradient technique underestimated the effluxes during the main winter period by 40 % but yielded similar fluxes on a seasonal basis. Cumulative budgets of CO_2 were smaller than emission reported for other sub-alpine meadows in the Swiss Alps and the Rocky Mountains. It remains unclear how GHG emissions are altered by changes in climate and according snow conditions.

1 Introduction

Identifying the sources and sinks of greenhouse gases (GHGs) in terrestrial ecosystems has become an important global research focus. Measurement networks such as GHG-Europe or FLUXNET (Aubinet et al., 2000; Baldocchi et al., 2001) deliver

BGD
10, 401–445, 2013

fundamental data to develop possible mitigation strategies for emissions originating from the burning of fossil fuels and current land-use and subsequent changes. While much of the research has focused on the biosphere-atmosphere exchange of carbon dioxide (CO_2) in most of the major global ecosystem types, including arctic ecosystems (Lohila et al., 2007; Schulze et al., 2010), little focus has been given to sub-alpine or alpine grasslands, particularly during winter (Brooks et al., 1997; Gilmanov et al., 2004; Filippa et al., 2009; Liptzin et al., 2009; Merbold et al., 2011).

Due to the projected changes in climate, such as rising winter temperatures, changes in precipitation and altered hydrology (IPCC, 2007), sufficient information on GHG exchange processes is necessary during winter in order to predict annual trace gas balances (Alm et al., 1999).

Complex processes drive the emissions of the three most important greenhouse gases – carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) – but a profound understanding of such processes exists only for CO_2. For example, the exchange of CO_2 between the ecosystem and the atmosphere during the dormant and often snow-covered periods is largely driven by soil temperature (often in deeper soil layers due to freezing at the soil surface), snow density and friction velocity above the snow (Liptzin et al., 2009; Merbold et al., 2011; Lohila et al., 2007; Mariko et al., 2000). Unfortunately, driving factors of CH_4 and N_2O emissions are less understood and knowledge of fluxes for all three gases remains sparse (Flechard et al., 2005; Kato et al., 2011; Kroon et al., 2010; Neftel et al., 2000, 2007; Soussana et al., 2007). Methane fluxes are characterized by two antagonistic processes – methanogenesis and methanotrophy – which both occur year-round (Bowden et al., 1998; Nykänen et al., 2003; Panikov and Dedysh, 2000; Zhuang et al., 2004; Zimov et al., 1993) and are primarily dependent on the aerobic/anaerobic conditions of soils as well as other factors, such as vegetation type (Le Mer and Roger, 2001). Nitrous oxide emissions are more difficult to explain due to the limited understanding of the potential microbial source processes – nitrification, denitrification and nitrifier denitrification (Brumme et al., 1999; Firestone and Davidson, 1989) – with an even more substantial lack of knowledge regarding winter

BGD
10, 401–445, 2013

processes. N_2O emissions from deeply frozen soils have been found to make a major contribution to annual flux estimates (Wolf et al., 2010). The reason for the high N_2O fluxes is most likely suppressed consumption in the soil, rather than enhanced N_2O production (Goldberg et al., 2010).

Globally, rice paddies, wetlands but also husbandry of ruminants are known as one of the major CH_4 sources while grassland soils and agricultural ecosystems are often mentioned as CH_4 sinks (Blankinship et al., 2010; Chen et al., 2011b; Dijkstra et al., 2011; Kato et al., 2011; Li et al., 2012; Stiehl-Braun et al., 2011; Wu et al., 2010). In addition, agriculturally managed soils, similar to soils under natural vegetation are known as the most important N_2O sources (Snyder et al., 2009; Stehfest and Bouwman, 2006).

Worldwide, only about 25 case studies have been conducted on winter respiration in high latitude and altitude system (reviewed by Liptzin et al., 2009 in a recent Special Issue on winter processes in Biogeochemistry) with only two of them being conducted in the Alps (Schindlbacher et al., 2007; Merbold et al., 2011). There is also only one study that explicitly measured the spatial variability of soil CO_2 effluxes for different ecosystem types during winter in Arctic Alaska (Jones et al., 1999). Moreover, up to date only few studies (< 10) on sub-alpine grasslands investigated the exchange of other greenhouse gases such as methane (CH_4) and nitrous oxide (N_2O) during periods of snow-cover (Gilmanov et al., 2004; Liptzin et al., 2009; Lohila et al., 2007; Wang et al., 2010; Schurmann et al., 2002; Filippa et al., 2009). These case studies showed that soil CO_2 efflux ranged between 30 and 200 g CO_2-C m^{-2} during the long snow-covered season which corresponded to 10 to 40 % of the annual effluxes in arctic and subalpine ecosystems (Winston et al., 1997; Clein and Schimel, 1995; Melloh and Crill, 1996; Nykanen et al., 1995; Aurela et al., 2002; Fahnestock et al., 1999; Jones et al., 1999; Björkman et al., 2010b). Much less studies include other GHGs which may offset possible annual carbon sink capacities of terrestrial ecosystems even further (Nykanen et al., 1995; Zimov et al., 1993, 1996; Sommerfeld et al., 1996; Dise, 1992; Bubier

BGD
10, 401–445, 2013

et al., 2002; Chen et al., 2011b; Merbold et al., 2011; Oechel et al., 1997; Groffman et al., 2006; Schurmann et al., 2002; Yashiro et al., 2006; Filippa et al., 2009).

Measurement of GHG fluxes in winter is a logistical and methodological challenge. Many snow-covered sites have poor access in winter and cold temperatures provide difficult working conditions for both humans and equipment. Primarily, there are three experimental approaches – surface chambers, snowpack concentration gradient measurements, and eddy covariance (EC). The comparability of the methods is controversial, and winter GHG fluxes vary more as a result of the method used than as a result of the actual variation in fluxes (Björkman et al., 2010b). The gradient method seems to underestimate fluxes compared to the EC method (Suzuki et al., 2006) as well as compared to the chamber method (Mariko et al., 2000). In contrast, Schindlbacher et al. (2007) observed that the chamber method underestimates CO_2 fluxes in comparison to the gradient method. To complete this contradicting discussion, Lohila et al. (2007) finds CO_2 emission rates measured by the eddy covariance method that are significantly lower than the rates measured by the chamber method.

In this study we quantified winter trace gas fluxes from a sub-alpine grassland in Switzerland. Our specific objectives were (i) to compare different approaches for measuring GHG emissions, the instantaneous gradient method, the permanent automatic monitored gradients, and eddy covariance, (ii) to define the spatial variation of GHGs across a subalpine valley and to identify the variables driving GHG emissions from different land-use type in a subalpine valley, and (iii) to quantify the emissions of CO_2, CH_4 and N_2O from the ecosystem during the snow covered season.

2 Material and methods

2.1 Study site

The grassland site is located in the Dischma valley near Davos in the Eastern Swiss Alps (46°47′ N, 9°52′ E, 1590 m a.s.l.). Davos is characterized by a mean annual

BGD
10, 401–445, 2013

temperature of 2.8 °C and an average of 139 to 175 days of snow cover (Beniston, 1997). Total annual precipitation in Davos amounts to 1000 mm yr^{-1} with maximum values recorded during the summer months (July–September) (MeteoSchweiz, 2011). Long-term averages of the study site showed a permanent snow cover from 19 November until 22 April (data not shown, measured at a nearby snow station at the same elevation with the same site characteristics, WSL Institute for Snow and Avalanche Research SLF). An overview of the monthly mean air temperature during 2010/2011 is given in Table 1.

The vegetation at the site consists of a species mixture of ryegrass (*Lolium* sp.), meadow foxtail (*Alopecurus pratensis*), dandelion (*Taraxacum officinale*), white clover (*Trifolium repens*) and buttercup (*Ranunculus* sp.). The sub-alpine grassland studied is moderately managed with grazing of cattle in spring and two harvest events for fodder production during summer, each being followed by manure applications. Soils are acidic with pH values ($CaCl_2$) of 4.1–4.6, have soil organic carbon contents of 8 ± 1 % in the uppermost 5 cm and contain 65–70 % sand and 10 % clay. For a more detailed explanation of the site see (Steinlin, 2011) and Mohn et al. (2013).

2.2 Greenhouse gas flux measurements

Greenhouse gas flux measurements of CO_2, CH_4 and N_2O were undertaken from early December 2010 until mid-April 2011 covering most of the snow-covered period in the Dischma valley. Two majorly different techniques – eddy covariance and manual gradient measurements – were used to derive independent GHG flux estimates and are explained in the following paragraph.

2.3 Eddy covariance flux measurements of CO_2

An eddy covariance (EC) tower was set-up at the end of November 2010 in the center of the grassland ecosystem in the Dischma valley (Fig. 1a, b). The dominant wind directions were NW and SE, following the Dischma valley surrounded by steep mountains.

BGD
10, 401–445, 2013

The EC tower approach was used for continuous measurements of the turbulent fluxes of CO_2, water vapor, sensible heat and momentum (Aubinet et al., 2000; Baldocchi, 2003). Measurement height was 1.5 m above the snowpack with regular adjustments following snow accumulation. A three-dimensional ultrasonic anemometer (CSAT3, Campbell Scientific, Logan, USA) was installed to measure wind velocity, wind direction and temperature fluctuations. Carbon dioxide and water vapor concentrations were measured with an open-path infrared gas analyzer (LI-7500, LI-COR Inc., Lincoln, Nebraska, USA) while both instruments sampled at a resolution of 20 Hz.

Data processing followed CarboEurope standards (Papale et al., 2006; Mauder et al., 2008). The vertical turbulent flux (F) was calculated from the covariance of the fluctuations (half-hourly averages) of the vertical wind velocity and the CO_2 concentration (c, µmol, Eq. 1)

$$F = \overline{w'c'} \quad (\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}) \tag{1}$$

where the overbar denotes time averages. c' was obtained by subtracting the linear trend in CO_2 concentration from each half hour interval. A positive flux–sign indicates a net loss of CO_2 from the ecosystem, whereas a negative sign indicates net uptake.

Flux processing included the necessary corrections for high frequency damping losses (Eugster and Senn, 1995) and density fluctuations according to Webb et al. (1980). In addition fluxes were further corrected with an additional heat flux correction term due to instrument heating (Burba et al., 2008). A specific description of the modified correction for instruments, which are not setup vertically is given in Merbold et al. (2011) and Rogiers et al. (2008). After the application of the various corrections to the processed fluxes data were filtered for clearly out of range values (±10SD), negative flux rates at night as well as values below a u^* threshold of 0.01 to avoid an overestimation of night time respiration under low turbulence (Goulden et al., 1996).

BGD
10, 401–445, 2013

2.4 Gradient measurements of CO_2, CH_4, N_2O and ^{222}Rn

Gas concentrations of CO_2, CH_4, N_2O and ^{222}Rn were measured in five profiles surrounding the EC tower on a weekly basis (Fig. 1c). In addition, two automatic profiles with a continuous monitoring of CO_2 concentrations were installed within the snowpack surrounding the EC and meteorological towers.

The gradient method is based on measured concentration gradients and the diffusivity of gases across the snowpack (Hubbard et al., 2005). This approach relies on the assumption that the gas production is continuous, limited to the soil and that the gas does not bind or react with snow. We used a one-dimensional steady-state diffusion model (Fick's law of diffusion) for calculating GHG fluxes through the snow (Eq. 2),

$$J = -D \times \frac{\mathrm{d}c}{\mathrm{d}z} \tag{2}$$

where J is the flux rate (µmol CO_2 $m^{-2}s^{-1}$/nmol CH_4/N_2O $m^{-2}s^{-1}$) and D the diffusion coefficient of each GHG in the snow (m^2s^{-1}). The concentration gradient $\frac{\mathrm{d}c}{\mathrm{d}z}$ is the slope of the linear regression (µmol $m^{-2}s^{-1}$). D is estimated from porosity (f) and turtuosity (τ) of the medium and the diffusion coefficient of CO_2 in air (Eq. 3).

$$D = f \times \tau \times D_{\mathrm{air}} \tag{3}$$

D_{air} has a value of 0.138×10^{-4} m^2s^{-1} for CO_2, 0.195×10^{-4} m^2s^{-1} for CH_4 and 0.144×10^{-4} m^2s^{-1} for N_2O (Massman, 1998). Porosity and tortuosity are derived from snow density following Eqs. (4) and (5),

$$f = 1 - \frac{\varrho}{\varrho_{\mathrm{ice}}} \tag{4}$$

where ϱ is the mean density of the snow layer and ϱ_{ice} is the density of ice (973 kg m^{-3}). Turtuosity is then calculated as a function of porosity.

$$\tau = f^{\frac{1}{3}} \tag{5}$$

BGD
10, 401–445, 2013

For weekly instantaneous measurements of the GHG fluxes using the gradient method, we sampled all gases across the snowpack with a "ski-pole". The ski pole had 10 cm interval depth markings along the pole, contained a tube inside and had a perforated tip allowing gas collection at any snow depth (Wetter, 2009). Measurements of the collected gas were made either in the field via a portable gas analyzer (LI-820, LI-COR Inc., Lincoln, Nebraska, USA) directly connected to the ski pole or later in the laboratory following gas sampling. While the gas analyzer only measures CO_2, gas chromatography was used to measure CO_2, CH_4 and N_2O concentrations within the collected samples. Gas was collected from the ski pole with 60 mL. Samples were immediately transferred into pre-evacuated 12 mL vials (Labco Limited, Buckinghamshire, UK). The gas analysis was carried out few hours later by gas chromatography (Agilent 6890 gas chromatograph equipped with a flame ionization detector and an electron capture detector, Agilent Technologies Inc., Santa Clara, USA). For more gas chromatography details see Hartmann et al. (2011).

The permanent automatic monitored gas gradients involved the use of another gas analyzer (LI-840, LI-COR Inc., Lincoln, Nebraska, USA) to measure CO_2 concentrations in situ and continuously within the snowpack at four different heights (Fig. 1b). Closed loops of tubing (Synflex 1300 aluminium coated tubing, Eaton Industries II GmbH, Effretikon, Switzerland), about 10 m length in total, were installed for GHG measurements. The closed loops included 1 m of an air permeable, hydrophobic, polypropylene tube (Accurel PP V8/2) (Gut et al., 1998) to sample the air within the snowpack over the course of the winter season. The first sampling depth was installed at the beginning of the winter season between the soil and the first snow layer. The following tube layers were set up on top of the snow pack preferably after a period of snow compaction and before severe snowfall events. We favored flexible tubes as compared to rigid "snow towers" used in other winter studies (e.g. Filippa et al., 2009), because the latter are likely to alter the build-up of an undisturbed snow structure. For the actual gas measurement, air was flushed through the tubes and sampled at a 10-minute interval using a self-made profile unit consisting of a switching-unit, a gas-analyzer

BGD
10, 401–445, 2013

(LI-840, LI-COR Inc., Lincoln, Nebraska, USA) and a Radon analyzer (Alpha Guard, Genitron Instruments, Frankfurt a.M., Germany) incorporating a pulse-counting ionization chamber (alpha spectroscopy). The radon analyzer was capable of measuring concentrations between 2 and 2×10^6 Bq m^{-3}. Radon (^{222}Rn) flux measurements were undertaken to determine diffusion properties in the snowpack. This method was successfully applied to measure soil diffusivity by Lehmann et al. (2000) since radon is of geological origin and is produced continuously in the α-decay chain of uranium and thorium in all natural soils. Furthermore, radon is a noble gas and shows no chemical or microbial reaction in the soil, snow or air. Since the canton of Grisons, and specifically the region of Davos, has been identified as a region of high radon by Deflorin (2004), we decided to use ^{222}Rn as a natural tracer to define the specific snow diffusion properties of other GHGs. Automated data were stored continuously on a data logger (CR10X, Campbell Scientific Inc. USA).

2.5 Spatial measurements of GHG fluxes

To determine the transversal and longitudinal variability across the grassland, 33 profiles were sampled manually using the ski-pole method during an intensive field campaign on the 23 February 2011. At each location samples for CO_2, CH_4 and N_2O analysis were taken at 10, 30 and 50 cm depth at a horizontal resolution of 5 m. Snow density measurements (explained below) were performed every 10 m. In addition, 150 CO_2 concentration gradients were measured on a transversal cut across the different vegetation types of the valley, in distances ranging from 0.2 to 5m. These gradients were measured on-site in a vertical resolution of 10 cm.

2.6 Meteorological data

Meteorological data such as air temperature and relative humidity (3 m height, Rotronic Hydroclip MP100A, ROTRONIC AG, Bassersdorf, Switzerland) soil temperature (3 cm depth, 107-L Campbell Scientific Inc. USA), soil water content (10HS soil moisture

BGD
10, 401–445, 2013

sensor, Decagon Devices Inc., Hopkins, Nebraska, USA), snow height (SR50-L, Campbell Scientific Inc. USA), wind speed and direction (3.4 m height, 05103 RM Young Windmonitor, Campbell Scientific Inc. USA), snow surface temperature (AlpuG IR, AlpuG GmbH, Davos, Switzerland) and short wave radiation (SP-110, Apogee Instruments Inc., Logan, UT, USA) were collected as 10 min averages at a nearby snow station run by the Institute of Snow and Avalanche Research (SLF).

2.7 Measurements of snow density

Manual measurements of snow density were conducted in combination with the manual GHG gradient measurements by weighing snow samples of a defined volume directly in the field. These measurements were done in 10 cm increments with 2–3 replicates per depth. Information on depth and thickness of ice layers was recorded additionally. Mean snow density was than calculated by the density of the different snow layers, where borders were defined by either an ice layer or the middle between two density measurements.

3 Results

3.1 Weather and snow condition

A continuous snow cover from mid-November until the beginning of April characterized the study site during the winter season 2010/2011 (Fig. 2). Air temperature varied distinctly over the course of the season, reaching lowest values of −20 °C on the 27 December and the 20 January. In March 2011, temperature started to rise rapidly. Temperatures at the soil-snow interface decreased at the beginning of the winter season and stayed mostly stable around 0 °C until complete snowmelt at the beginning of April 2011. Topsoil temperatures dropped slightly below zero during February and March (Fig. 2a–c). Snow accumulated rapidly with the continuous snowfall until the 11 December. Maximum snow height (63 cm) was reached the 27 February (Fig. 2d), which

BGD
10, 401–445, 2013

was well below the long-term average of 89 cm (SLF; unpublished data). Snow density remained stable at around 0.25 g m^{-3} over most of the season and reached maximum values of 0.45 g m^{-3} only at the end of the season (Fig. 2e). Ice layers within the snowpack developed due to short temperature changes during the months December and January and the associated freeze – thaw cycles of the snow (Fig. 2a).

In this study we defined the winter season as the period of continuous snow cover – lasting from 16 November 2011 until the 4 April totaling 140 days.

3.2 Temporal variation of greenhouse gas fluxes

Concentrations of CO_2 showed a linear increase from the snow to the soil surface, with significant linear relationships between concentrations and snow depths (not shown). Fluxes of CO_2 calculated from the gradient measurements followed a seasonal course with largest efflux rates occurring at the beginning of the snow-covered period (Fig. 3a, 2.3 ± 2.2 µmol CO_2 $m^{-2} s^{-1}$ in December 2010). Decreasing CO_2 fluxes were measured during the peak winter period (January/February 2011) reaching a minimum of 0.02 µmol CO_2 $m^{-2} s^{-1}$ on the 23 February. Thereafter and with the beginning of snowmelt CO_2 fluxes started to increase along with high concentrations of CO_2 at the soil-snow interface (0.51 ± 0.23 µmol CO_2 $m^{-2} s^{-1}$ in March and April) (Fig. 3a). In comparison to the gradient approach, CO_2 fluxes measured by the eddy covariance method showed much larger efflux rates associated with larger variation (Fig. 4, grey polygon), while having a better temporal resolution. Fluxes were characterized by continuous but temporally declining release of CO_2 until snowmelt at the end of March (Fig. 4). With the appearance of the first snow-free patches within the EC footprint at the beginning of April 2011 net ecosystem exchange (NEE) rates decreased towards zero indicating photosynthetic activity (Fig. 4, grey polygon).

Methane was taken up continuously by the grassland during the winter 2010/2011 (Fig. 3b). Largest uptake rates were recorded on 8 December with rates as negative as -0.62 nmol CH_4 $m^{-2} s^{-1}$. Fluxes of methane towards the ecosystem decreased over

BGD
10, 401–445, 2013

the course of the winter season and fluctuated slightly below zero at the end of the season (March/April: -0.09 ± 0.08 nmol CH_4 m^{-2} s^{-1}, Fig. 3b).

Emission of nitrous oxide varied largely during the winter season 2010/2011 (Fig. 3c) with peaks up to 1.63 nmol N_2O m^{-2} s^{-1} on 15 February. However the average seasonal loss of N_2O from the ecosystem was significantly lower (0.23 ± 0.23 nmol N_2O m^{-2} s^{-1}, Fig. 3c).

3.3 Driving factors of GHG fluxes

In this study we tested the influence of air temperature (T_a), temperature at the soil-snow interface (T_{s-s}), soil moisture (Θ), snow height (h_s), snow density (ϱ_s), snow water equivalent (SWE) and wind speed (WS) on measured CO_2 fluxes. SWE was calculated by the product of snow depth and relative snow density with respect to the density of liquid water. Therefore, SWE represents a measure for the mass of the snowpack. T_{s-s} and SWE explained 78 % and 80 % of the variability of CO_2 fluxes, respectively (Fig. 5a, b). Measurements from April were discarded from this analysis due to the absence of a continuous snow cover on the grassland and a likely CO_2 dissolution in melt water altering CO_2 gradients. Both variables were then included in the following General Linear Model (GLM), explaining 84 % of the variation in CO_2 fluxes (Eq. 6).

$$CO_2\text{flux} = 2.26 + 5.09 \times T_{s-s} - 0.12 \times \text{SWE} - 0.35 \times T_{s-s} \times \text{SWE} \quad (6)$$

This model was further applied to interpolate the weekly gaps in the data to derive cumulative sums of CO_2 emission for the snow-covered period in 2010/2011.

In contrast to the profile measurements, fluxes measured by eddy covariance could not be explained by any of the above given meteorological variables. Average flux magnitudes of the gradients were lowest when looking at measured values only, but highest when including the modeled data. EC fluxes were commonly bigger than the values derived from the gradients (Table 2). Largest deviations between gradient and eddy covariance derived values were found during the beginning and the end of the season,

BGD
10, 401–445, 2013

whereas measurements derived by the gradient method were about 40 % lower during the main winter period than those estimated by EC (Table 2, Figs. 3, 4).

Variability in CH_4 fluxes was similarly explained as CO_2 fluxes by the temperature at the soil-snow interface ($r^2 = 0.43$) and snow water equivalent ($r^2 = 0.57$). However a combination of both driving variables in a GLM did not improve the explanatory power of variation in CH_4 fluxes ($r^2 = 0.50$). Therefore the relation between CH_4 flux and SWE was used to calculate annual sums of CH_4 uptake (Eq. 7).

$$CH_4 \text{flux} = -0.46 + 0.02 \times \text{SWE} \quad (7)$$

In contrast to the CO_2 and CH_4 fluxes, none of the meteorological variables measured were able to explain the variation in N_2O flux. Relating N_2O fluxes to soil water content (10 cm depth) as done in previous studies did not result in sufficient explanatory power (Fig. 5e). Extrapolation of N_2O fluxes was based on a running mean of the weekly measured fluxes. The days before actual start of measurement were filled with the overall mean of measured N_2O fluxes.

3.4 Seasonal GHG budget

Seasonal budgets of CO_2, CH_4 and N_2O during the period of 16 November until 4 April (140 days) were 670 g CO_2 m^{-2}, −0.5 g CH_4 m^{-2} and 0.13 g N_2O m^{-2}, respectively. Measurements were extrapolated according to Eqs. (6) and (7) given above. Cumulated emissions for CO_2 measured by EC were slightly lower than the values given by the profile measurements (630 g CO_2 m^{-2}). The ecosystems global warming potential (GWP) during the winter season 2010/2011 (winter defined as the snow-covered time period) was 669–709 g CO_2-eq., respectively. N_2O fluxes contributed ±5 % to the seasonal GHG budget and CH_4 fluxes reduced the GHG budget of the grassland site by less than 1 %.

BGD
10, 401–445, 2013

3.5 Automatic gradient measurements

Besides monitoring GHGs during winter in the Dischma valley we aimed at testing an in-house developed automatic gradient measurement technique for continuous ^{222}Rn and CO_2 concentrations measurements within the snowpack. Although we have chosen long tube lengths (10 m) to avoid heating of the air when passing the instruments measuring CO_2 concentrations we observed ice-channels surrounding the tubing during the end of the measurement campaign (Fig. 6). As a result, the continuously measured CO_2 gradient was much smaller than the instantaneous manually measured one using the ski-pole (data not shown). Further development including active cooling of the air circulating in the tubes is needed.

3.6 Spatial variation of CO_2, CH_4 and N_2O fluxes on the grassland

CO_2 fluxes during the intensive measurement campaign varied between 0.04 µmol CO_2 m^{-2} s^{-1} and 1.14 µmol CO_2 $m^{-2}s^{-1}$. The variation of CO_2 fluxes was stronger along the transversal cut of the grassland than along the longitudinal cut of the valley (Fig. 7a). Coefficients of variation were 75 % for the whole grassland, 76 % for the transversal and 72 % for the longitudinal transect.

Methane fluxes were significantly below zero (−0.06 nmol CH_4 $m^{-2}s^{-1}$, one sample *t*-test, Fig. 7b) along the two transects. Maximum uptake rates were −0.16 nmol CH_4 $m^{-2}s^{-1}$. Single points of methane efflux were located across the grassland with values up to 0.10 nmol CH_4 $m^{-2}s^{-1}$ (Fig. 7b). Concentrations of methane within the snowpack were less variable than the concentrations of CO_2 (not shown). Fluxes of CH_4 along the transversal and longitudinal cut through the grassland did not differ significantly (Fig. 7b). Coefficients of spatial variation were slightly higher than the values reported for CO_2 fluxes (110 % whole grassland, 103 % and 101 % for the transversal and the longitudinal transects, respectively).

N_2O fluxes were variable across the grassland, with mean fluxes of 0.03 nmol N_2O $m^{-2}s^{-1}$ (Fig. 6c). However a significantly larger efflux of N_2O (0.33 nmol N_2O $m^{-2}s^{-1}$)

BGD
10, 401–445, 2013

was measured at one profile (at 75m) along the longitudinal transect (Fig. 7c). The coefficients of spatial variation were highest for N_2O in relation to CO_2 and CH_4, with values up to 256 % on the grassland, 165 % for the transversal and 254 % for the longitudinal cut.

3.7 Spatial variation of CO_2 fluxes across vegetation types

The mean CO_2 fluxes between the different ecosystems varied considerable with largest emissions of 0.85 ± 0.38 µmol CO_2 $m^{-2} s^{-1}$ from the grassland ecosystem (Figs. 8, 9) and smallest from the filled ground and the grassland slope (0.31 ± 0.16 µmol CO_2 $m^{-2} s^{-1}$). Intermediate fluxes of CO_2 occurred from the forest (0.41 ± 0.22 µmol CO_2 $m^{-2} s^{-1}$) having the lowest snow cover across the measurement transect (Fig. 8).

4 Discussion

The gradient method has been most frequently applied to investigate winter CO_2 emissions during previous studies (van Bochove et al., 2000; Wolf et al., 2011; Wetter, 2009). However, its accuracy is highly uncertain due to the difficulties in validating gas diffusivity across snow packs and comparisons with chamber and eddy covariance approaches have yielded contradicting results (Björkman et al., 2010b; Suzuki et al., 2006; Schindlbacher et al., 2007). Our comparison of the gradient approach with CO_2 effluxes estimated by the EC method indicated a 40 % underestimation during the main winter period (January–March) and stronger deviations during snowmelt. One bias for this conclusion could be the different scales of the two methodologies. While the gradient method enables to quantify emissions at the plot scale (Hubbard et al., 2005), eddy covariance integrates flux measurements over a whole ecosystem (the so-called footprint area) and can cover several hectares of land (Baldocchi and Meyers, 1998). Our spatial measurement campaign showed that the average CO_2 effluxes along the

BGD
10, 401–445, 2013

longitudinal transect (main wind direction) and the transversal cut were in the same order of magnitude than the ones that were monitored throughout the peak winter season (0.35 µmol m^{-2} s^{-1} vs. 0.52 µmol m^{-2} s^{-1}). Contrastingly, eddy covariance fluxes showed considerably higher results for the peak winter season (January-March).

The underlying approach of the gradient method derives gas diffusivity across the snowpack indirectly estimated from snow density measurements assuming steady-state conditions (Eq. 2). Therefore it seems likely that the estimated fluxes include a high uncertainty. Effects such as pressure pumping may lead to adjective movement of snow air and therefore increased CO_2 efflux. The quantification of such effects remains still a challenge (Mast et al., 1998). Bowling & Massman (2011) were able to identify an 8–11 % contribution of pressure pumping to a winter CO_2 budget in Niwot Ridge, USA. We did not observe such a relationship between CO_2 flux and wind speed (not shown) at our site suggesting that wind pumping played a minor role in this study.

In addition, nonlinearities of the concentration gradient often caused by ice-layers have been shown to generate problems when calculating CO_2 fluxes. Mast et al. (1998) suggested to choose a linear part of the gradient with constant snow density, whereas Schindlbacher et al. (2007) proposed including sections of the gradient above an ice-layer only. More complex approaches were recommended by Monson et al. (2006b). In our study, we did not observe nonlinearities, which could not be related to a specific ice layer. Therefore the entire concentration gradient was chosen for flux calculation.

The estimation of porosity and tortuosity bares the largest uncertainties when applying the gradient method for GHG flux calculation (Monson et al., 2006b; Sommerfeld et al., 1996). We estimated both variables from measurements of snow density following Eqs. (3) and (4) similar to the majority of biogeochemical studies on soil CO_2 effluxes during winter (Hubbard et al., 2005; Filippa et al., 2009; Liptzin et al., 2009; Mast et al., 1998). Pinzer et al. (2010) found aged snow mainly being composed of rounded grains whereas fresh snow consisted of dendritic or plate-like particles. Such microstructure can have a crucial influence on the gas flux, by affecting the linkage and connectivity of pores (Pinzer et al., 2010). These properties can not completely

BGD
10, 401–445, 2013

be derived from snow density and tortuosity alone. One possible but costly and time-consuming approach could be the use of X-ray microtomography to determine the microscopic snow structure and derive the theoretical effective gas diffusion coefficient (Pinzer et al., 2010). Other suggestions to estimate the effective diffusivity from the snow structure (tortuosity) would be the use of inert gases such as NO, NO_2, CO_2 or SF_6 as tracers. A severe drawback of such approach is the possibility of dissolving CO_2 in liquid water, which may store significant amounts of CO_2. Further dissolved CO_2 may be leached from the system by downward fluxes of water. However Sommerfeld et al. (1996) estimated that the magnitude of CO_2 flux in the liquid phase was two orders of magnitude less than the upward flux through diffusion of CO_2 in the gaseous phase.

Our results indicated the largest discrepancy between fluxes measured by eddy covariance and the gradient approach late in the year (Table 3). The likely reason is the beginning of snowmelt at the end of March and beginning of April, where CO_2 dissolves in liquid water. Dissolved CO_2 may be leached from the system and the downward flux may have led to a smaller diffusion coefficient and thus to slower gas exchange resulting in an underestimation of the calculated CO_2 flux rates. However due to the rather fast melting of snow at the end of the season we expected only minor underestimation in CO_2 fluxes on a seasonal basis. In contrast, given the results presented in Table 2 the gradient methods underestimates fluxes derived using the EC technique by 40 % though having a much larger variation.

Last but not least, the use of tracers is a powerful tool to quantify gas diffusion in snow required for the gradient method. While studies in the Arctic used SF_6 as an artificial tracer (Björkman et al., 2010a,b) in comparison with other techniques showing reasonable results we decided to use ^{222}Rn as a natural tracer. ^{222}Rn was chosen since it has two major advantages. First, the production in the subsoil leads to a small but constant flux from the soil surface to the atmosphere. Secondly, the release of ^{222}Rn over the entire soil surface does not lead to lateral diffusion as found for SF_6 (Björkman et al., 2010a). However, gradients of ^{222}Rn as well as CO_2 could not be measured by

BGD
10, 401–445, 2013

the permanently monitored gradients in this study due to the formation of ice channels around the permanently installed tubing system. The likely reason is the heating of the air when passing the instruments because snow structures are very sensitive to slight temperature changes around freezing. Based on our experience we propose the following improvements for the use of the automatic gradient measurements of CO_2, ^{222}Rn and possibly other GHGs in the future: (i) longer tubes between the analyzer and the measurement spot with the disadvantage of extended lag times, and (ii) lower flow rates to allow cooling of the circulating air and most importantly active cooling of the gas leaving the instruments measuring GHGs and ^{222}Rn in direct conjunction with a temperature sensor located in the airstream. (iii) Alternatively, the gases could be sampled with an open system, which, however, may alter the gas gradient within the snow pack due to the permanent sampling of air and which alters the snow structure by the installation of a fixed air sampling unit.

Eddy covariance (EC) measurements on the other hand were undertaken to receive an ecosystem integrated signal of CO_2 efflux from the snow-covered grassland. We did not encounter extended periods of stable or neutral conditions in the Dischma valley due the topography of the valley, which was further underlined by our measured wind data (not shown). The site was chosen since it represented a typical managed high altitude grassland ecosystem in the Swiss Alps and was further characterized by the convenient accessibility and power availability in winter. These features enabled us to use the setup as explained in the material & methods paragraph. The second limitation when using the EC method in winter was overcome by applying an additional correction term for the sensor heating as suggested by Burba et al. (2008). Since the gas analyzer was not set up vertically we used a similar approach as explained by Merbold et al. (2011) and Rogiers et al. (2005).

4.1 Seasonal GHG fluxes

CO_2 flux measurements reported in this study were generally in the upper range of winter emissions reported in the literature (Lohila et al., 2007; Skinner, 2007;

BGD
10, 401–445, 2013

Sommerfeld et al., 1996; Filippa et al., 2009; Liptzin et al., 2009; Seok et al., 2009; Rogiers et al., 2008; Brooks et al., 1997; Fahnestock et al., 1999). Whereas our results showed a clearly seasonal pattern with (I) gradual decreases at the beginning of the snow-covered period, (II) a mid-winter minimum and (III) increases in CO_2 flux during snowmelt, studies undertaken in the Rocky Mountain showed completely opposite behavior of steadily increasing CO_2 fluxes with progressing winter (Sommerfeld et al., 1996; Filippa et al., 2009; Liptzin et al., 2009; Seok et al., 2009). The only similarities were the higher fluxes of CO_2 during the period of snowmelt. This increase in CO_2 fluxes was shown to be related to soil water content (approx. $0.2\,m^3\,m^{-3}$) (Liptzin et al., 2009). In contrast, in the Dischma valley, soil moisture did not show an influence on CO_2 fluxes measured. Apparently soil water content was not limiting in the valley floor and remained almost constant over the whole winter period (Fig. 2e).

Decreases in CO_2 fluxes during winter period could be related to declining substrate availability, as suggested by Liptzin et al. (2009) and Schindlbacher et al. (2007). Further, decreasing soil temperatures may have additionally contributed to mid-winter minima (Fig. 2b) as similarly reported for a sub-alpine forest by Monson et al. (2006a). Increases in CO_2 efflux during snowmelt are most likely caused by a combination of factors occurring simultaneously, increases in soil temperature and soil moisture but also carbon availability (e.g. Hubbard et al., 2006; Monson et al., 2006a). While we found a close relationship between temperatures at the soil-snow interface and CO_2 fluxes as commonly reported for growing season soil CO_2 fluxes (e.g. Merbold et al., 2009; Monson et al., 2006b) and the according relation between temperature and microbial activity, several studies only found weak or insignificant relations between CO_2 fluxes and soil temperature during winter (Sommerfeld et al., 1996; Schindlbacher et al., 2007; Litzin et al., 2009; Björkman et al., 2010a). Snow water equivalent (SWE) largely explained the variability in CO_2 fluxes in the Dischma valley. This correlation was largely due to the variation in snow height since snow density remained almost constant during the winter period 2010/2011. These findings are in contrast to the results shown by Monson et al. (2006b) whom showed lower rates of CO_2 flux with reducing snow

BGD
10, 401–445, 2013

height. However the negative relationship between snow height and respiration might be misleading since snow height includes a time factor, meaning snow height commonly increases with the progress of the winter season. This is particularly underlined by the calculated values of SWE at our site with SWE > 12 cm mainly occurring during December and January and larger values only occurring during February and March. This indicates that snow cover was highest at low temperatures in the air and at soil-snow and at times of a reduced carbon availability.

Methane uptake was as large as $-0.14\,\mathrm{nmol\,CH_4\,m^{-2}\,s^{-1}}$ on the Dischma grassland. Similar uptake rates were found for a sub-alpine meadow by Sommerfeld et al. (1993) and a completely drained fen in Eastern Finland, by Alm et al. (1999). Still, the reported uptake rates were considerably lower (-0.8 and $-0.1\,\mathrm{nmol\,CH_4\,m^{-2}\,s^{-1}}$, respectively) than the values measured at our site. Mast et al. (1999) reported uptake rates of $-0.19\,\mathrm{nmol\,CH_4\,m^{-2}\,s^{-1}}$ on dry sub-alpine soils and net CH_4 production under moist and water saturated conditions. Our results indicate that even at a volumetric water content of $0.4\,\mathrm{m^3\,m^{-3}}$ the grassland in the Dischma valley is still characterized by net methane consumption. The seasonal pattern of CH_4 uptake with decreasing uptake rates during the winter period and a re-increase towards the end of the winter season is in contrast to the increasing uptake over the winter period and rapid decreases during snowmelt observed in a subalpine soil in the Rocky Mountains (Mast et al., 1998).

Besides a different seasonal pattern compared to previous studies our results did not indicate a strong relationship of CH_4 fluxes to commonly observed drivers. Soil temperatures only showed a weak relation to CH_4 uptake while soil moisture was not significantly related to CH_4 fluxes. Although volumetric soil water content of the soil is one crucial factor limiting CH_4 diffusion into soils (Wang et al., 2005; 2010; Borken and Beese, 2006; Chen et al., 2011a,b; Hartmann et al., 2011), Chen et al. (2011a) found that this is only valid for soil temperatures > 5 °C. The lacking relationship in the Dischma valley might either be due to the small range of soil moisture the measurements covered during the winter 2010/2011 or that we are still missing an important variable driving the CH_4 uptake on this grassland. Since we found a larger variability of CH_4

BGD
10, 401–445, 2013

fluxes along the transversal cut of the valley than on the longitudinal transect we assume a stronger influence of topography along the transversal transect, e.g. distance to the river, to the stream and/or the slope of the grassland.

Measured N_2O fluxes averaging 0.23 nmol m^{-2} s^{-1} were significantly larger than values reported for a subalpine meadow in the Rocky Mountains (0.008 nmol m^{-2} s^{-1}, Sommerfeld et al., 1993) as well as for a drained fen in Eastern Finland (0.006 nmol m^{-2} s^{-1}, Alm et al., 1999). However, a grassland site fertilized with inorganic NPK fertilizers showed four times larger emissions than the Dischma grassland (1.08 nmol m^{-2} s^{-1}, Nykanen et al., 1995). We could not identify a seasonal pattern for the N_2O fluxes measured, which is most likely due to the complex controls of production and consumption of N_2O as well as the reactivity of NO, N_2O and NO_2. N_2O fluxes were neither explained by temperatures at the soil-snow interface nor by SWE. However there seemed to be some response to soil moisture (Fig. 5e). A study by Dalal and Allen (2008) showed the dependency of N_2O fluxes to water filled pore space (WFPS). The authors reported increasing N_2O emission up to a WFPS of 70 % when denitrification is the most important process in the soil caused by limited oxygen diffusion. However when WFPS exceeded 70 % N_2O consumption in the soil is favored, leading to decreasing N_2O emissions (Dalal and Allen, 2008). The possible relation between N_2O fluxes and soil moisture remains highly hypothetical due to the unavailability of soil porosity information at the Dischma valley. A different approach using the natural abundance of N isotopes was applied to gain further insight in the source and sink processes of N_2O emissions at the Dischma grassland (Mohn et al., 2013).

Seasonal budgets derived by two different measurement techniques and further extrapolation to the whole snow-covered season lead to almost similar emissions (631 g CO_2 (EC) and 670 g CO_2 (gradient)). The larger budget derived by the gradient methods, while generally underestimating fluxes during the peak winter season, occurs most likely from an overestimation of fluxes at the beginning (November) and end (April) of the winter season. During this period the model, including temperature and snow water equivalent, clearly overestimates the CO_2 losses from the grassland ecosystem

BGD
10, 401–445, 2013

(Table 3). Budgets of CO_2 (172–182 g C-CO_2 eq. m^{-2} season^{-1}) were within the range of the budget reported for another sub-alpine meadow located in the Rocky Mountains (131–232 C-CO_2 eq. m^{-2} season^{-1}, Sommerfeld et al., 1993). Methane fluxes had only minor influence on the total GHG Budget of the grassland and N_2O fluxes contributed about 5 % to the overall GHG-budget which is similar to the results for other managed grasslands in Switzerland during summer (Imer et al., 2013) and considerably less than the contribution of N_2O fluxes to the annual GHG balance on a site in Inner Mongolia (Chen et al., 2011a).

4.2 Spatial variation of GHG fluxes

Methane and carbon dioxide fluxes varied only slightly on the grassland under investigation. In contrast, N_2O was characterized by the largest spatial variation compared to CO_2 and CH_4, showing coefficients of variation > 200 %. We assume this being a result of the manure application shortly before the start of the winter season resulting in considerable patchiness of available nitrogen in the topsoil since manure can not be applied uniformly. This hypothesis can only be underlined by results from a mountain meadow in Inner Mongolia showing coefficients of variation in N_2O fluxes of 130 % during summer (Yao et al., 2009).

5 Conclusions

Total greenhouse gas emissions during the winter 2010/2011 in the Dischma valley were primarily determined by CO_2 fluxes. Even when calculating the Global Warming Potential (GWP) for all three GHGs the contribution of N_2O and CH_4 was minor, 5 % and < −1 %, respectively. GHG fluxes of CO_2 and CH_4 varied largely with changes in temperatures at the soil-snow interface and the duration of winter. Given the fact that the duration of winter (snow-covered season) is likely to decrease under common climate change scenarios (reduced snow cover, increasing temperatures and moisture

BGD
10, 401–445, 2013

regimes, IPCC 2007) we assume a lower contribution of winter emissions (here defined as snow-covered season) to the annual budget. However taking a more conservative meteorological/calendric definition of winter the contribution to annual budgets may increase due to longer microbial activity in the soil. More detailed knowledge on the driving variables of N_2O fluxes in grassland ecosystems is crucially needed.

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BGD
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BGD
10, 401–445, 2013

Table 1. Monthly means of the most important meteorological variables between November 2010 and April 2011.

	Nov	Dec	Jan	Feb	Mar	Apr
mean air temp. (°C)	−1.8	−7.3	−6.2	−3.7	−0.8	4.6
mean soil temp. (°C)	1.4	0.2	−0.1	−0.3	−0.3	5.5
mean snow height (cm)	15	38	46	52	43	8
monthly snowfall (cm)	52	46	30	16	2	0

BGD
10, 401–445, 2013

Table 2. Monthly averaged (measured and modeled) and overall mean of CO_2 flux ($\mu mol\,m^{-2}\,s^{-1}$) data derived by the gradient approach and the eddy covariance method.

CO_2 flux ($\mu mol\,m^{-2}\,s^{-1}$)	Gradient (meas.)	Gradient (mod.)	EC (meas.)	EC (mod.)
Nov	na	4.1 ± 1.25	na	1.67 ± 0.85
Dec	1.36 ± 0.68	1.63 ± 0.56	1.53 ± 2.06	1.41 ± 1.5
Jan	0.56 ± 0.16	0.73 ± 0.13	1.07 ± 1.53	1.16 ± 1.03
Feb	0.41 ± 0.31	0.54 ± 0.03	1.02 ± 1.69	0.81 ± 0.96
Mar	0.62 ± 0.23	0.58 ± 0.11	1.33 ± 1.74	1.07 ± 1.06
Apr	0.29	2.16 ± 0.89	1.25 ± 0.92	1.26 ± 0.74
winter season	0.71 ± 0.62	1.26 ± 1.2	1.09 ± 1.9	1.18 ± 1.04

BGD
10, 401–445, 2013

Table 3. Total CO_2, CH_4, N_2O and GHG (CO_2-eq.) budget for the Dischma valley grassland for the snow-covered period in winter 2012/2011.

	CO_2	CH_4	N_2O	GHG
Cumulative Flux ($g\,m^{-2}$)[a]	670	−0.05	0.13	
Cumulative Flux ($g\,m^{-2}$)[b]	631	−0.05	0.13	
Total GHG Budget (CO_2 eq. m^{-2})[a]	670	−1.14	39.7	708.5
Total GHG Budget (CO_2 eq. m^{-2})[b]	631	−1.14	39.7	669.5
contribution to the overall budget (%)[a]	94.6	0.16	5.6	100
contribution to the overall budget (%)[b]	94.4	0.17	5.9	100

[a]Derived by the gradient technique.
[b]Derived by the EC technique.

BGD
10, 401–445, 2013

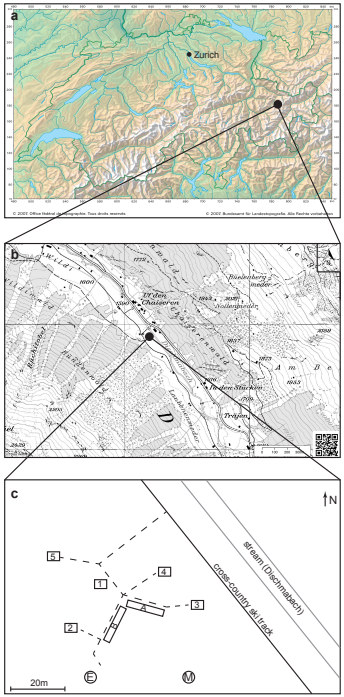

Fig. 1. (a) and **(b)** location of the research site in the Dischmavalley south of Davos, GR, Switzerland (copyright geo.admin.ch, swiss federal authorities, 2007, http://www.disclaimer.admin.ch/terms_and_conditions.html). **(c)** Scheme of the sampling set up in the field. "M" is the location of the meteo tower run by the Swiss Federal Institute for Snow and Avalanche Research and "E" refers to the location of the eddy covariance tower and the automatic profile sampling unit. Profiles 1–5 were used for manual measurement, where as A and B were automatically gradient measurements. The dashed lines are walking tracks to approach the profiles.

BGD
10, 401–445, 2013

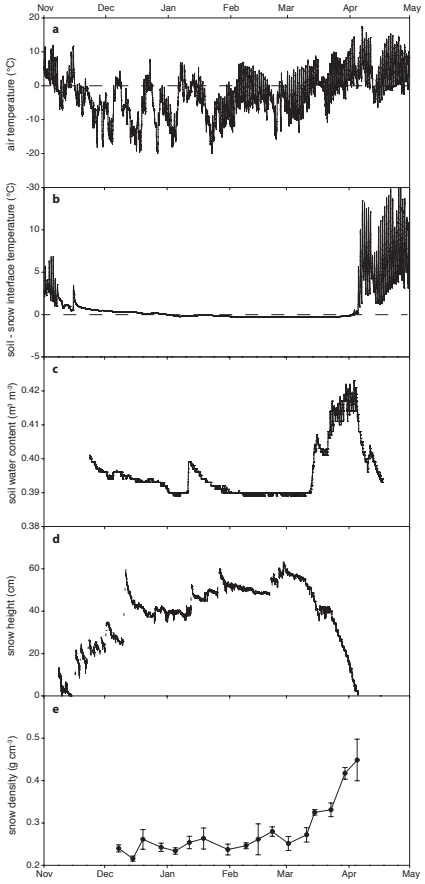

Fig. 2. Meteorological conditions between November 2010 and April 2011, **(a)** air temperature (°C), **(b)** temperature at the soil-snow interface (°C), **(c)** soil water content ($m^3\,m^{-3}$), **(d)** snow height (cm) and **(e)** snow density ($g\,m^{-3}$).

BGD
10, 401–445, 2013

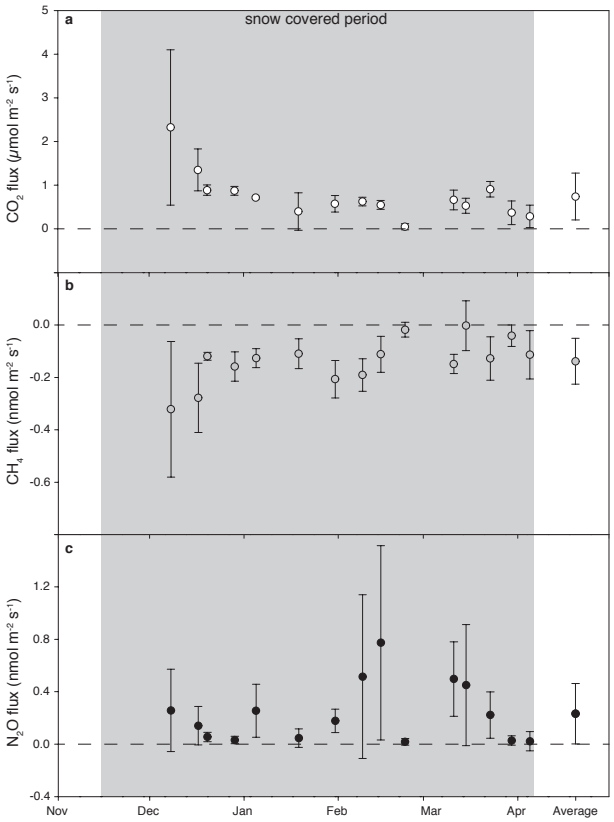

Fig. 3. Fluxes, calculated from the gradient measurements, of **(a)** CO_2, **(b)** CH_4 and **(c)** N_2O during the 2010/2011 winter season in the Dischma valley. Average seasonal fluxes are given at the right side of the figure, respectively. The grey shaded area indicated the period of permanent snow cover.

BGD
10, 401–445, 2013

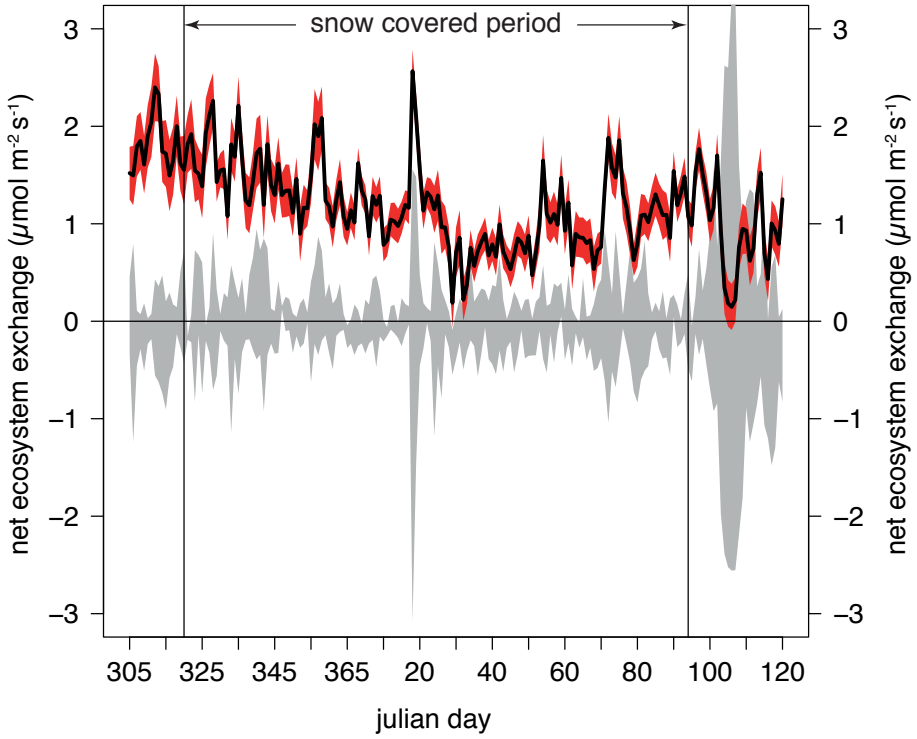

Fig. 4. CO_2 fluxes measured by eddy covariance in the Dischma valley from 1 November 2010 until May 2011. The black line represents the CO_2 flux in µmol m^{-2} s^{-1} and the associated error calculated using standard procedures (for details see Reichstein et al., 2005) is visualized by the red polygon. The grey polygon visualizes the deviation of CO_2 fluxes from the daily mean. The area between the two vertical lines shows the time of snow cover.

BGD
10, 401–445, 2013

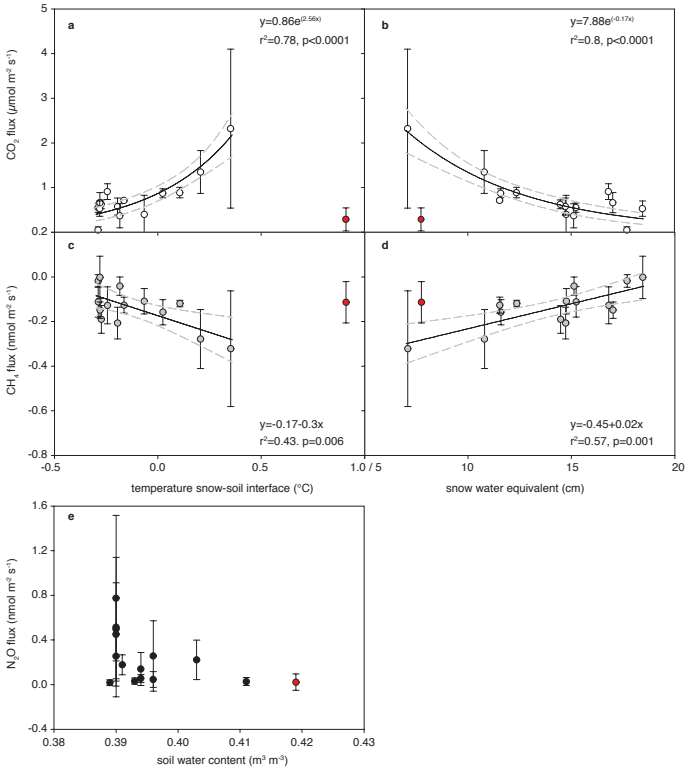

Fig. 5. Response functions of CO_2 and CH_4 to **(a)**/**(c)** the temperature at the soil-snow interface and **(b)**/**(d)** snow water equivalent. While CO_2 and CH_4 fluxes could be explained well, **(d)** N_2O fluxes could not be explained by any of the meteorological variables measured. Red dots indicate measurements in April, which were excluded from the analysis, since the snow cover at site was already non-continuous at this time of the year. Dashed lines indicate the 95 % confidence intervals.

BGD
10, 401–445, 2013

Fig. 6. Ice channels, which developed over the course of the season around the tubing of the automatic gradient measurement system. Therefore CO_2 and ^{222}Rn measurements incorrect (photocredit L. Merbold).

BGD
10, 401–445, 2013

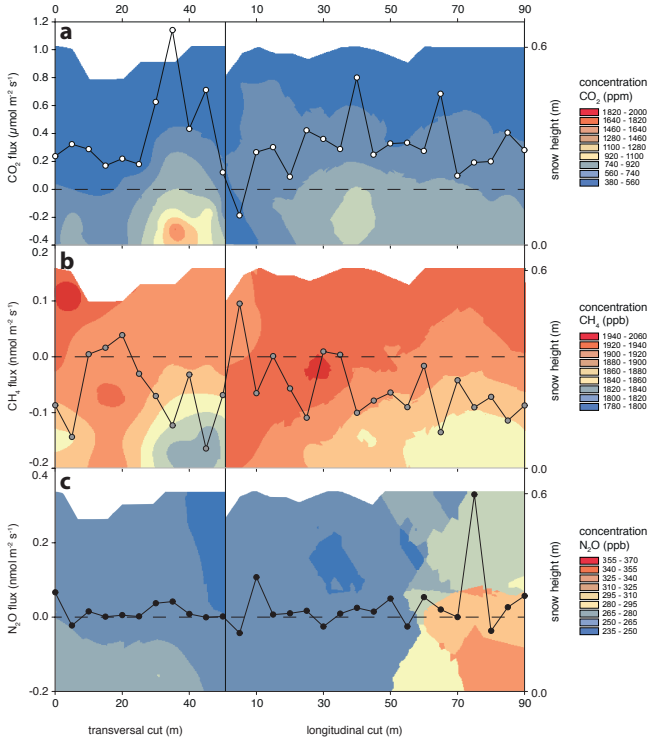

Fig. 7. Spatial variation of **(a)** CO_2 fluxes ($\mu mol\,m^{-2}\,s^{-1}$), **(b)** CH_4 and **(c)** N_2O fluxes ($nmol\,m^{-2}\,s^{-1}$) along a transversal and a longitudinal cut through the grassland in the Dischma valley. Lengths of the transversal ($n = 11$) and longitudinal cut ($n = 18$) were 50 and 90 m, respectively. Both transects crossed each other at the 20 m mark. Concentrations of CO_2 (ppm), CH_4 and N_2O (ppb) in the snow profile are given as colored polygons interpolated between the gas concentration measurements at each point.

BGD
10, 401–445, 2013

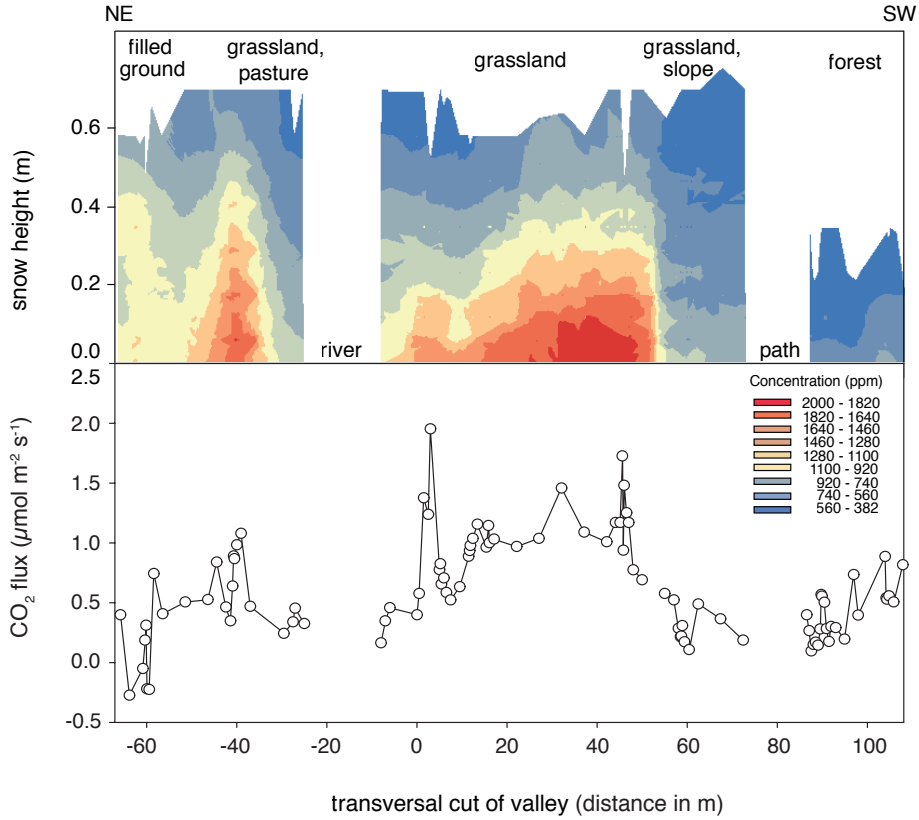

Fig. 8. Spatial variation of CO_2 fluxes across ecosystems in the Dischmavalley using the ski-pole method connected to a gas-analyzer. Colors indicate the concentration of CO_2 in the snowpack. Interpolation of the CO_2 concentration was done using conventional kriging in ArcGIS.

BGD
10, 401–445, 2013

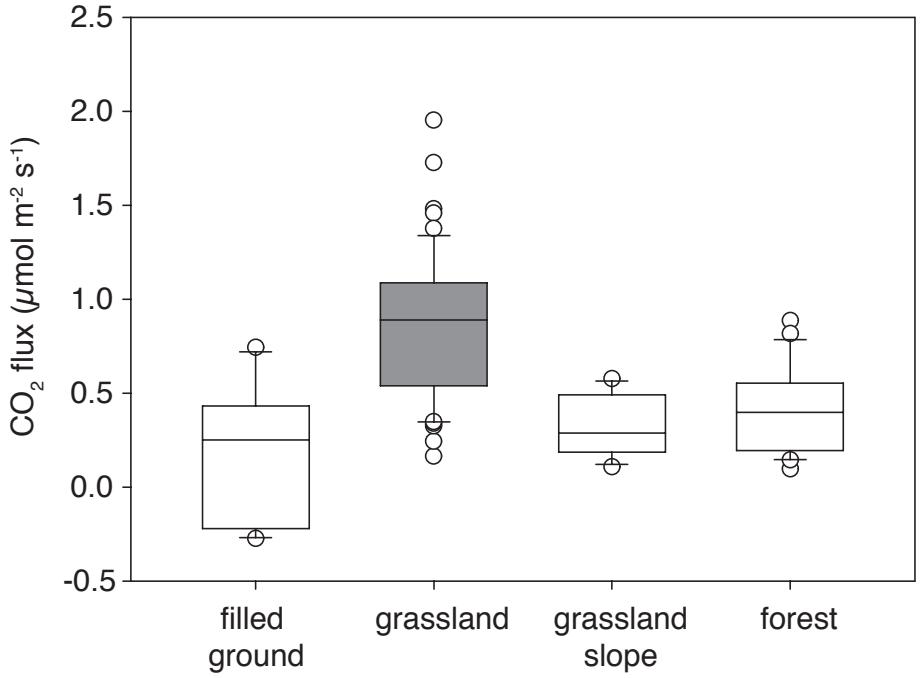

Fig. 9. Boxplot of the CO_2 flux measurement across the Dischma valley. The grey highlighted box of the grassland data indicates significantly different fluxes from the other three ecosystem types.

BGD
10, 401–445, 2013