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Winter greenhouse gas fluxes (CO_2, CH_4 and N_2O) from a subalpine grassland

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Abstract. Although greenhouse gas emissions during winter contribute significantly to annual balances, their quantification is still highly uncertain in snow-covered ecosystems. Here, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) fluxes were measured at a subalpine managed grassland in Switzerland using concentration gradients within the snowpack (CO_2, CH_4, N_2O) and the eddy covariance method (CO_2) during the winter 2010/2011. Our objectives were (1) to identify the temporal and spatial variation of greenhouse gases (GHGs) and their drivers, and (2) to estimate the GHG budget of the site during this specific season (1 December–31 March, 121 days). Mean winter fluxes (December–March) based on the gradient method were $0.77 \pm 0.54\,\mu mol\,m^{-2}\,s^{-1}$ for CO_2 ($1.19 \pm 1.05\,\mu mol\,m^{-2}\,s^{-1}$ measured by eddy covariance), $-0.14 \pm 0.09\,nmol\,m^{-2}\,s^{-1}$ for CH_4 and $0.23 \pm 0.23\,nmol\,m^{-2}\,s^{-1}$ for N_2O, respectively. In comparison with the CO_2 fluxes measured by eddy covariance, the gradient technique underestimated the effluxes by 50 %. While CO_2 and CH_4 fluxes decreased with the progressing winter season, N_2O fluxes did not follow a seasonal pattern. The major variables correlating with the fluxes of CO_2 and CH_4 were soil temperature and snow water equivalent, which is based on snow height and snow density. N_2O fluxes were only explained poorly by any of the measured environmental variables. Spatial variability across the valley floor was smallest for CO_2 and largest for N_2O. During the winter season 2010/2011, greenhouse gas fluxes ranged between $550 \pm 540\,g\,CO_2\,m^{-2}$ estimated by the eddy covariance approach and $543 \pm 247\,g\,CO_2\,m^{-2}$, $-0.4 \pm 0.01\,g\,CH_4\,m^{-2}$ and $0.11 \pm 0.1\,g\,N_2O\,m^{-2}$ derived by the gradient technique. Total seasonal greenhouse gas emissions from the grassland were between 574 ± 276 and $581 \pm 569\,g\,CO_2\,eq.\,m^{-2}$, with N_2O contributing 5 % to the overall budget and CH_4 reducing the budget by 0.1 %. Cumulative budgets of CO_2 were smaller than emissions reported for other subalpine meadows in the Swiss Alps and the Rocky Mountains. Further investigations on the GHG exchange of grasslands in winter are needed in order to (1) deepen our currently limited knowledge on the environmental drivers of each GHG, (2) to thoroughly constrain annual balances, and (3) to project possible changes in GHG flux magnitude with expected shorter and warmer winter periods.

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 deliver fundamental data to investigate biogeochemical processes at the ecosystem scale (Aubinet et al., 2000; Baldocchi et al., 2001). Much of the research to date has focused on the biosphere–atmosphere exchange of carbon dioxide (CO_2) and more recently also on methane (CH_4) and nitrous oxide (N_2O) in most of the major global

ecosystem types, including arctic ecosystems (Lohila et al., 2007; Schulze et al., 2010). In comparison, less focus has been paid to subalpine or alpine grasslands (Gilmanov et al., 2007; Soussana et al., 2007; Ammann et al., 2007), particularly during winter (Brooks et al., 1997; Gilmanov et al., 2004; Filippa et al., 2009; Liptzin et al., 2009; Merbold et al., 2012). For the full greenhouse gas balance of ecosystems, CH_4 and N_2O have to be included, which may offset possible annual carbon sink capacities of terrestrial ecosystems (Nykanen et al., 1995; Zimov et al., 1996, 1993; Sommerfeld et al., 1996; Dise, 1992; Bubier et al., 2002; Chen et al., 2011a; Merbold et al., 2012; Oechel et al., 1997; Groffman et al., 2006; Schurmann et al., 2002; Yashiro et al., 2006; Filippa et al., 2009). Globally, rice paddies, wetlands and ruminant husbandry are the major CH_4 sources. In contrast, grassland soils and agricultural ecosystems are often considered as CH_4 sinks (Blankinship et al., 2010; Chen et al., 2011a; Dijkstra et al., 2011; Kato et al., 2011; Li et al., 2012; Stiehl-Braun et al., 2011; Wu et al., 2010), while agriculturally managed soils, similar to soils under natural vegetation, are known as considerable N_2O sources (Snyder et al., 2009; Stehfest and Bouwman, 2006).

Complex processes drive the emissions of the three most important greenhouse gases – CO_2, CH_4, and 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 growing season – namely photosynthesis and respiration – is driven by light, water availability and temperature. However, the dominant process during the dormant and often snow-covered periods, respiration, is largely driven by soil temperature. Due to freezing at the soil surface, soil-respired CO_2 often originated from deeper soil layers, while snow density and friction velocity above the snow control the CO_2 exchange with the atmosphere (Liptzin et al., 2009; Merbold et al., 2012; Lohila et al., 2007; Mariko et al., 2000). Worldwide, only about 25 case studies have been conducted on winter respiration in high-latitude and -altitude systems (reviewed by Liptzin et al., 2009 in a recent special issue on winter processes in Biogeochemistry) with only two of them conducted in the Alps (Schindlbacher et al., 2007; Merbold et al. 2012). There is also only one single 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). Case studies showed that soil CO_2 efflux ranged between 0.7 and 770 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).

Driving factors of CH_4 and N_2O emissions are much less understood than for CO_2, and detailed process knowledge remains sparse (Flechard et al., 2005; Kato et al., 2011; Kroon et al., 2010; Neftel et al., 2000, 2007; Soussana et

al., 2007). CH_4 fluxes are characterized by two antagonistic processes, methanogenesis and methanotrophy, both occurring year round (Bowden et al., 1998; Nykanen 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 biological factors such as vegetation type (Le Mer and Roger, 2001). Considerable contributions of CH_4 fluxes to annual trace gas balances have been shown for several "hot-spot" ecosystems such as wetlands and peatlands (Merbold et al., 2009; Corradi et al., 2005; Alm et al., 2007; Dise, 1992; Huang et al., 1997; Kroon et al., 2010), whereas known CH_4 sinks contributed only little to annual GHG balances (Chen et al., 2011a; Blankinship et al., 2008; Hartmann et al., 2011).

Emissions of N_2O are more difficult to predict due to the limited understanding and interaction 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 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). For a fen in the Netherlands, Kroon et al. (2010) showed a contribution of winter N_2O emissions of up to 465 % to the annual trace gas balances, while in nine European grasslands N_2O emissions during winter contributed to less than 6 % to annual balances (Soussana et al., 2007).

Measurement of GHG fluxes in winter is a logistical and methodological challenge as many snow-covered sites have poor access in winter and cold temperatures provide difficult working conditions for both humans and equipment. Primarily, there are four experimental approaches – surface chambers, snowpack concentration gradient measurements (GM), isotopic tracers and eddy covariance (EC). The comparability of the methods is controversial since each method covers different spatial and temporal scales. Therefore, annual estimates of winter GHG fluxes are often variable as a result of the method used (McDowell et al., 2000; Björkman et al., 2010a). The gradient method has been documented 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 underestimated CO_2 fluxes relative to the gradient method, and McDowell et al. (2000) found no difference between the chamber and the gradient method at three sites in the Rocky Mountains. To complete this contradictory discussion, Lohila et al. (2007) measured significantly lower CO_2 emissions rates by the eddy covariance method than by the chambers.

Up to date only a few studies (< 10) on subalpine grasslands have investigated the exchange of the other greenhouse gases (CH_4 and N_2O) during periods of snow-cover

Table 1. Monthly means of the basic meteorological variables between November 2010 and April 2011. The soil temperature sensor was installed at 3 cm depth.

	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

(Gilmanov et al., 2004; Liptzin et al., 2009; Lohila et al., 2007; Wang et al., 2010; Schurmann et al., 2002; Filippa et al., 2009); therefore, in this study we quantified all three GHG fluxes from a subalpine grassland during winter in Switzerland. Our specific objectives were (i) to compare different approaches for measuring GHG emissions; the instantaneous gradient method, permanent automatically monitored gradients and eddy covariance, (ii) to identify the variables driving GHG emissions from the grassland and (iii) placing the grassland CO_2 fluxes in context with the surrounding ecosystems, and (iv) to estimate the cumulative 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 represents a typical managed high-altitude grassland ecosystem in the Swiss Alps and is located in the Dischma Valley near Davos, Canton of Graubünden, (46°47′ N, 9°52′ E, 1590 m a.s.l., Fig. 1a) with convenient accessibility and power availability in winter. Davos is characterized by a mean annual temperature of 2.8 °C, and snow cover typically lasts 155 days (Beniston, 1997). Total annual precipitation in Davos amounts to 1022 mm yr^{-1}, with maximum values recorded during the summer months (July–September, MeteoSchweiz, 2011). During the winter season 2010/2011, mean monthly air temperatures ranged from −7.3 °C in December to 4.6 °C in April. Snow covered the site from 16 November until the 5 April (Table 1).

The vegetation at the grassland 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 subalpine grassland studied is considered 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. The surrounding ecosystems are a sloping grassland, forest and a filled ground. For a more detailed explanation of the site see Steinlin (2011) and Mohn et al. (2013).
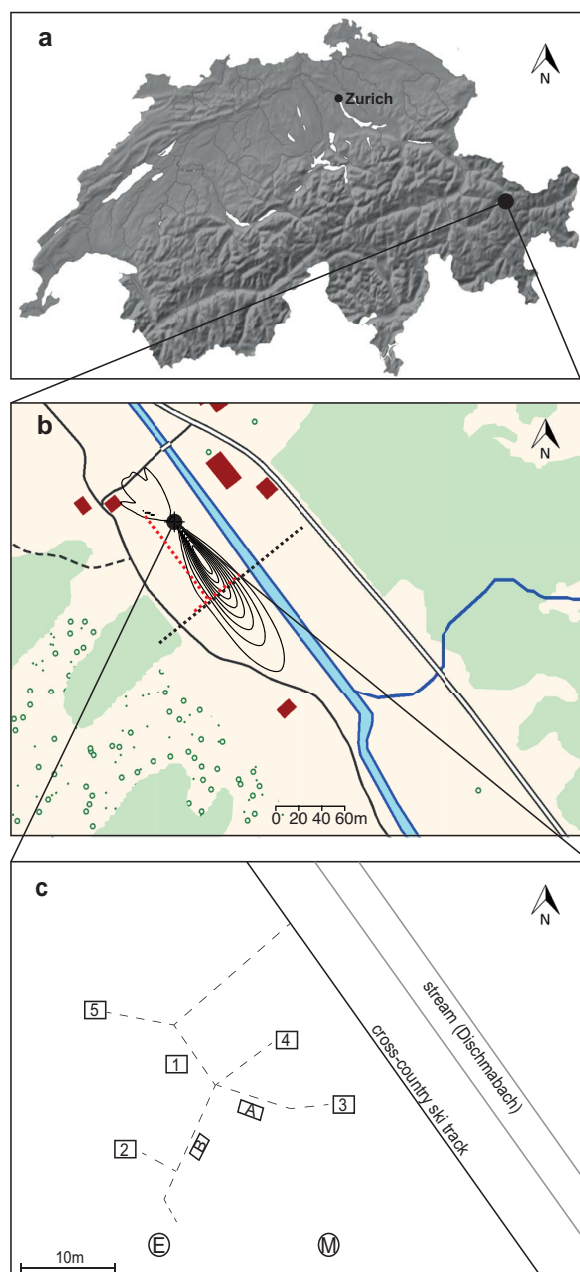

Fig. 1. (a) and **(b)**: location of the research site in the Dischma Valley south of Davos, GR, Switzerland (copyright www.geo.admin.ch, swiss federal authorities, 2007, http://www.disclaimer.admin.ch/terms_and_conditions.html). Panel b further shows the footprint calculated after Kljun et al. (2004) for the eddy covariance tower and the transects (red dashed lines) of the spatial GHG flux measurement campaign. **(c)** visualizes a scheme of the sampling setup in the field. "M" is the location of the meteorological 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 units. Profiles 1–5 were used for manual measurement, whereas A and B were automatic gradient measurements. The dashed lines are walking tracks to approach the profiles. **(b)** Reproduced with permission of swisstopo (JA100120).

2.2 Greenhouse gas flux measurements

Gas flux measurements of CO_2, CH_4 and N_2O were undertaken from early December 2010 until the beginning of April 2011, covering most of the snow-covered period in the Dischma Valley. Two different techniques – eddy covariance and manual gradient measurements – were used to derive independent GHG flux estimates. In addition, we tested a permanent automatic monitoring of CO_2 gradients.

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. 1). The dominant wind directions were NW and SE, following the orientation of the Dischma Valley. 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. CO_2 and water vapor concentrations were measured with an open-path infrared gas analyzer (LI-7500, LI-COR Inc., Lincoln, Nebraska, USA) and both the anemometer and gas analyzer 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 (30 min averages) of the vertical wind velocity and the CO_2 concentration (c, µmol) (Eq. 1)

$$F_{CO_2} = \overline{w'c'}, \tag{1}$$

where the overbar denotes time averages. c' was obtained by subtracting the linear trend in CO_2 concentration from each half-hour interval, and w' represented the vertical wind speed. 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 a heat flux correction term due to instrument heating (Burba et al., 2008). A specific description of the modified correction for instruments that are not setup vertically is given in Merbold et al. (2012) 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 (± 10 standard deviations, SD), negative flux rates at night, and values below a u^* (friction velocity) threshold of $0.1\,\mathrm{m\,s^{-1}}$ to avoid an underestimation of nighttime respiration under low turbulence (Goulden et al., 1996).

Gas concentrations of CO_2, CH_4, and N_2O were measured in four profiles surrounding the EC tower on a weekly basis. In addition, two automatic profiles with continuous monitor-ing of CO_2 concentrations were installed north of the EC and meteorological towers (Fig. 1c).

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),

$$J = -D\frac{d_c}{d_z}, \tag{2}$$

where J is the flux rate ($\mathrm{\mu mol\,CO_2\,m^{-2}\,s^{-1}}$; $\mathrm{nmol\,CH_4\,m^2\,s^{-1}}$ and $\mathrm{nmol\,N_2O\,m^2\,s^{-1}}$) and D the diffusion coefficient of each GHG in the snow ($\mathrm{m^2\,s^{-1}}$). The concentration gradient d_c/d_z is the slope of the linear regression between the single concentration measurements in each profile ($\mathrm{\mu mol\,m^{-4}}$). D is estimated from porosity (f) and tortuosity (τ) of the medium and the diffusion coefficient in air (D_{air}, Eq. 3). diffusion) for calculating GHG fluxes through the snow (Eq. 2),

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

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

$$f = 1 - \frac{\rho}{\rho_{ice}}, \tag{4}$$

where ρ is the mean density of the snow layer and ρ_{ice} is the density of ice ($973\,\mathrm{kg\,m^{-3}}$). Tortuosity is then calculated as a function of porosity (Eq. 5).

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

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 to determine the insertion depth into the snow. The pole contained tubing inside and had a perforated tip, allowing gas collection at any snow depth (Wetter, 2009). Gas measurements were made at 10 cm increments either in the field via a portable gas analyzer directly connected to the ski pole or later in the laboratory following gas sampling. A different hole was used for each sampling date. Gas was collected from the ski pole using a diaphragm gas pump (NMP 015M, KNF Neuberger, Balterswil, Switzerland) to pull the air at a rate of approximately $0.4\,\mathrm{L\,min^{-1}}$ through the infrared gas analyzer (LI-820, LI-COR Inc., Lincoln, Nebraska, USA) until CO_2 concentrations remained constant (usually after 30–60 s). In addition, gas samples were taken from the ski pole using a

60 mL syringe, which were immediately transferred into pre-evacuated 12 mL vials (Labco Limited, Buckinghamshire, UK) with a needle. In these samples CO_2, CH_4 and N_2O concentrations were measured by gas chromatography (Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) combined with a methanizer to measure CO_2 and CH_4 and an electron capture detector (ECD) to measure N_2O, Agilent Technologies Inc., Santa Clara, USA). For more gas chromatography details see Hartmann et al. (2011).

The permanent automatically monitored gas gradients were set up to measure CO_2 and Rn^{222} concentrations in situ and continuously within the snowpack at four different heights. Closed loops of tubing (Synflex 1300 aluminium coated tubing, Eaton Industries II GmbH, Effretikon, Switzerland), about 10 m length in total, were installed for CO_2 and Rn^{222} concentration measurements. The closed loops included 1 m section 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 snowpack, 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; Seok 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 min interval using a self-made profile unit consisting of a switching unit, the gas analyzer (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 was measured 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 for the specific snow diffusion properties needed for the quantification of other GHG fluxes using the gradient approach. To quantify the actual ^{222}Rn flux, we measured the increase in ^{222}Rn with time in chambers placed on the soil surface in snow pits every week.

To determine the transversal and longitudinal variability across the grassland, 33 profiles along two transects (transversal length 50 m, longitudinal 90 m) were sampled manually using the ski-pole method during an intensive field campaign on 23 and 24 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 (Fig. 1b). 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 5 m on 24 February (Fig. 1b). These gradients were measured on site using the portable gas analyzer (LI-820, LI-COR Inc., Lincoln, Nebraska, USA) connected to the ski pole in a vertical resolution of 10 cm.

Statistical differences in ecosystem fluxes were analyzed using an analysis of variance (ANOVA). Spatial data evaluation and interpolation was achieved by conventional kriging approaches in ArcGIS (ArGIS Desktop 9.3.1, ESRI Inc.)

2.3 Environmental variables

Environmental data including 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 (10 cm depth, 10HS soil moisture 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 global radiation (SP-110, Apogee Instruments Inc., Logan, UT, USA) were collected as 10 min averages at a nearby meteorological station run by the Institute of Snow and Avalanche Research (SLF). Measurements of snow density were conducted in combination with the manual GHG gradient measurements by weighing snow samples ($100\,cm^3$) directly in the field. These measurements were done in a 10 cm vertical resolution with 2–3 replicates per depth.

2.4 Calculation of seasonal GHG balances

Gaps in eddy covariance CO_2 fluxes were filled using a marginal distribution sampling (MDS) procedure according to Reichstein et al. (2005) in order to receive a complete seasonal dataset. Gap-filled 30 min flux averages were thereafter integrated.

Gradient technique based seasonal flux estimates were derived by averaging the weekly repeated profile measurements and relating the flux values to a set of environmental variables (air temperature (T_a), soil temperature (T_s), soil moisture (Θ), snow height (h_s), snow density (ϱ_s), snow water equivalent (h_{SWE}) and wind speed (WS)). Snow water equivalent was calculated by the product of snow depth and relative snow density with respect to the density of liquid water. Therefore, h_{SWE} represents a measure for the mass of the snowpack and includes a time component since snow accumulates over the course of the season. The identified
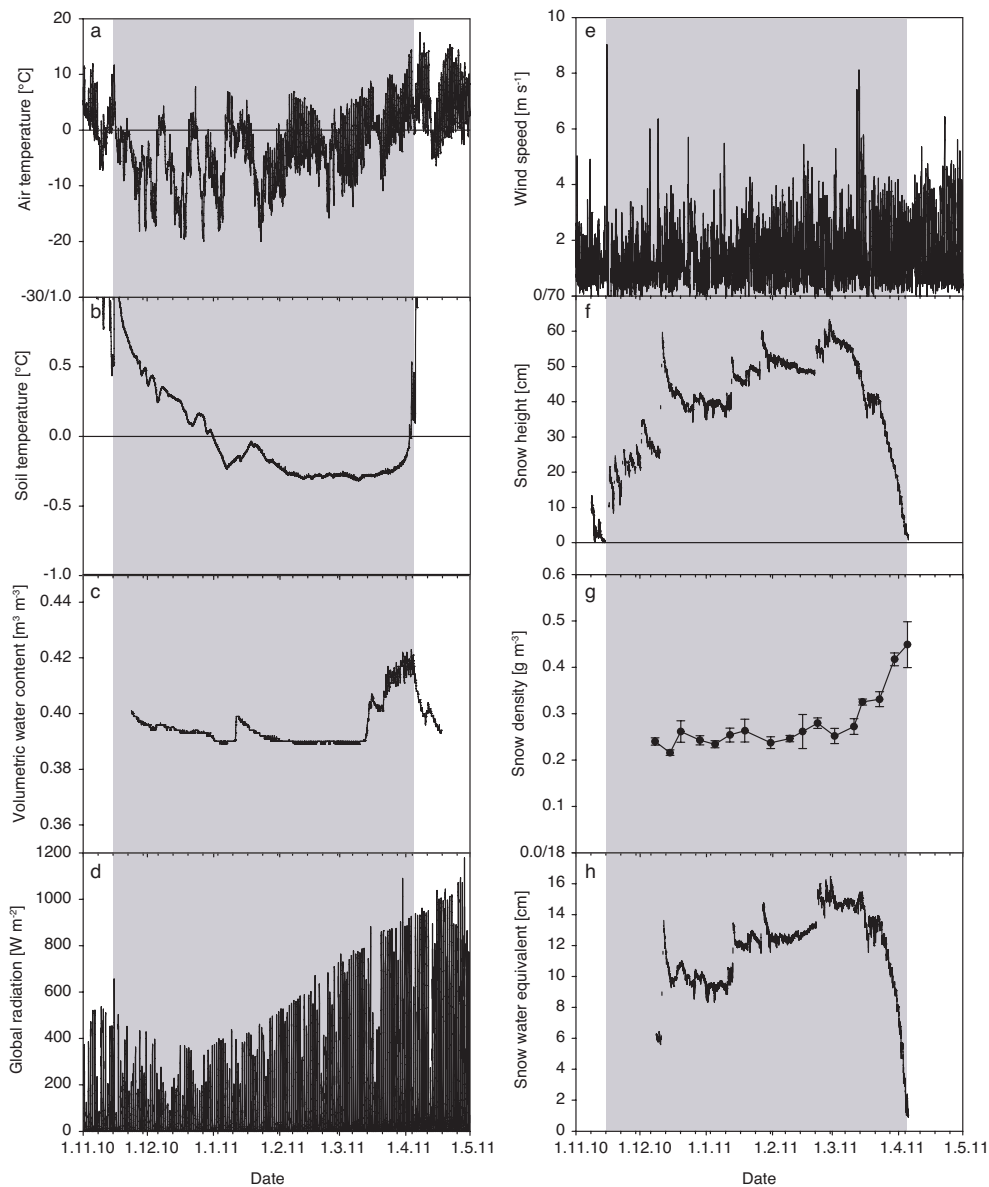
Fig. 2. Environmental variables between November 2010 and April 2011, **(a)** air temperature, **(b)** soil temperature, **(c)** soil water content, **(d)** radiation, **(e)** wind speed, **(f)** snow height, **(g)** snow density ±SD and **(h)** snow water equivalent. Data are 30 min averages except for **(g)**, which is based on 4 measurements per sampling date. The grey shaded area represents the time of continuous snow cover.

functional relations on a weekly basis were then used to extrapolate flux values for each day of the snow-covered season and thereafter integrated.

Seasonal budgets were calculated for the time period when actual measurements were available (1 December 2010–31 March 2011) representing 85 % of the snow-covered period during the winter 2010/2011.

3 Results

3.1 Weather and snow condition

There was continuous snow cover at the study site from mid-November until the beginning of April during the winter season 2010/2011 (Fig. 2). Air temperature varied strongly over the course of the season, reaching lowest values of −20 °C on 27 December and 20 January. In March 2011 temperature started to rise rapidly (Fig. 2a). Soil temperatures decreased at the beginning of the winter season and stayed mostly stable around 0 °C until complete snowmelt

at the beginning of April 2011 (Fig. 2b). Soil water content fluctuated only slightly during the peak winter period and increased with the beginning of snowmelt in March (Fig. 2c). Global radiation decreased until mid-December and rose continuously thereafter due to extended hours of daylight (Fig. 2d). Wind speed fluctuated generally between 0.1–$4 \, \mathrm{m \, s^{-1}}$ with maxima of $8 \, \mathrm{m \, s^{-1}}$ observed during single days in November 2010 and March 2011 (Fig. 2e). Snow accumulated rapidly with the regular snowfall events until 11 December. Maximum snow height (63 cm) was reached 27 February (Fig. 2f) and was below the long-term average of $89 \pm 30 \, \mathrm{cm}$ (T. Jonas; unpublished data). Snow density remained stable at around $0.25 \, \mathrm{g \, m^{-3}}$ over most of the season and reached maximum values of $0.45 \, \mathrm{g \, m^{-3}}$ only in the beginning of April (Fig. 2g). Ice layers within the snowpack developed due to short temperature changes during the months of December and January and the associated freeze–thaw cycles of the snow (Fig. 2a). Snow water equivalent was shown to be lowest at the beginning of the season and highest at the end with reduced snow height and higher snow density (Fig. 2h).

3.2 Temporal variation of greenhouse gas fluxes

Concentrations of CO_2 showed a decrease from the soil to the snow surface with significant linear relationships between concentrations and snow depths (not shown). Fluxes of CO_2 calculated from the gradient measurements showed largest efflux rates at the beginning and end of the snow-covered period (Fig. 3a, $2.3 \pm 2.2 \, \mathrm{\mu mol \, CO_2 \, m^2 \, s^{-1}}$ in December 2010). Decreasing CO_2 fluxes were measured during the peak winter period (January/February 2011), reaching a minimum of $0.02 \, \mathrm{\mu mol \, CO_2 \, m^2 \, s^{-1}}$ on 23 February. Thereafter, and with the beginning of snowmelt, CO_2 fluxes started to increase ($0.51 \pm 0.23 \, \mathrm{\mu mol \, CO_2 \, m^{-2} \, s^{-1}}$ in March and April) along with high concentrations of CO_2 at the soil–snow interface (Fig. 3a). In comparison to the gradient approach, CO_2 fluxes measured by the eddy covariance method provided a better temporal resolution, showing a much larger variation (Fig. 4a–c). EC fluxes were commonly larger than the values derived from the gradients (Table 2). For the main winter period (December–March), CO_2 fluxes measured by EC were twice as high as the gradient measurements (Table 2, Fig. 3a). The CO_2 fluxes were characterized by a continuous but temporally declining release of CO_2 until snowmelt at the end of March (Fig. 4a–c). With the appearance of the first snow-free patches within the EC footprint in April 2011 net ecosystem exchange (NEE) rates dropped below zero indicating photosynthetic activity (Fig. 4a and b).

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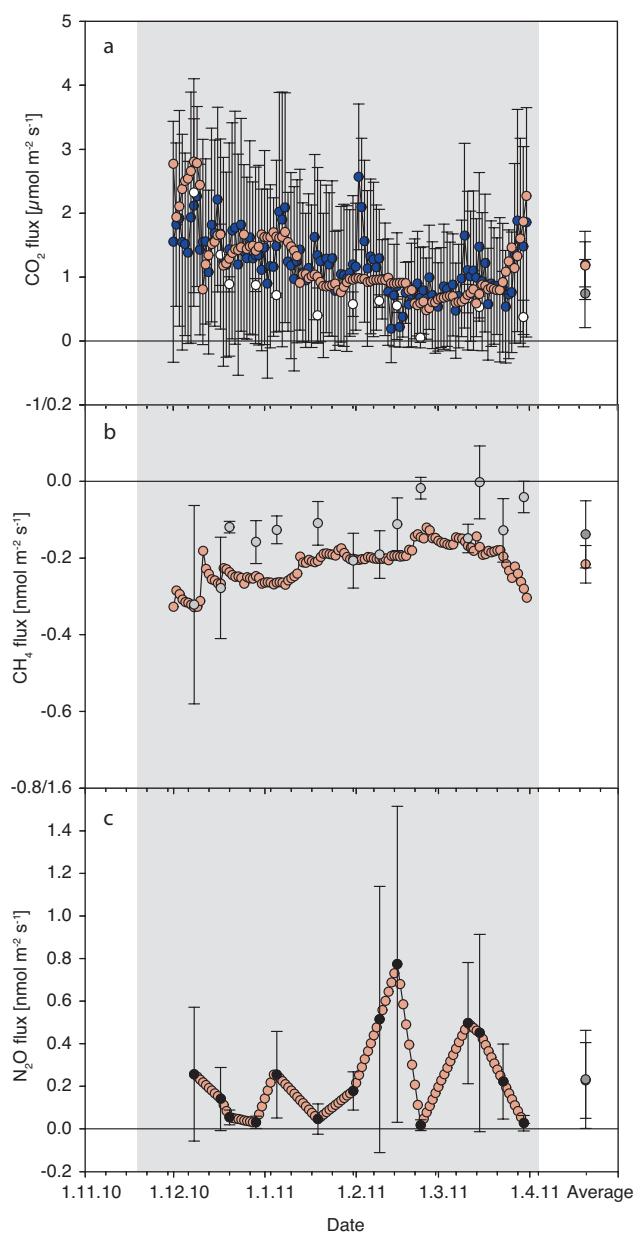

Fig. 3. Flux estimates from the gradient and EC measurements for **(a)** CO_2 (white circles), **(b)** CH_4 (grey circles) and **(c)** N_2O (black circles) during the 2010/2011 winter season in the Dischma Valley. Modeled gradient fluxes are indicated as orange circles. Gap-filled EC of $CO_2 \pm$ uncertainty (Reichstein et al., 2005) are highlighted in blue **(a)**. Average seasonal flux estimates are given at the right side of each figure. The grey shaded area represents the time of continuous snow cover. Error bars for the gradient-derived fluxes are shown $\pm$ SD.

son and fluctuated slightly below zero in March and April ($-0.09 \pm 0.08 \, \mathrm{nmol \, CH_4 \, m^2 \, s^{-1}}$, Fig. 3b).

Emission of N_2O varied largely during the winter season 2010/2011 (Fig. 3c) with peaks up to $1.63 \, \mathrm{nmol \, N_2O \, m^2 \, s^{-1}}$ on 15 February. In comparison, the

Table 2. Monthly averaged (measured and gap-filled) and overall mean of CO_2, CH_4 and N_2O flux data $\pm SD$ derived by the gradient approach and the eddy covariance method.

| | CO$_2$ fluxes (μmol m^{-2} s^{-1}) | | | | CH$_4$ fluxes (nmol m^{-2} s^{-1}) | | N$_2$O fluxes (nmol m^{-2} s^{-1}) | |
	Gradient (meas.)	Gradient (mod.)	EC (meas.)	EC (GF)	Measured	Modeled	Measured	Modeled
Nov	na	na	na	1.81 ± 0.96	na	na	na	na
December	1.36 ± 0.68	1.76 ± 0.56	1.53 ± 2.05	1.57 ± 0.99	-0.22 ± 0.10	-0.27 ± 0.04	0.12 ± 0.10	0.14 ± 0.09
Jan	0.56 ± 0.16	1.17 ± 0.33	1.07 ± 1.53	1.23 ± 0.88	-0.15 ± 0.05	-0.22 ± 0.03	0.16 ± 0.11	0.14 ± 0.1
Feb	0.41 ± 0.31	0.82 ± 0.17	1.01 ± 1.69	0.95 ± 1.15	-0.11 ± 0.09	-0.18 ± 0.03	0.44 ± 0.38	0.37 ± 0.31
Mar	0.62 ± 0.23	0.88 ± 0.4	1.33 ± 1.74	1.00 ± 1.03	-0.08 ± 0.07	-0.19 ± 0.04	0.30 ± 0.22	0.31 ± 0.2
Apr	0.29 ± 0.26	na	0.66 ± 2.28	1.12 ± 1.35	-0.11 ± 0.9	na	0.02 ± 0.07	na
Winter season (Dec–Mar)	**0.77 ± 0.54**	**1.18 ± 0.54**	**1.24 ± 1.75**	**1.19 ± 1.05**	**-0.14 ± 0.09**	**-0.22 ± 0.05**	**0.23 ± 0.23**	**0.24 ± 0.21**

average N_2O flux from the ecosystem was significantly lower (0.23 ± 0.23 nmol N_2O m^2 s^{-1}, Fig. 3c).

3.3 Driving factors of greenhouse gas fluxes

The weekly measured CO_2 effluxes using the gradient approach correlated most closely with snow water equivalent (h_{SWE}, $r^2 = 0.8$, Fig. 5d) and with soil temperature at 3 cm depth ($r^2 = 0.78$, Fig. 5b). No significant relationship existed with air temperature, wind speed, snow density and snow height. Measurements from April were discarded from this analysis due to the absence of continuous snow cover on the grassland and altered CO_2 gradients. In order to derive cumulative sums of CO_2 emissions for the snow-covered period in 2010/2011, we used the observed relationship between h_{SWE} and CO_2 flux to interpolate weekly gaps in the data (Fig. 3a). This relationship explained 80 % of the variability in flux from the ecosystem (Fig. 5d):

$$F_{CO_2} = 7.88 e^{(-0.17 h_{SWE})} \tag{6}$$

Similar to the profile measurements, CO_2 fluxes measured by eddy covariance (EC) were correlated with h_{SWE} explaining 38 % of the variation (Fig. 5c). In addition, soil temperature at 3 cm depth showed a weaker but still significant relationship with CO_2 emissions ($r^2 = 0.32$). Other environmental variables did not correlate with EC-based fluxes (not shown).

CH_4 flux variability was also explained by snow water equivalent ($r^2 = 0.57$), resulting in decreasing uptake rates with increasing values of h_{SWE} (Figs. 3b and 5e). Therefore, the relationship between CH_4 flux and h_{SWE} was used to calculate seasonal sums of CH_4 uptake (Eq. 7).

$$F_{CH_4} = 0.02 h_{SWE} - 0.45 \tag{7}$$

In contrast to the CO_2 and CH_4 fluxes, none of the meteorological variables measured were able to explain the variability 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 (not shown) and neither did the correlation with h_{SWE} (Fig. 5f). Therefore, we extrapolated

the N_2O fluxes on a seasonal basis by linearly interpolating the weekly measured fluxes (Fig. 3c).

3.4 Spatial variability of CO_2, CH_4 and N_2O fluxes in the grassland

During the intensive measurement campaign, CO_2 fluxes ranged between 0.09 μmol CO_2 m^{-2} s^{-1} and 1.14 μmol CO_2 m^2 s^{-1}. We observed similar variation in CO_2 fluxes along the transversal cut of the grassland and along the longitudinal cut of the valley (Fig. 6a). Coefficients of variation were 75 % for the whole grassland, 76 % for the transversal and 72 % for the longitudinal transect. Our spatial measurement campaign showed that the average CO_2 effluxes along the longitudinal transect (main wind direction) and the transversal cut were in the same order of magnitude as those that were monitored throughout the peak winter (0.36 ± 0.24 μmol m^2 s^{-1} vs. 0.54 ± 0.23 μmol m^2 s^{-1}, January–March). By comparison, eddy covariance fluxes showed considerably higher fluxes (1.14 ± 1.65 to 1.06 ± 1.02 μmol m^2 s^{-1}, January–March).

Fluxes of CH_4 were significantly below zero (-0.06 ± 0.06 nmol CH_4 m^2 s^{-1}, one sample t test, Fig. 6b) along the two transects. Maximum uptake rates were -0.16 nmol CH_4 m^2 s^{-1}. Single points of CH_4 efflux were located across the grassland with values up to 0.10 nmol CH_4 m^{-2} s^{-1} (Fig. 6b). Fluxes of CH_4 along the transversal and longitudinal cut through the grassland did not differ significantly (Fig. 6b). Coefficients of 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 across the grassland averaged 0.03 ± 0.07 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}) was measured at one profile (at 75 m) along the longitudinal transect (Fig. 6c). Only few locations on the grassland were characterized by N_2O uptake (-0.03 ± 0.008 nmol N_2O m^2 s^{-1}). The coefficients of spatial variation were highest for N_2O in relation to CO_2 and CH_4, with values up to 256 % on
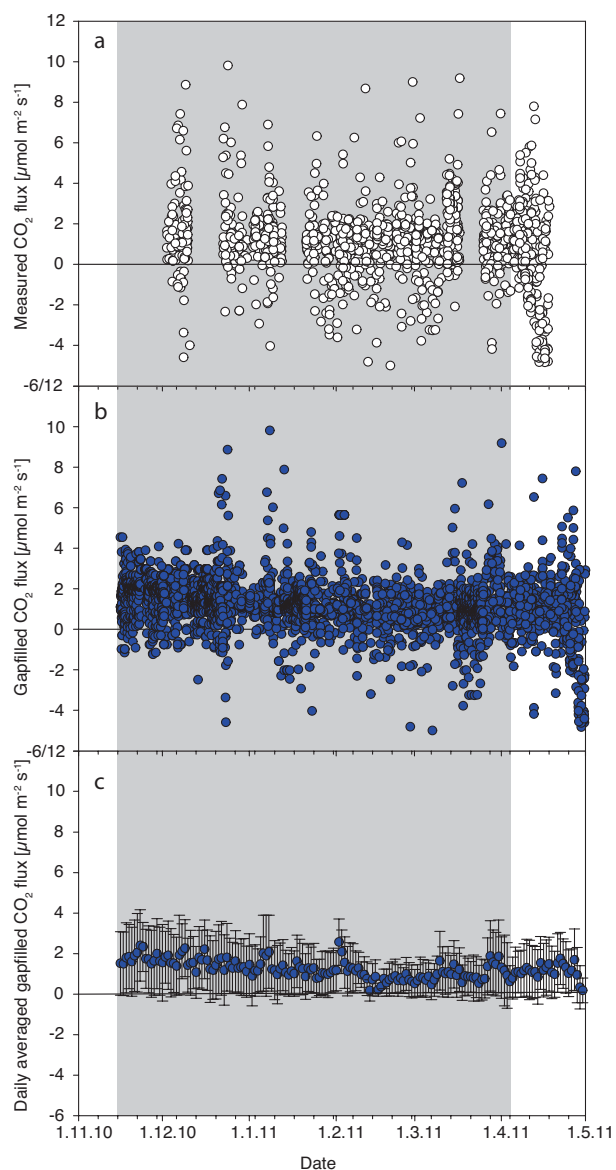
Fig. 4. CO_2 fluxes based on eddy covariance measurements in the Dischma Valley from mid-November 2010 until April 2011: **(a)** measured 30 min averages (white circles), **(b)** gap-filled 30min averages and (blue circles) **(c)** gap-filled daily averages $\pm$ uncertainty (blue circles) calculated using standard procedures (for details see Reichstein et al., 2005). The grey shaded area represents the time of continuous snow cover.

the grassland, 165 % for the transversal and 254 % for the longitudinal cut.

3.5 Spatial variation of CO_2 fluxes across vegetation types

The mean CO_2 fluxes differed considerably among the ecosystems, with the largest emissions of $0.85 \pm 0.38 \, \mu\text{mol} \, CO_2 \, m^2 \, s^{-1}$ from the grassland ecosys-

tem (Figs. 7 and 8) and smallest from the filled ground and the grassland slope $(0.31 \pm 0.16 \, \mu\text{mol} \, CO_2 \, m^2 \, s^{-1})$. Intermediate fluxes of CO_2 occurred from the forest $(0.41 \pm 0.22 \, \mu\text{mol} \, CO_2 \, m^2 \, s^{-1})$ (Figs. 7 and 8). Snow height was largest in the open areas (filled ground, grassland and grassland slope) and lowest in the forest (Fig. 7).

3.6 Automatic gradient measurements

Besides monitoring GHGs during winter in the Dischma Valley, we aimed at testing an in-house development of an automatic gradient measurement technique for a continuous monitoring of ^{222}Rn and CO_2 concentrations within the snowpack. Although we chose long tube lengths (10 m) to avoid heating of the air passing the infrared gas analyzer, we observed ice channels around the tubing at the end of the measurement campaign (Fig. 9). 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.

3.7 Seasonal GHG budget

Seasonal budgets derived by the gradient measurements of CO_2, CH_4 and N_2O during the period of 1 December until 31 March (121 days) were $543 \pm 247 \, \text{g} \, CO_2 \, m^{-2}$, $-0.4 \pm 0.01 \, \text{g} \, CH_4 \, m^{-2}$ and $0.11 \pm 0.1 \, \text{g} \, N_2O \, m^{-2}$, respectively. Cumulative emissions for CO_2 measured by EC were slightly larger $(550 \pm 540 \, \text{g} \, CO_2 \, m^{-2})$ than the values calculated from the concentration gradients. The ecosystem's global warming potential (GWP) during the winter season 2010/2011 (winter defined as the snow-covered time period) was 547–574 g CO_2-eq., using the range of values derived from the EC and gradient approaches (Table 3). N_2O fluxes contributed 5 % to the seasonal GHG budget and CH_4 fluxes reduced the GHG budget of the grassland site by 0.1 %.

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 snowpacks and comparisons with chamber and eddy covariance approaches have yielded contradicting results (Björkman et al., 2010a; 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 50 % underestimation by the gradient method during the main winter period (January–March) and stronger deviations during snowmelt (Fig. 3a).

One potential bias for our conclusion could be the different spatial scales captured by the two methodologies. While the gradient method enables the quantification of emissions
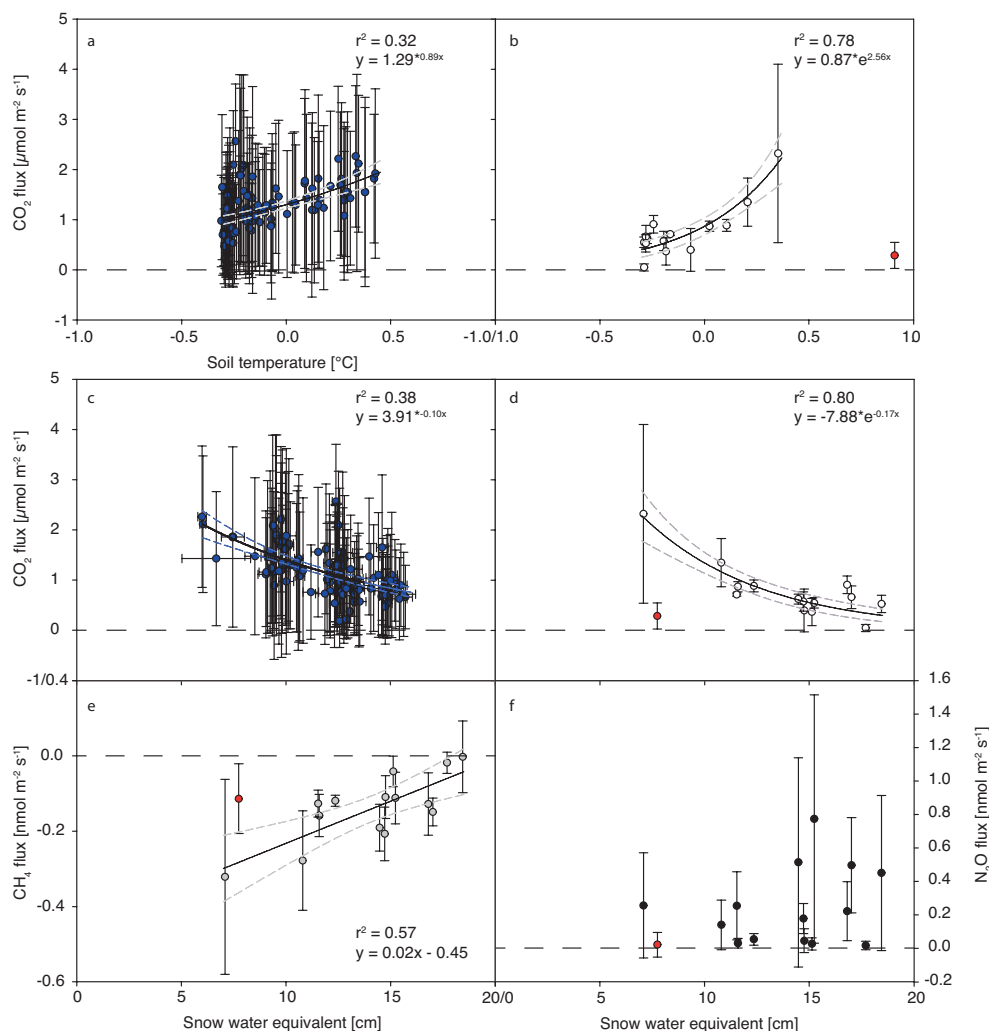
Fig. 5. Response functions of CO_2, (eddy covariance **a, c** and gradient based **b, d**) CH_4 (**e**), and N_2O (**f**) to soil temperature and snow water equivalent. While CO_2 and CH_4 fluxes could be explained well, N_2O fluxes could not be explained by any of the meteorological variables measured. Red dots indicate measurements in April, which were excluded from the analysis, since the snow cover at site was already noncontinuous at this time of the year. Dashed lines indicate the 95 % confidence intervals.

at the plot scale (Hubbard et al., 2005), eddy covariance integrates flux measurements over a whole ecosystem (footprint area) and can cover several hectares of land (Baldocchi and Meyers, 1998). The underlying approach of the gradient method is the estimation of gas diffusivity across the snowpack by measurements of snow density 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 advective movement of snow air and consequently increased CO_2 efflux (Colbeck, 1997; Sturm and Johnson, 1991). Recently, Bowling and Massman (2011) were able to identify an 8–11 % contribution of pressure pumping to a winter CO_2 budget in Niwot Ridge, USA. However, the quantification of such effects remains a challenge (Mast et al., 1998). We did not observe 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 choosing 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 observed few 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 contributes the largest uncertainties for GHG flux calculation when applying the gradient method (Monson et al., 2006b; Seok et al., 2009;
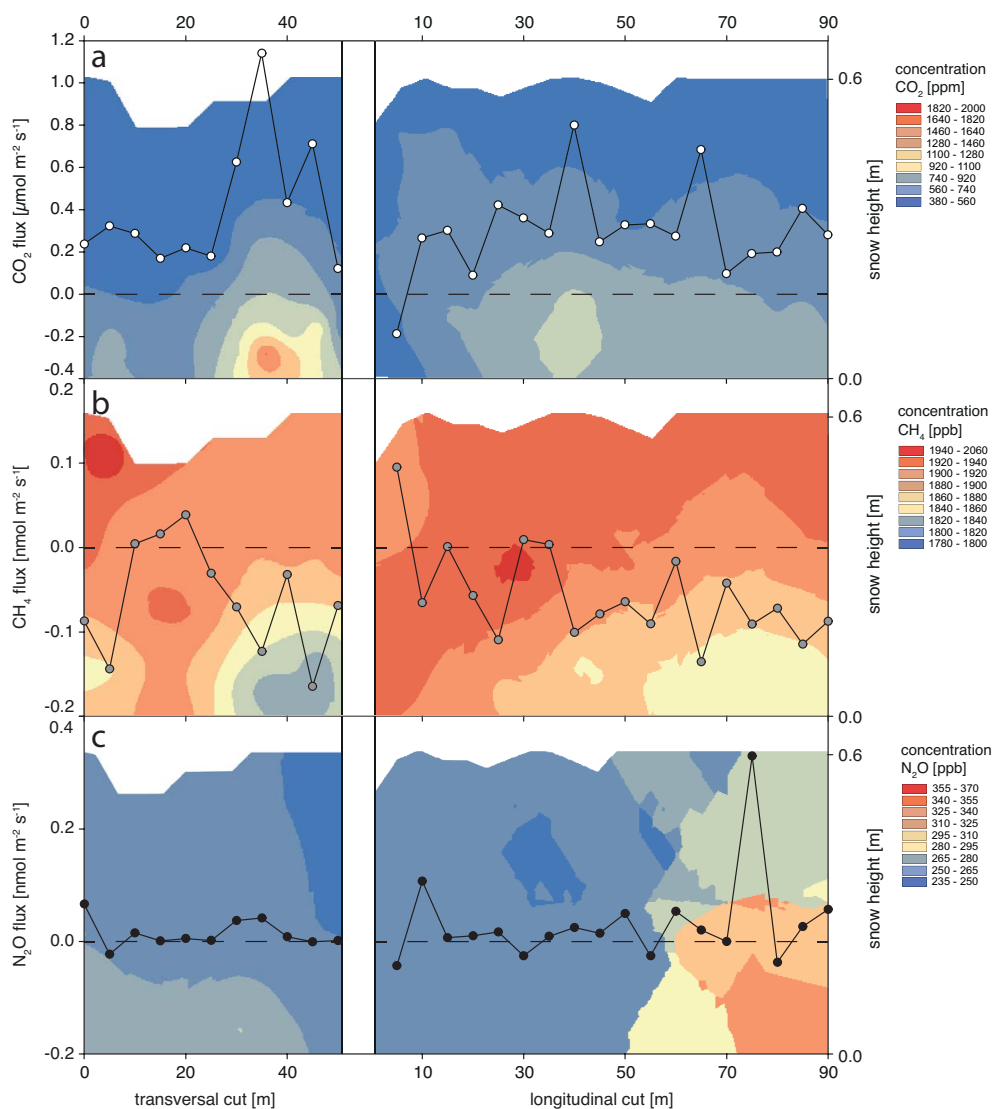
Fig. 6. Spatial variation of **(a)** CO_2 fluxes **(b)** CH_4 and **(c)** N_2O fluxes along a transversal and a longitudinal cut through the grassland in the Dischma Valley. Lengths of the transversal ($n = 11$) and longitudinal cut ($n = 18$) were 50 and 90 m, respectively. Both transects crossed each 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. Interpolation of the GHG concentrations was performed using conventional kriging in ArcGIS (ArcGIS Desktop 9.1, ESRI Inc.).

Table 3. Total CO_2, CH_4, N_2O and GHG budget for the Dischma grassland for the peak winter period in 2010/2011 (peak winter period lasted from 1 December 2010 until 31 March 2011, totaling 121 days).

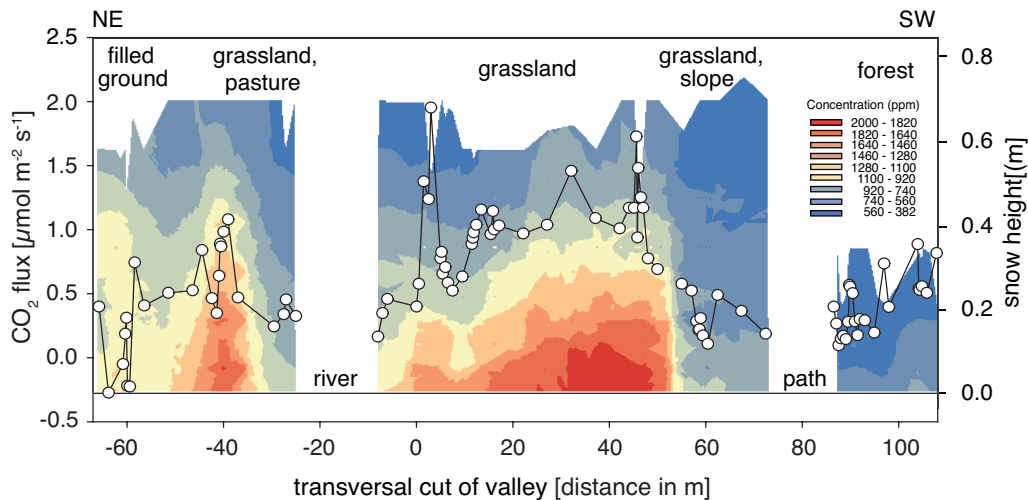|	CO_2	CH_4	N_2O	Total
Cumulative Flux ($\mathrm{g\,m^{-2}}$) – Gradient	543 ± 247	-0.04 ± 0.01	0.11 ± 0.1	
Cumulative Flux ($\mathrm{g\,m^{-2}}$) – EC	550 ± 540			
Total GHG Budget (CO_2 eq. $\mathrm{m^{-2}}$) – Gradient	543 ± 247	-0.9 ± 0.2	32.39 ± 29.31	574 ± 276
Total GHG Budget (CO_2 eq. $\mathrm{m^{-2}}$) – EC	550 ± 540	-0.9 ± 0.2	32.39 ± 29.31	581 ± 569
Contribution to the overall budget (%) – Gradient	94.5	-0.1	5.6	100
Contribution to the overall budget (%) – EC	94.6	-0.1	5.5	100

Fig. 7. Spatial variation of CO_2 fluxes (white circles) across ecosystems in the Dischma Valley 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 performed using conventional kriging in ArcGIS (ArcGIS Desktop 9.1, ESRI Inc.).
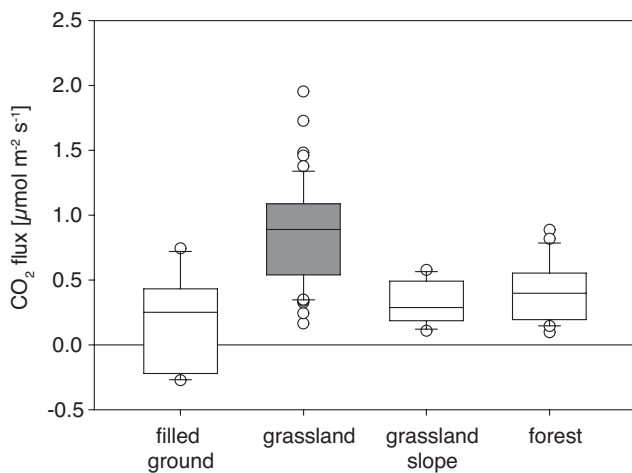

Fig. 8. Boxplot of the CO_2 flux calculations based on CO_2 concentration gradients across the Dischma Valley. The grey highlighted box of the grassland data indicates significantly different fluxes from the other three ecosystem types.

Fig. 9. 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 were incorrect (photo credit L. Merbold).

Sommerfeld et al., 1996). We estimated both variables from measurements of snow density following the 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 to be mainly composed of rounded grains, whereas fresh snow consisted of dendritic or plate-like particles. Such microstructures can have a crucial influence on the gas flux by affecting the linkage and connectivity of pores (Pinzer et al., 2010). These properties cannot completely be derived from snow density and tortuosity alone. One possible but costly and time-consuming ap-
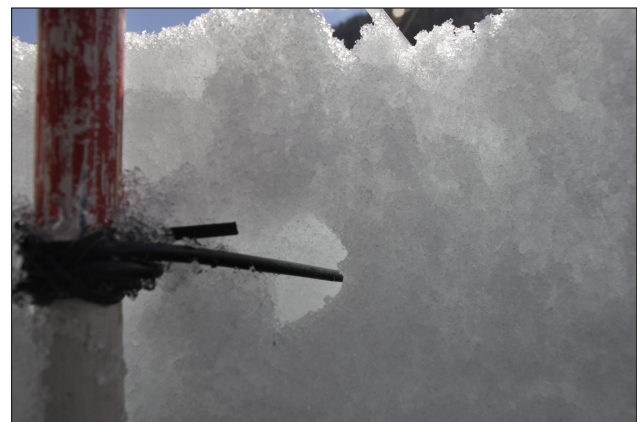
proach could be the use of X-ray tomography to determine the microscopic snow structure and derive the theoretical effective gas diffusion coefficient (Pinzer et al., 2010). Another approach to quantify gas diffusion through the snow could be the application of automatic gas gradients, including the application of traces (e.g., Rn^{222}). 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, (ii) lower flow rates to allow cooling of the circulating air and, more importantly, (iii) active cooling of the gas leaving the instruments measuring GHGs and ^{222}Rn in direct conjunction with a temperature sensor located in the

airstream. Alternatively, the gases could be sampled with an open system; however, this may alter the gas gradient within the snowpack due to the permanent sampling of air. Moreover, the installation of a fixed air sampling unit may alter the snow structure.

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; 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 clear 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 Mountains showed completely opposite behavior of steadily increasing CO_2 fluxes with progressing winter (Sommerfeld et al., 1996, Monson et al., 2006a). The only similarity between these two studies was the higher CO_2 flux during the period of snowmelt, which has found to be related to increases in soil water content (approx. $0.2 \, \mathrm{m}^3 \, \mathrm{m}^{-3}$) (Liptzin et al., 2009). In contrast, CO_2 fluxes measured in the Dischma Valley were not related to soil moisture. Apparently, soil water content was not limiting in the valley floor and remained almost constant over the whole winter (Fig. 2c).

Decreases in CO_2 efflux throughout the winter have been related to declining substrate availability and lower soil temperature (Liptzin et al., 2009; Schindlbacher et al., 2007). 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 that may also induce higher carbon (C) availability (e.g., Hubbard et al., 2006 and Monson et al., 2006a). In our study both soil temperature and h_{SWE} correlated closely with CO_2 efflux. The temperature dependency of CO_2 efflux with a Q_{10} value > 25 across the narrow temperature range between -0.5 and $+0.5\,°C$ was much higher than values typically observed for unfrozen soils ranging between 2 and 6 (e.g., Davidson et al., 2006). However, these unusually high increases in CO_2 efflux with increasing temperature are consistent with other winter studies in forest ecosystems (Monson et al., 2006b; Schindlbacher et al., 2007). One reason for the extraordinary high temperature sensitivity is the limitation of substrate diffusion by freezing water. In our study a progression of the snow-covered period that was associated with a declining C availability due to decreasing soil temperatures might have contributed to the unusually high Q_{10} values. The typical application of manure just before the first snow fall, providing an easily available but rapidly depleting C source during the first phase of the winter, has very likely reinforced this temporal pattern. Besides soil temperature, snow water equivalent can be regarded as a measure for both (1) the progressing winter season with an increasing snowpack but declining substrate availability, as discussed above, and (2) the snowpack properties affecting gas diffusivity and hence the calculation of efflux rates using Fick's law. For instance, towards the end of the winter season – when snow height was similar but snow density was higher than during the peak winter – the estimated CO_2 flux rates dropped by about 50 % as compared to the previous months (Table 2). By comparison, EC-based CO_2 fluxes remained constant, indicating that the fluxes were particularly underestimated with the gradient approach during the late winter. The likely reason is an incorrect estimation of gas diffusivity in wet and dense snow with snow porosity and tortuosity, which were inferred from snow density measurements being the most uncertain variables (Seok et al., 2009). In their evaluation of CO_2 concentration profiles measured at high frequencies in a subalpine meadow, Seok et al. (2009) concluded that potential errors are highest at high snow densities (and hence late in the winter season). Moreover, their results revealed a strong impact of wind pumping, which decreased the CO_2 effluxes calculated by the diffusion method by an average of 57 % as compared to the actual flux.

The CH_4 uptake rates observed in our study were similar to those in dry subalpine soils ($-0.14 \, CH_4 \, \mathrm{m}^2 \, \mathrm{s}^{-1}$, Mast et al., 1998) and in a completely drained fen in eastern Finland ($-0.09 \, CH_4 \, \mathrm{m}^2 \, \mathrm{s}^{-1}$, Alm et al., 1999). By comparison, Sommerfeld et al. (1993) measured uptake rates up to $-0.8 \, \mathrm{nmol} \, CH_4 \, \mathrm{m}^2 \, \mathrm{s}^{-1}$ for a subalpine meadow in the Rocky Mountains, USA. While Mast et al. (1998) found net CH_4 production under moist and water-saturated conditions, our results indicate that even at a volumetric water content of $0.4 \, \mathrm{m}^3 \, \mathrm{m}^{-3}$, the grassland in the Dischma Valley is still characterized by net CH_4 consumption. The seasonal pattern of CH_4 uptake with decreasing uptake rates during the winter period and subsequent increasing towards the end of the winter season agrees with the trend found in dry subalpine soils of the Rocky Mountains in western USA, but contrasts with the seasonal course of CH_4 emissions reported for water-saturated soils in the Rockies (Mast et al., 1998). CH_4 fluxes measured in this study correlated moderately with soil temperature but showed no strong relationship with soil moisture (not shown). Although volumetric soil water content of the soil is one crucial factor limiting CH_4 diffusion into soils (Wang et al., 2010, 2005; 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 $> 5\,°C$. Soil temperatures above $5\,°C$ were only observed after snowmelt at our site (Fig. 2b). The lack of correlation with soil moisture in the Dischma Valley might either be due to the small range of soil moisture 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 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, could be the driving force.

Measured N_2O fluxes averaging 0.23 ± 0.23 nmol m^2 s^{-1} were significantly larger than wintertime 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). A synthesis by Eichner (1990) showed increased emissions of N_2O following fertilizer application. She found larger emissions from the usage of an inorganic fertilizer than form usage with an organic fertilizer, such as manure added to our study site shortly before the first snowfall in the Dischma Valley. 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. N_2O fluxes were neither explained by soil temperatures, soil water content (not shown) or by snow water equivalent (Fig. 5d). In mid-February, high-precision N_2O isotopomer analysis using laser spectroscopy indicated that the main N_2O source processes were heterotrophic denitrification and nitrifier denitrification (Mohn et al., in review). However, both processes might partly be outbalanced by N_2O consumption, which prevent a correlation with environmental variables. 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 becomes 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 relationship between N_2O fluxes and soil moisture remains highly hypothetical due to the unavailability of soil porosity information in the Dischma Valley. A different approach using the natural abundance of N isotopes was applied to gain further insight into the source and sink processes of N_2O emissions at the Dischma grassland, identifying heterotrophic denitrification and nitrifier denitrification as the main N_2O source processes (Mohn et al., 2013).

Seasonal budgets of CO_2 derived from two different measurement techniques and extrapolated to most of the snow-covered season lead to almost identical results of approximately 150 g CO_2-C eq. m^{-2}. The reason for similar fluxes estimated by the two methods, despite an underestimation of CO_2 fluxes calculated by the gradient approach during peak winter, is the higher modeled CO_2 fluxes in the beginning and at the end of winter (Tabler 2, Fig. 3a). The seasonal CO_2 flux estimates were within the range of the budget reported for another subalpine meadow located in the Rocky Mountains (131–232 g CO_2-C eq. m^{-2} season^{-1}, Sommerfeld et al., 1993). However, our flux estimates were substantially smaller than ecosystem respiration measured for a subalpine pasture on a peaty soil in Switzerland (Merbold et al., 2012).

CH_4 fluxes had only a 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 (Hiltbrunner et al., 2012; 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). These low contributions of N_2O and CH_4 to the total GHG budget strongly suggest that the hypothesized offset of a net carbon sink by other GHGs other than CO_2 is negligible for the grasslands under observation.

4.2 Spatial variability of GHG fluxes across different land uses

While CH_4 and CO_2 fluxes varied only slightly on the grassland, N_2O fluxes were characterized by the largest spatial variation showing coefficients of variation > 200 %. One possible explanation for such large variation could be the manure application shortly before the start of the winter season that results in a patchy distribution of available nitrogen in the topsoil. This hypothesis is supported by results from a fertilized mountain meadow in Inner Mongolia showing coefficients of variation in N_2O fluxes of 130 % during summer (Yao et al., 2010).

The significantly higher winter CO_2 fluxes in the grassland compared to the forest (Fig. 8) are consistent with the observation of decreasing summer soil respiration rates during afforestation of a subalpine pasture (Hiltbrunner et al., 2013). In their study the lower rates in the forest were explained with a smaller root turnover, a lower litter quality and a less favorable microclimate in the forest than in the adjacent grassland. In our study the thinner snow cover in the forests (< 30 cm) leading to colder soils (Groffman et al., 2006) might have contributed to the lower CO_2 effluxes in the forest.

5 Conclusion

Total greenhouse gas emissions during the winter 2010/2011 in the Dischma Valley were primarily dominated by CO_2 fluxes. Even when calculating the global warming potential (GWP) for all three GHGs the contributions of N_2O and CH_4 to the seasonal budget were minor, 5 % and < -0.1 %, respectively. GHG fluxes of CO_2 and CH_4 varied largely with changes in soil temperature and snow water equivalent. Snow water equivalent was identified as a physically relevant variable affecting gas diffusion of CO_2 and CH_4 through the snowpack. Our method comparison indicated that during peak winter, the CO_2 fluxes based on the manual gradient approach were 50 % smaller than those estimated by eddy covariance, probably due to an inappropriate estimation of gas diffusion in the snow. This implies that additional efforts are needed to accurately measure CO_2 fluxes at the plot scale.

GHG fluxes varied strongly within the grassland, with N_2O showing the largest coefficients of variation, which was most probably occurring due to an application of organic fertilizer shortly before the first snow event. CO_2 emission across different land-use types in the Dischma Valley were shown to be largest on the grassland with about 50 % higher rates than in an adjacent forest.

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