

N₂O emissions from snow-covered soils in the Swiss Alps

By A. SCHÜRSMANN, J. MOHN and R. BACHOFEN*, *Institute of Plant Biology/Microbiology,
University of Zurich, Zollikerstrasse 107, CH-8008 Zurich, Switzerland*

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ABSTRACT

N₂O emissions were investigated at two sites in the Swiss Alps, Alptal (SZ) and Piora Valley (TI), using the closed, vented chamber method during the snow-free period and the snowpack diffusion method during snow cover. Significant spatial variations in surface N₂O effluxes between different sampling subsites were observed in both summer and winter. While in winter N₂O fluxes from a raw humus site in Alptal and from a site of neutral pH in the Piora Valley were very low (0.01–0.02 mg N₂O-N m⁻² d⁻¹) and similar to other published values, N₂O emissions for acidic and alder-covered sites were 0.3–0.4 mg N₂O-N m⁻² d⁻¹ and reached 1.7–1.9 mg N₂O-N m⁻² d⁻¹ for nutrient-rich sites. This suggests that the soil temperatures close to the freezing point were not limiting microbial activity under snow. Snow-covered soils are insulated from extreme air temperatures and stay constant between –0.3 and –1.1°C. They represent an environment where micro-organisms may remain active while vegetation is dormant. N₂O liberation is repressed at neutral and raw humus sites, as nitrification is the main source of N₂O. During summer the soil microbial activity is strongly related to water availability and temperature: in contrast, in winter both factors are rather constant and the controlling factors of heterotrophic activity are unknown. Our data show that N₂O is a significant component of alpine N cycling and that winter N₂O fluxes should not be neglected in the calculation of the annual budget for alpine ecosystems, considering that snow covers (sub-) alpine regions for a large part of the year.

1. Introduction

The impact of steadily increasing atmospheric nitrous oxide (N₂O) concentrations on global-scale processes such as stratospheric ozone depletion and the greenhouse effect is still an important issue in research (Crutzen, 1981; IPCC, 1996; Vitousek et al., 1997). Large-scale budgets of trace gases are often based on extrapolations from relatively few ground-based data. We believe that an understanding of the factors controlling trace gas fluxes will be an important step in the development of global budgets and models. Identifying the sources and sinks of N₂O has been the focus of considerable research over the last decade, as

the global budget is not balanced. High spatial and temporal variability make its estimation particularly difficult (Kroeze et al., 1999). Most global gas budgets assume that microbial production of N₂O stops when soil is snow-covered (Bouwman, 1990). Approximately 50% of the Northern Hemisphere experiences a significant snow-covered season, including both high-elevation and high-latitude ecosystems. Snow-covered soils are insulated from extreme air temperatures and may stay unfrozen under the snowpack. These soils provide an environment where micro-organisms may adapt to low temperatures and remain active (Brooks et al. 1996; Hénault et al., 1998; Sommerfeld et al., 1993; Teepe et al., 2001). While soil microbial activity during the growing season is strongly related to soil moisture and temperature (Schürsmann et al., 1998), other factors must

* Corresponding author.
e-mail: bachofen@botinst.unizh.ch

control heterotrophic activity during the winter. Seasonal and diurnal variations in the physical environment of soil are absent during the winter, especially concerning temperature and moisture. Snow cover reduces energy exchange at the soil/snow interface, and soil moisture remains rather constant until the initiation of snow melt (Cline, 1995).

Little work has been done so far to quantify N₂O flux from alpine environments during the snow-covered season. Williams et al. (1995) have suggested that N₂O is not a significant component of alpine N cycling in the Sierra Nevada. Winter N₂O fluxes from both alpine (Sommerfeld et al., 1993) and subalpine (Mosier et al., 1993) sites in Wyoming are similar to summer fluxes. Here we present information from an alpine and a subalpine site showing that N₂O fluxes from beneath snowpacks in ecosystems with a long period of snow cover may be important, depending on soil conditions, and should not be neglected in ecosystem N₂O budgets.

2. Material and methods

2.1. Site description

N₂O emissions through the snow cover were investigated during winter 1998/1999 at two sites, an alpine valley in Southern Switzerland (Piora, TI) and a subalpine forest in the Northern Swiss Alps (Alptal, SZ). For comparison N₂O emissions were also measured at both sites during the snow-free period in 1997.

The experimental site Piora is located in a landlocked alpine valley of the Gotthard Massif in Southern Switzerland (46°33'N, 8°43'E). The north and south slopes of the Piora Valley are composed of metamorphic crystalline rock. The east-west oriented Piora trough, a band consisting of Rauwacke (dolomite and gypsum), runs through the valley. Glacial deposits, moraines, avalanches, land slides and accumulations of dolomite 'sand' have resulted in a mosaic of different soils. During summer up to 400 cattle spend 60–70 days on 300 ha of pasture in the Piora Valley (Knoll-Heitz, 1991).

Sampling subsites were five plots in the vicinity of the Centro di Biologia Alpina in Cadagno at 1960 m a.s.l. Annual precipitation averages approximately 1400 mm and the mean temper-

ature is 0°C (SMI-MeteoSwiss, 1997). Snow fall amounts to 70% of the yearly precipitation. Snow depth often exceeds 4 m in January and February, and snow cover usually lasts until the end of May or mid-June depending on orientation, slope and exposition to wind. Two plots (dystric Cambisols) were located on the lower north slope of Mount Mottone, which is covered with European green alder (*Alnus viridis*). The others were placed in pastureland, one with a thin humus layer rich in carbonates (Lithosol, referred to as neutral site), one with acidic soil (dystric Cambisol) and one at a nutrient-rich site close to the sheds where the cattle are milked twice daily. Here the soil is thoroughly mixed by bioturbation mainly by earthworms, and the ground flora is dominated by *Rumex alpinus*.

The second experimental site, Alptal, is located in the Northern Swiss Alps at an altitude of 1200 m (47°03'N, 8°43'E). The annual precipitation amounts to 2300 mm and the mean temperature is 5°C. Snow fall amounts to 30% of the yearly precipitation. Snow cover lasts for about 18 weeks and hardly exceeds 200 cm in height. The local atmospheric deposition of N is approximately 20 kg N ha⁻¹ yr⁻¹.

The soil is a Gleysol on poorly permeable clay-rich Flysch. Norway spruce (*Picea abies*) accompanied by about 15% silver fir (*Abies alba*) are the most abundant tree species in the Alptal forest. The heterogeneous micro-topography explains the mosaic distribution of wet depressions (anmoor humus) and drained mounds (raw humus). The mounds (water table >40 cm depth) have an oxidized Bw horizon and forest floor (umbric Gleysol). In the depressions the water table frequently reaches the surface, leading to an anmoor topsoil with a high carbonate content. The mineral soil is a permanently reduced Bg horizon, overlain by a BwA horizon in better drained spots. N₂O emissions were determined at two sampling subsites, one situated in a depression (anmoor humus), the other localized on a mound (raw humus).

2.2. N₂O flux measurement

The gas fluxes were determined using the snow-pack diffusion method during wintertime and a closed chamber method during the snow-free period.

2.2.1. Gradient measurements. Concentration profiles are the basis with which to estimate fluxes in porous media such as snow (Sommerfeld et al. 1993; 1996) or sediments (Morse, 1979; Tessier et al. 1994); the first derivative from the slope of the profile yields the flux. N₂O fluxes through the snow were estimated using the method of Sommerfeld et al. (1993). Gas collectors were of 10 cm diameter by 1 cm thick stainless-steel disks covered with 50 µm stainless-steel mesh. A hole was dug in the snow down to the soil surface and a collector was placed at the soil surface, one 10 cm below the snow–atmosphere interface, and two at regular distances in between. The collectors were placed horizontally in a distance of about 60–80 cm into the wall of the hole, which was then refilled with snow. Two weeks were allowed for equilibration after disrupting the initial gas gradient in the atmosphere of the snow layer. Two sets of collectors were installed at each subsite at a distance of 2 m. Collectors were connected to sampling ports located above the snow surface by 1/16 inch Teflon tubing. Samples were drawn using 50 ml nylon syringes fitted with three-way valves. Pre-evacuated Hungate tubes sealed with butyl rubber stoppers were used for gas storage and transport. The N₂O concentrations were determined the following day with a Carlo Erba gas chromatograph equipped with a ⁶³Ni electron capture detector (CE Instruments, Model 80, Milan, Italy). To avoid O₂ contamination of the detector a GC configuration with a 4-port valve was used. This allowed to bypass the electron capture detector until O₂ had eluted from the column. Operating temperatures were 350°C for the detector, 90°C for the capillary column (30 m × 0.53 mm I.D. molecular sieve 5 Å, Supelco 2-5463) and 100°C for the injector. The carrier gas was a 95:5 argon–methane (v/v) mixture at a flow rate of 3 ml min⁻¹.

Gas flux as a result of gradient-driven diffusion was calculated using Fick's law:

$$J_g = D_g(d[g]/dz)f$$

where J_g is the gas flux, D_g the diffusion coefficient, $[g]$ the measured gas concentration, z the depth of the snowpack, and f the snowpack porosity [$f = 1 - (\rho_{\text{snow}}/\rho_{\text{ice}}^{-1})$, where ρ is the density]. The diffusion coefficient was assumed to be 0.139 cm² s⁻¹, consistent with previous research

on N₂O flux through snow (Brooks et al., 1997; Massman, 1998; Sommerfeld et al., 1993; 1996).

2.2.2. Chamber measurements. A static chamber system was employed for the N₂O flux measurements during the snow-free period (Hutchinson and Mosier, 1981). The square sheet steel frame (1 m² and 15 cm in height) was permanently installed to a depth of about 5 cm. The chamber was closed with a lid only during the measurements. A rubber tube seal between the frame and the lid and clamps to tighten the lid to the frame excluded gas exchange between the chamber and the atmosphere during the measurements. Samples were extracted through a neoprene septum for gas chromatographic analysis at regular intervals (0, 10, 20 and 30 min) after closure of the chamber. Hungate tubes sealed with butyl rubber stoppers were used for gas storage and transport. The N₂O concentration was determined as described above. N₂O fluxes were calculated from the changes in N₂O concentrations over time.

2.3. Additional parameters

Temperature loggers [Tinytag, Gemini Data Loggers (UK) Ltd.] were installed at the different subsites at 5 cm soil depth. Soil temperature was measured year-round. Snow cover was indicated when the daily fluctuations stopped. Thus the length of snow cover with respect to the vegetation period could be estimated. Ambient air temperatures were determined simultaneously to the N₂O flux measurements.

Soil cores (diameter 6.3 cm, length 10 cm) were retrieved from every subsite within 1 m from the flux chamber at each day of sampling during the snow-free period. They were cut out several months before the experiments but kept in place to allow recovery of the soil system from disturbance. After retrieval the cores were stored at 4°C, taken to the laboratory and analyzed by absorption spectrophotometry for exchangeable NO₃⁻, NH₄⁺ (Uvikon 930, Kontron Instruments) (Kandeler, 1993; Keeney and Nelson, 1982), pH (0.01 M CaCl₂, soil to solution ratio 1:2.5) and soil water content (% WHC, Alef, 1991). N species were extracted (60 min) with 0.1 M CaCl₂. The biologically available organic carbon (mineralizable C) was determined with a Sapromat A6 instrument (Voith GmbH, Germany) according to

Beck (1993). Slurries of 15 g of field-moist sieved soil in 100 ml tap-water were stirred and incubated at 22°C and constant O₂ headspace concentration. The CO₂ liberated is absorbed by a NaOH trap. The loss of volume is compensated by electrolytically produced O₂. CO₂ production rates were calculated from the duration of the phases of O₂ production for the second incubation day.

3. Results and discussion

3.1. N₂O concentration profiles through the snowpack

The snow depth in Pióra varied considerably with values ranging from 1.6 m to 3.6 m. In Alptal the snow depth was only 1.0 to 1.2 m, enough to keep soils from freezing. The snow was relatively homogeneously packed, as seen in linear (neutral and nutrient-rich subsites) or slightly concave concentration curves (Figs. 1 and 2). Linearity in the emission curves indicates free upward diffusion through the snow; concavity may be caused by gas consumption in the upper pore spaces of the snowpit or a lower porosity of the snow in deeper layers due to compaction. Therefore gas samples

must be collected at several depths throughout the snowpack to observe potential accumulation of gases below less permeable layers of snow, which would result in overestimated flux rates.

Very high concentrations of N₂O accumulated at the soil-snow interface. A value 5300 ppm was measured at the nutrient-rich subsite in Pióra at the end of March 1999. In contrast, soil surface N₂O concentrations at the neutral subsite (Pióra) during snow melt and the raw humus subsite (Alptal) were not significantly different from atmospheric concentrations, indicating negligible N₂O production under these conditions.

3.2. Spatial and temporal variation of the N₂O emissions

Mean values of selected soil properties and N₂O emissions for the subsites during the growing season are shown in Table 1. In general, N₂O fluxes were more variable during the summer, reacting strongly to water availability. This is furthermore reflected by the large error bars for summer fluxes relative to the ones for winter (Fig. 3). An example is given for the alder forest II subsite (Fig. 4, from Schürmann et al., 1998),

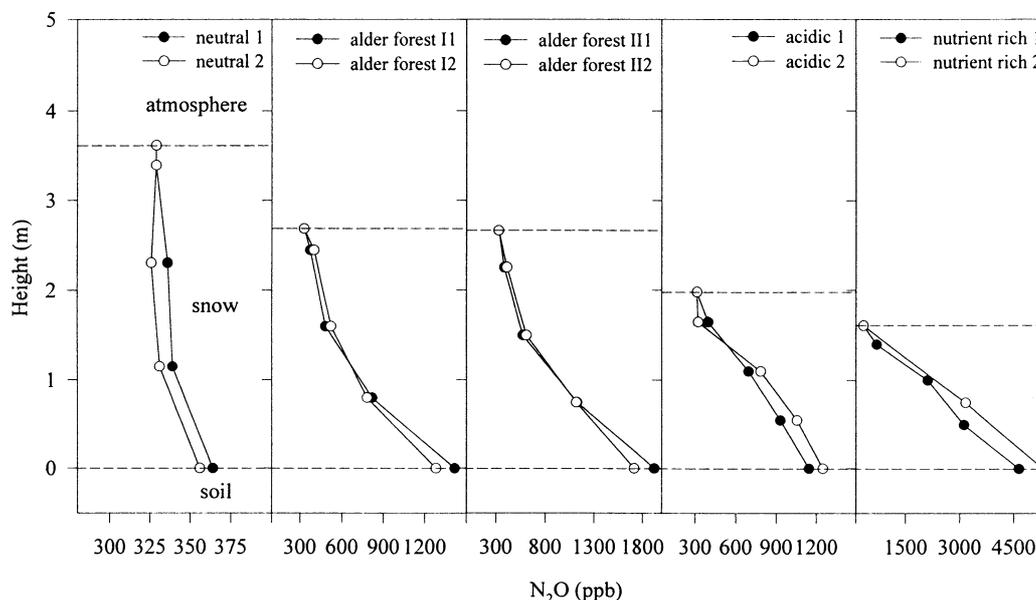


Fig. 1. Selected profiles of N₂O concentrations (ppbv) in snowpacks at the Pióra subsites in winter 1998/99. (Sampling date 2 March 1999. Thickness of snowpack varied strongly with exposition and slope.)

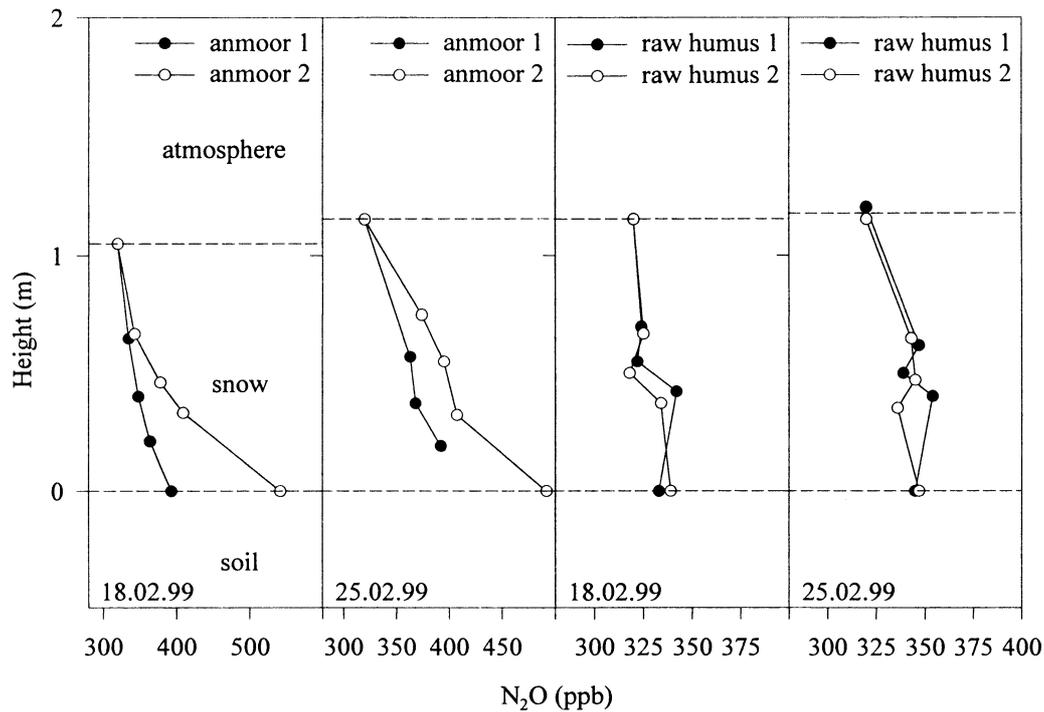


Fig. 2. Selected profiles of N_2O concentrations in snowpacks at the Alptal subsites in winter 1998/99 (sampling date 18 and 25 February 1999.)

Table 1. Selected soil properties and N_2O emissions during the growing season 1997 from Piora (Schürmann et al., 1998) and Alptal (Mohn et al., 2000)

Site	NO_3^- ($mg\ kg^{-1}\ dw$)	NH_4^+ ($mg\ kg^{-1}\ dw$)	Mineralized C (within 24 h) ($mg\ C\ kg^{-1}\ dw\ h^{-1}$)	pH	Water content ($g\ g^{-1}$)	Flux ($mg\ N_2O-N\ m^{-2}\ d^{-1}$)
Piora						
Neutral	ND (5)	11.7 ± 0.5 (5)	22.9 ± 4.3 (5)	6.5 ± 0.2 (5)	0.36 ± 0.02 (5)	0.15 ± 0.03 (6)
Alder forest I	11.7 ± 2.0 (6)	9.7 ± 1.1 (6)	31.6 ± 7.1 (6)	3.5 ± 0.1 (6)	0.50 ± 0.02 (6)	0.21 ± 0.01 (12)
Alder forest II	1.8 ± 0.6 (8)	17.6 ± 1.3 (8)	27.9 ± 1.6 (7)	4.1 ± 0.1 (8)	0.40 ± 0.03 (8)	0.24 ± 0.05 (16)
Acidic	0.1 ± 0.1 (4)	4.9 ± 1.0 (4)	22.0 ± 6.5 (4)	4.4 ± 0.2 (4)	0.29 ± 0.02 (4)	0.19 ± 0.08 (4)
Nutrient rich	1.4 ± 0.8 (5)	9.1 ± 0.7 (5)	20.5 ± 5.2 (5)	5.4 ± 0.1 (5)	0.35 ± 0.03 (5)	0.35 ± 0.11 (8)
Alptal						
Anmoor	0.3 ± 0.1 (5)	17.9 ± 2.1 (5)	38.9 ± 2.8 (5)	5.3 ± 0.1 (5)	0.79 ± 0.01 (5)	ND (5)
Raw humus	0.7 ± 0.04 (5)	63.5 ± 18.9 (5)	45.7 ± 3.4 (5)	3.4 ± 0.1 (5)	0.75 ± 0.04 (5)	0.16 ± 0.01 (5)

Numbers are given as means with standard deviation, (*n*) is the number of measurements. ND, not detected.

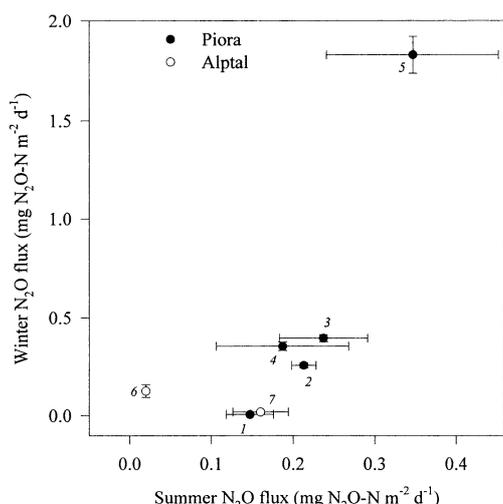


Fig. 3. Mean N₂O surface emissions during winter and summer at the Piora and Alptal subsites. (Piora: 1 neutral, 2 alder forest I, 3 alder forest II, 4 acidic, 5 nutrient-rich; Alptal: 6 anmoor, 7 raw humus). Standard deviations are given as error bars: horizontally for summer values (number of measurements as in Table 1), vertically for winter values (4 measurements).

0.37 mg N₂O-N m⁻² d⁻¹. Addition of acetylene to the forest soil reduced N₂O emissions (by inhibiting nitrification); thus nitrification was the main source of N₂O. After rainfall, emission of N₂O decreased to 0.02 mg N₂O-N m⁻² d⁻¹ but increased when acetylene was added (by inhibiting N₂O reductase of denitrifiers), demonstrating that N₂O production originated from denitrification.

There was clear spatial variation in surface N₂O effluxes between the sampling subsites during snow cover (Table 2), while N₂O production within the same subsite was more uniform (Figs. 1 and 2). N₂O emissions ranged from 0.01 to 1.96 mg N₂O-N m⁻² d⁻¹ at the Piora site and from 0.02 to 0.23 at the Alptal site. As the soil temperature is rather constant under the snow cover, the spatial heterogeneity in production observed in this study indicates that factors other than temperature are regulating microbial activity. Soil temperatures at 5 cm below the surface in Piora dropped below 0°C during November 1998 and increased rapidly to above 0°C only in mid-June the following year. During this period the soil temperature remained constant in a narrow range between -1.1 and -0.3°C.

illustrating that fluxes of N₂O (and N₂) were susceptible to water availability. A precipitation event from 6 to 7 October clearly illustrates this inter-relation. Before rainfall N₂O emission was

The low N₂O fluxes observed at the neutral site in Piora, and the raw humus site in Alptal are similar in magnitude to those measured in other studies (Brooks et al., 1996; Hénault et al., 1998;

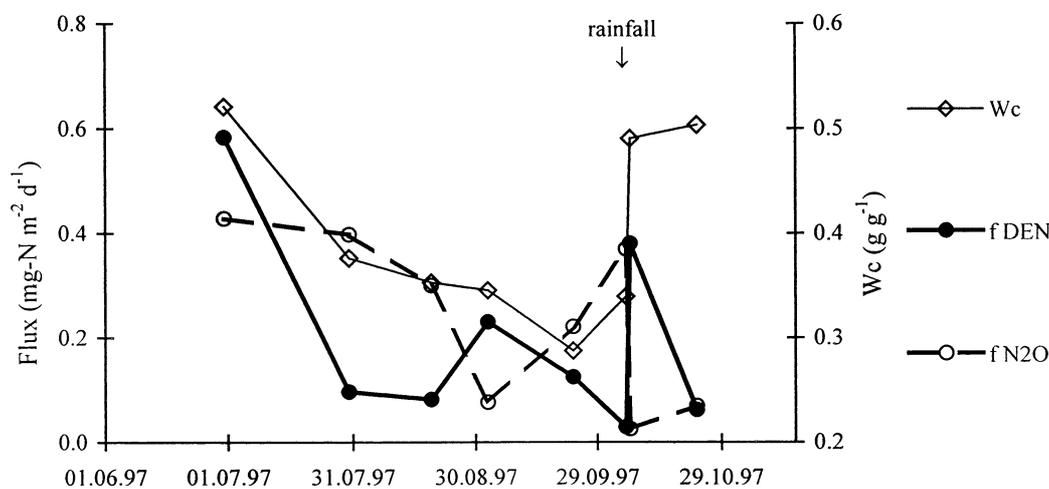


Fig. 4. Soil water content (Wc), fluxes of N₂O (fN₂O), and mean rates of denitrification (fDEN) during the summer season 1997 for the alpine alder forest II plot in Piora. Denitrification was measured using the acetylene inhibition method with soil cores. Each point is the mean of four independent measurements. Soil temperature ranged from 5.5–15.0°C (mean 9.6 ± 3.4°C). Adapted from Schürmann et al. (1998).

Table 2. Seasonal emissions of N_2O ($mg\ N\ m^{-2}$) at different subsites in winter 1998/99 and summer 1998

Site	Subsite	N_2O emissions ($mg\ N\ m^{-2}$)	
		Snow-free period	Snow-covered period
Piora	Neutral	22.5	1.3
	Alder forest I	36.9	49.0
	Alder forest II	41.0	75.8
	Acidic	32.8	67.2
	Nutrient rich	60.7	346.8
Alptal	Anmoor	4.8	15.6
	Raw humus	38.2	2.3

For Piora a 2-yr average (winter, 195 d; summer: 170 d) and for Alptal a 9-yr average (winter, 126 ± 38 d; summer, 239 ± 38 d) was used for the calculation.

Sommerfeld et al., 1993). However, N_2O emissions measured at other subsites are considerably higher, with maximum values of 1.69–1.96 $mg\ N_2O-N\ m^{-2}\ d^{-1}$ at the nutrient-rich site. These high N_2O fluxes suggest that the effect of low temperatures on denitrification is overcome by an adaptation of the microbial population and the high substrate availability in the absence of plants competing for nutrients. This is supported by studies which have identified a pulse of denitrification activity in early spring from previously snow-covered soils, when substrate concentrations are high (Alm et al., 1999; Groffman and Tiedje, 1989; Hénault et al., 1998; Mosier et al., 1993; Teepe et al., 2001; Wagner-Riddle and Thurtell, 1998). Hixson et al. (1988) reported that N_2O fluxes from saturated soils at $0^\circ C$ were not significantly different from soils at $5-10^\circ C$.

High N_2O fluxes were observed during snow melt at the end of May at the two alder forest subsites, 0.57 and $0.62\ mg\ N_2O-N\ m^{-2}\ d^{-1}$ at subsite I, and 0.67 and $0.64\ mg\ N_2O-N\ m^{-2}\ d^{-1}$ at subsite II. These high emissions during thawing are a result of denitrification activity and the physical release of accumulated N_2O in the soil (Teepe et al., 2001). The snowpack was reduced to about 0.7 m and snow density reached values around $0.62\ g\ cm^{-3}$. The neutral subsite was still covered by 1.9 m of snow at this time and fluxes of N_2O were below $0.01\ mg\ N_2O-N\ m^{-2}\ d^{-1}$.

3.3. The importance of winter fluxes to ecosystem N_2O fluxes

Figure 3 shows a comparison of N_2O surface emission rates during winter and summer. Except for the neutral site, mean winter fluxes in Piora were up to 5 times higher than mean fluxes during the growing season. Multiplying the mean daily N_2O flux by the duration gives estimates of the sum of N_2O emitted during snow cover and during the snow-free period (Table 2). For Piora a 2-yr average of 195 d for winter and 170 d for summer was employed for the calculation (SMI-MeteoSwiss, 1997), and for Alptal a 9-yr average of 126 ± 38 d for winter and 239 ± 38 d for summer was used (P. Schleppei, personal communication). These data demonstrate that at many sites the soil is a larger N_2O source while snow covered (190–212 d) than during the snow-free period (153–175 d). Exceptions are the neutral subsite in Piora and the raw humus (mor) subsite in Alptal. At these subsites nitrification is the main source of N_2O during summer (Mohn et al. 2000; Schürmann et al., 1998). In winter, nitrification is repressed, resulting in small N_2O emissions. Oxygen availability is reduced by prevailing more humid soil conditions and by heterotrophic activity. This would favor denitrification; however, denitrification does not seem to be of importance for N_2O loss in these two soils.

Denitrification in the soil did not cease in winter when the temperature is buffered within a narrow range slightly below $0^\circ C$ for many months by snowpacks that insulate the soil from extreme air temperatures. Micro-organisms remain active while vegetation is dormant and does not compete for nitrate. The extended period of snow cover in alpine areas combined with uniform and high fluxes of N_2O suggests that these fluxes must play a major role in the alpine N cycle.

4. Conclusions

Most trace gas budgets assume that trace gas production is negligible when soil is snow covered (Bouwman, 1990). Even small N_2O fluxes represent an important part of the annual budget for these ecosystems, considering the length of snow cover in (sub-) alpine regions. Winter fluxes have clearly to be included in model calculations of annual global budgets. A considerable fraction of

the land surface in the Northern Hemisphere has soils with topsoil temperatures near the freezing point, indicating that winter fluxes of N₂O are underestimated in the global budget. The seasonal variability of these fluxes suggests that even small changes in climate (e.g. timing and depth of snow cover) may have a significant effect on N₂O cycling in such environments with extended periods of snow cover.

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