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TELLUS

Fluxes and production of N_2O, CO_2 and CH_4 in boreal agricultural soil during winter as affected by snow cover

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ABSTRACT

Agricultural soils are important source of atmospheric nitrous oxide (N_2O) and a considerable part of annual N_2O release occurs during the cold season in the boreal region. According to recent studies N_2O can be produced in soils at low temperatures, below 0 °C. We studied if removal of the snowcover lowers soil temperatures and whether this would affect flux rates of N_2O, carbon dioxide (CO_2) and methane (CH_4) from an agricultural soil in eastern Finland. Gas flux rates and concentrations in soil were measured from study plots with undisturbed snow cover and from plots with snow removed. This experiment simulates changes in the soil thermal conditions with less snowfall. Plots without snow had even 15 °C lower temperature at the depth of 5 cm and they had higher N_2O emissions during soil freezing and thawing. However, there were only minor changes in CH_4 or CO_2 flux rates after removal of snow over the cold season. N_2O and CO_2 accumulated in the soil during winter and were then released rapidly during thawing in spring. CH_4 concentrations in the soil remained lower than the atmospheric levels during winter and subsequently increased to the ambient levels after thawing. Future climate scenarios suggest possible decline in snowfall in northern Europe resulting in lower soil temperatures. This could lead to higher N_2O emissions from boreal agricultural soils.

1. Introduction

Greenhouse gases, nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) are produced and consumed in soils in microbial processes. These microbial processes are greatly regulated by soil chemical and physical characteristics. Production of CO_2 (respiration) and CH_4 is regulated, for example, by temperature and soil moisture as are denitrification and nitrification, the latter two being the key processes for N_2O production in soil. Agricultural soils are the most important global sources of N_2O and the concentration of N_2O in the atmosphere is increasing annually at the rate of 0.2–0.3% (Houghton et al., 2001). Also the concentration of CH_4 in the atmosphere is increasing (Houghton et al., 2001). Soils, for example, forest soils and drained agricultural soils, may act as sinks for atmospheric CH_4 whereas waterlogged soils (e.g. wetlands and rice fields) emit CH_4.

There are studies suggesting that large amount of N_2O can be produced and emitted from agricultural and forest soils even at temperatures below 0 °C (Holtan-Hartwig et al., 2002; Öquist et al., 2004; Groffman et al., 2006; Koponen et al., 2006a). Emissions of N_2O during winter are important because they may account for more than half of the annual emissions in boreal and temperate areas (e.g. Röver et al., 1998; Teepe et al., 2000; van Bochove et al., 2000; Schürmann et al., 2002; Maljanen et al., 2003a; Regina et al., 2004).

The main mechanism for N_2O production in frozen soils is presumably denitrification (Mørkved et al., 2006; Öquist et al., 2007). N_2O can be produced in unfrozen water films in an anaerobic soil matrix in frozen soil (Teepe et al., 2001), and the production is limited by NO_3^- availability (Mørkved et al., 2006; Öquist et al., 2007). High N_2O emissions during winter have been explained by sudden release of accumulated N_2O (Goodroad and Keeney, 1984; van Bochove et al., 2001) or by increasing denitrification activity due to high availability of organic C and N during freezing-thawing events (e.g. Christensen and Tiedje, 1990). It is also possible that at low temperature N_2O reductase is suppressed increasing the production of N_2O over that of N_2 (Holtan-Hartwig et al., 2002). However, the reasons for high N_2O emissions during winter and the production of N_2O in frozen soils are not well understood.

Snow is a good insulator regarding soil temperature during winter and therefore removal of snow can enhance soil freezing

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and amplify the depth of frost (Schürmann et al., 2002). According to the recent climate scenarios the snow cover in the boreal region may decrease (Houghton et al., 2001) resulting in lower soil temperature.

Our hypothesis in this study was that without the insulating snow cover (lower soil temperature) N_2O emissions would increase and CO_2 production (respiration) would decrease as compared to the soil with a natural snow cover. The snow cover limits diffusion of CH_4 from the atmosphere into the soil and therefore thinner snow cover may enhance soil CH_4 uptake (Borken et al., 2006). We examined how snow cover affects the flux rates of N_2O, CO_2 and CH_4 by keeping half of the study plots free from snow during one winter period.

2. Methods

2.1. Study site and experimental design

The study site is located in eastern Finland (63°09′N, 27°20′E). The soil type according to FAO classification is Dystric Regosol, medium textured. The soil profile (0–25 cm) consisted mainly of fine sand (71%), silt (15%), and clay (6%). Organic matter content is 5.65% and soil pH (H_2O) is 5.8 in the 0–10 cm of the soil profile. Mean annual temperature (1971–2000) in the region is 2.8 °C and mean annual precipitation is 609 mm, of which approximately 50% falls as snow (Drebs et al., 2002). The long-term (1971–2000) average maximum snow depth has been 50 cm in the middle of March (Drebs et al., 2002). The study was conducted on timothy—meadow fescue lawn (*Phleum pratense* and *Festuca pratensin,* Huds.) which was fertilized in May 2004 with 90 kg N ha^{-1}, 15 kg P ha^{-1}, 25 kg K ha^{-1} and in July 2004 with 96 N kg ha^{-1}.

There were four experimental plots in the study area of which two were kept free from snow (referred to as bare soil). The area of one plot was 3 × 6 m. Snow was removed from the bare plots with a spade on each day the snow height exceeded about 5 cm. The remaining two plots had an undisturbed snow cover. There were three gas sampling points on each plot.

2.2. Environmental variables

Soil frost was measured using frost-depth gauge filled with methylene blue (Gandahl, 1957) and soil temperatures (depth 5 cm) were recorded with iButton® temperature loggers (Dallas Semiconductor Corp., USA). Air temperature was recorded at a weather station, located 100 m from the study site.

Soil samples for the analysis of NO_3^- and NH_4^+ were collected at 0–10 cm depth six times (28 October, 12 November and 20 December 2004, 2 February, 18 April and 2 June 2005). NO_3^- was extracted with distilled water and NH_4^+ with 1 M KCl solution. NO_3^- was analysed by an ion chromatograph and NH_4^+ with a spectrophotometer (Fawcett and Scott, 1960).

2.3. Gas measurements

Gas flux measurements started in the snow-free period in October 2004 and continued weekly to biweekly until early June 2005. N_2O, CO_2 and CH_4 flux rates were measured with a static chamber method using aluminium chambers, equipped with a fan, (60 × 60 cm, h 30 cm) and aluminium collars (60 × 60 cm, h 15 cm) pre-installed in the soil (Maljanen et al., 2003a). After closing the chamber a gas sample was taken with a polypropylene syringes at 5, 10, 15 and 25 min intervals from the headspace of the chamber. Gas concentrations were analysed within 24 h after sampling with a gas chromatograph (Shimadzu GC-14B, Shimadzu Corp. Japan) equipped with electron capture (EC), thermal conductivity (TC) and flame ionization (FI) detectors (see Maljanen et al., 2003a). Compressed air containing 1.98 μl l^{-1} of CH_4, 396 μl l^{-1} of CO_2 and 0.389 μl l^{-1} of N_2O was used for daily calibration. Gas fluxes were calculated from the linear change in gas concentrations in the headspace of the chamber. The regression coefficient r^2 was computed for the sample sets from each chamber. If the r^2 was low ($<$0.8) or if there were any indications of failures in the gas sampling or gas analysis the results were discharged. However, if fluxes were negligible (especially during the midwinter) the r^2 was always low and it was not used as a criterion for omission whenever such conditions occurred.

Gas flux rates from the snow-covered soil were determined by measuring gas concentration gradients and by calculating associated diffusion rates in the snow (Sommerfeld et al., 1993; Maljanen et al., 2003b). Gas samples (40 ml) from the snow pack were drawn with a stainless steel probe (Ø 3 mm, length 50 cm). For the calculation of the diffusive fluxes, an ambient gas sample was taken above the snow pack and another sample inside the snow pack 2 cm above the soil surface. The linearity of gas gradient in the snow pack was checked during each sampling time by sampling gas at 10 cm intervals from the top of snow pack to the soil surface. Simultaneously, snow samples were collected with a PVC tube (Ø 10.2 cm, h 55 cm) for porosity measurements. The intact samples were weighed for calculation of the average porosity of snow using the density of pure ice (0.9168 g cm^{-3}).

Samples (30 ml) for the soil gas concentration measurement were taken with syringes from silicon tubes (Ø 1.0 cm, wall thickness 0.3 cm, length 110 cm, $V = 86$ cm^3) inserted horizontally at the depth of 5 cm in the soil (Kammann et al., 2001) close to the collars for the gas flux measurements. Gas samples were analysed as described above.

2.4. Statistical methods

The differences in the gas fluxes between the treatments were tested with Mann–Whitney *U*-test (SPSS statistical package 11.5). Correlations between gas concentrations and environmental parameters were tested with nonparametric Spearman rank correlation test.

3. Results

3.1. Weather conditions and soil properties

Snow started to accumulate in late November in 2004, reached a maximum height of 43 cm in early February 2005 and it thawed totally by mid-April (Fig. 1). Mean daily air temperature reached a minimum of –19.2°C in February (Fig. 1). The early winter from November to January was mild; monthly mean temperatures remained 3.2–5.5 °C higher than the long term average (Drebs et al., 2002). The first time topsoil (1–2 cm) frost was detected in early November. The topsoil remained continuously frozen from late November 2004 until April 2005 (Fig. 1). The soil frost was more severe in areas without snow, reaching a maximum depth of 104 cm in the middle of April. In contrast, under undisturbed snow cover the maximum depth of frost was 20 cm in late March (Fig. 1). Soil temperature (depth 5 cm) in the area with snow cover was almost constant (from –0.8 to 0.8) during the winter, whereas in bare plots it varied from –15.0 to 0.2 °C during the same period (Fig. 1). Removal of the snow cover affected also the survival of plants on the study plots, most perennial plants growing on bare plots died during the winter.

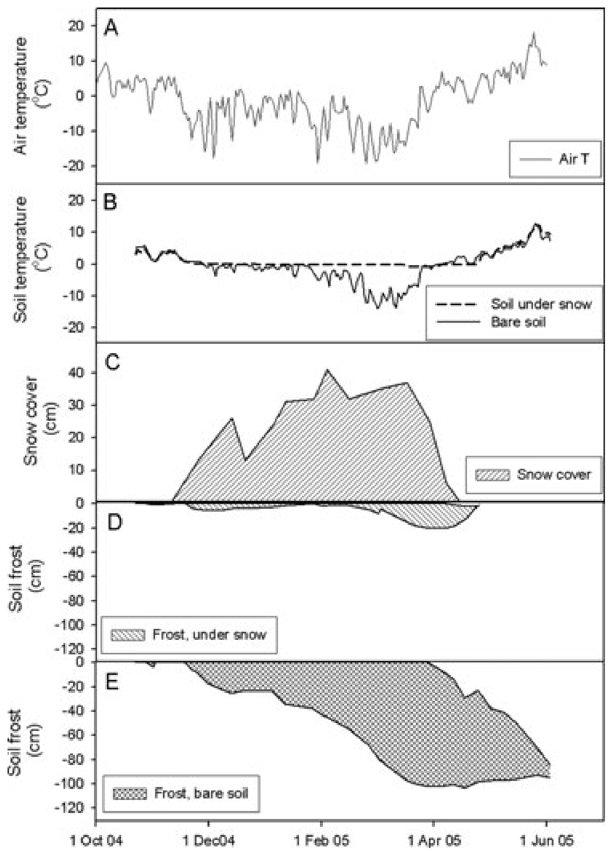

Fig. 1. Mean daily air temperature (A), soil temperature at depth of 5 cm (B), depth of snow cover (C), depth of soil frost under snow cover (D) and depth of soil frost on bare soil without snow (E).

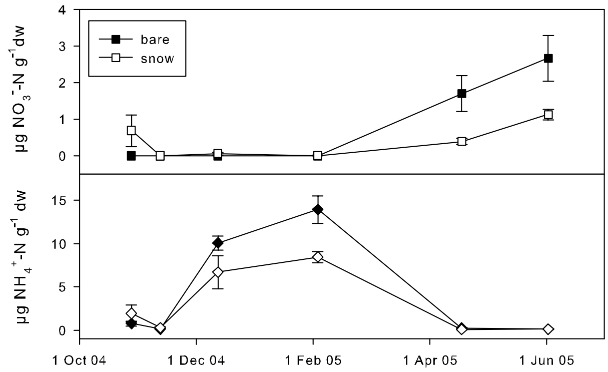

Fig. 2. Concentrations of NO_3^--N (squares) and NH_4^+-N (diamonds) in soil sampled from plots under snow (open symbols) or from plots without snow (black symbols).

Soil NH_4^+ concentrations were low in the unfrozen soil (<2 mg NH_4-N g^{-1}), increased after freezing up to 14.0 mg NH_4-N g^{-1} in bare soil and up to 8.4 mg NH_4-N g^{-1} under snow during the coldest months and decreased again to <0.10 mg NH_4-N g^{-1} after thawing (Fig. 2). NO_3^- concentrations were low, <0.01 mg NO_3-N g^{-1}, during the winter but increased after thawing to 2.6 mg NO_3-N g^{-1} in bare soil and to 1.1 mg NO_3-N g^{-1} in soil under snow (Fig. 2).

3.2. Gas fluxes

The bare plots emitted more N_2O than those with an undisturbed snow cover during soil freezing (a period of 3 weeks) ($p < 0.001$) and during thawing (a period of 8 weeks) ($p < 0.001$) (Fig. 3a). High emissions during freezing lasted about 3 weeks in November and December. Following high fluxes, N_2O emissions from all plots remained low (no statistical differences between the treatments). During thawing in April, N_2O emissions increased more from the bare plots, and remained at higher level until the end of the study period (Fig. 3a). The mean N_2O emissions from the bare plots during freezing (23.5 μg $m^{-2}h^{-1}$) and thawing (44.6 μg $m^{-2}h^{-1}$) were 35 and 4 times those from the plots under snow cover.

In contrast to N_2O emissions, CO_2 emissions were low during soil freezing (Fig. 3c). Also, CO_2 emissions from soils under snow and from the bare plots were low in mid-winter (Fig. 3c). When the soil started to thaw in April, CO_2 emissions increased first from the bare plots and a week later from the snow-covered plots (Fig. 3c). In late May and early June the soil with snow cover emitted more CO_2 than the bare plots (Fig. 3c).

The average CH_4 flux rate from all plots was negative during the study period implying that the soil was a small CH_4 sink (Fig. 3e). During the coldest part of the winter and spring thaw there were no statistical differences in the CH_4 fluxes between the treatments.

3.3. *Gas concentrations in soil*

The N_2O concentrations in soil probes started to increase from an ambient concentration of 0.3 $\mu l\ l^{-1}$ after the topsoil was frozen (Fig. 3b) and reached a maximum of 30 $\mu l\ l^{-1}$ in the bare plots and 5 $\mu l\ l^{-1}$ in plots with snow. After thawing, they decreased rapidly close to the ambient levels. N_2O concentration in soil with snow cover correlated positively with the development of soil frost ($r = 0.722$, $p = 0.002$) whereas in bare plots it did not. N_2O concentration under snow cover correlated also with the depth of snow ($r = 0.786$, $p < 0.001$).

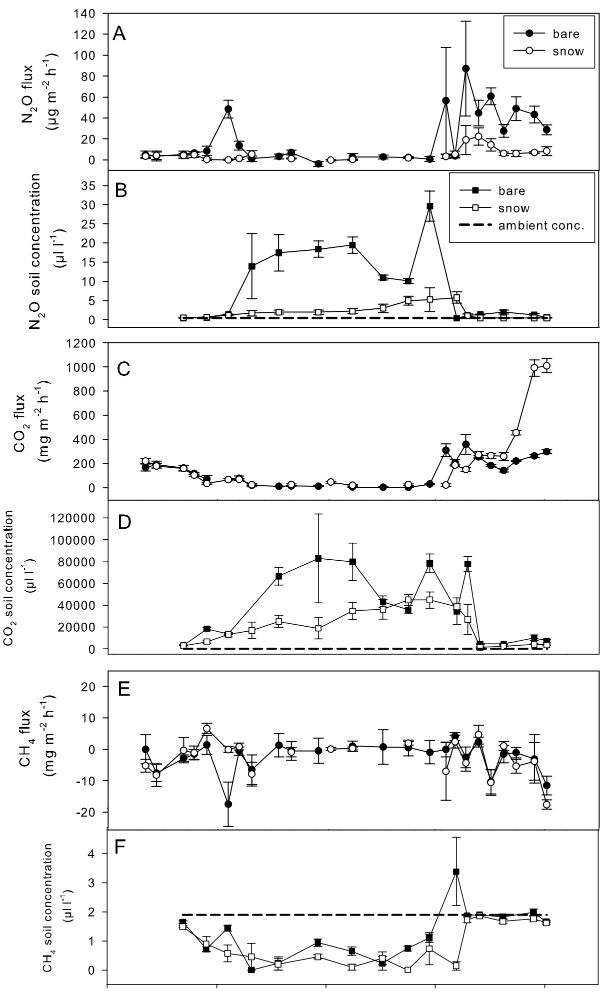

Fig. 3. Flux rates of N_2O (A), CO_2 (C) and CH_4 (E). Values are mean with standard error of six replicates. Concentration of N_2O (B), CO_2 (D) and CH_4 (F) in soil at depth of 5 cm. Values are mean with standard error of three replicates. Dashed lines indicate the ambient concentrations of gases.

Table 1. Mean concentrations ($\mu l\ l^{-1}$) of N_2O and CO_2 in unfrozen soil in autumn and in frozen soils with snow or without snow (bare) from January to February. Ratio U/F is the relative increase in the gas concentrations (concentration in unfrozen soil/concentration in frozen soil)

	N_2O		CO_2	
	Concentration	Ratio U/F	Concentration	Ratio U/F
Unfrozen	0.455		3023	
Frozen (snow)	2.27	3.98	28 700	8.51
Frozen (bare)	16.1	35.4	65 100	21.5

As with N_2O, CO_2 also accumulated in the frozen soil (Fig. 3d). In bare soil the relative concentration of N_2O (the increase from the concentration before freezing) increased after soil freezing more than the relative concentration of CO_2. However, in the soil with snow the reverse was true (Table 1). The maximum concentration in bare plots was 80 and 45 ml l^{-1} CO_2 under the snow cover. After thawing, CO_2 concentrations in soil decreased rapidly to a level of 2.0 ml l^{-1}(with snow) and 6.5 ml l^{-1} (bare soil). The concentration of CO_2 under snow-covered soil correlated positively with the depth of soil frost ($r = 0.771$, $p < 0.001$) and with the depth of snow cover ($r = 0.690$, $p = 0.003$), but it did not correlate with the depth of frost in bare plots.

CH_4 concentration began to decrease after the topsoil was frozen and it remained at a level lower than the ambient concentration during the winter months. After thawing CH_4 concentration in soil increased close to the ambient level of 1.8 $\mu l\ l^{-1}$. During thawing there was a slight increase in CH_4 concentration in the bare soil (Fig. 3e).

4. Discussion

4.1. *Soil properties*

Removal of snow resulted in more severe soil frost and lower soil temperatures than those under natural snow cover. Under the snow pack the top soil temperature remained relatively constant during winter months supporting the observations reported in previous studies (e.g. Schürmann et al., 2002). The death of vegetation on bare plots illustrates the importance of insulating function of snow cover for perennial plant species. It is likely that mechanical shovelling itself was not the reason for the death of *Phleum pratense* and *Festuca pratensin* plants because the over wintering parts of these plants are located under the soil surface (Virkajärvi and Järvenranta, 2001).

NH_4^+ concentration increased during the winter indicating N mineralization also in frozen soil. Nitrogen mineralization was expected to occur because decomposition of organic matter continued in frozen soil as indicated by the CO_2 production and CO_2 accumulation in soil (see later). NO_3^- concentration remained low during the mid-winter. It is possible that part of the accumulated NH_4^+ is nitrified but NO_3^- is then used rapidly in denitrification. Therefore, the availability of NO_3^- is an important factor limiting denitrification rate in frozen soil (Öquist et al., 2007).

4.2. N_2O and CO_2 emissions

The bare plots had higher mean N_2O emissions and lower soil temperature compared to plots with natural snow cover supporting studies from forest soils by Groffman et al. (2006). Many field and laboratory studies have shown high emissions only during soil thawing (e.g. Christensen and Tiedje, 1990; Teepe et al., 2000; Regina et al., 2004; Syväsalo et al., 2006) but there are only few field (Kammann et al., 1998; Röver et al., 1998; Teepe et al., 2000) and laboratory studies (Teepe et al., 2001; Koponen et al., 2004, 2006a) that have reported high N_2O emission pulses during soil freezing. In our study, enhanced N_2O emissions were seen not only during soil thawing in the spring but also during soil freezing in the autumn. The freezing related N_2O pulse occurred only from the bare plots with lower soil temperature.

Enhanced denitrification in bare plots may be related to more severe frost causing the death of some microbes and therefore release of microbially available organic carbon which stimulates respiration and depletion of O_2 (Christensen and Tiedje, 1990; Mørkved et al., 2006) thus providing favourable conditions for denitrification. Enhanced emissions could also result from changes in the microbial community. However, there are some contradictory results on whether freezing and thawing can change the microbial community structure in soil (Koponen et al., 2006b; Sharma et al., 2006), but evidently thawing increases microbial activity in soil as seen here from the increased CO_2 production.

Thawing related N_2O emission pulse was seen on bare and snow plots. In bare plots during thawing there was first an N_2O emission pulse simultaneously with a rapid decrease in the N_2O concentration in soil. This first pulse is a result of release of trapped gas from the soil (Goodroad and Keeney, 1984; Teepe et al., 2001). The second N_2O pulse occurred in April when the snow was melting but there was still frost deeper in the soil. The high soil moisture probably favoured denitrification and N_2O production after soil thawing (Goodroad and Keeney, 1984). The higher N_2O emissions from bare plots in the early summer may result from higher availability of NO_3^- because all vegetation had died and did not consume NO_3^-.

The removal of snow altered the soil physical–biological conditions and this affected the CO_2 emissions after thawing. The CO_2 emissions in the autumn and during the winter period until thawing were similar in the plots under snow cover and the bare plots. During thaw, enhanced CO_2 emissions were first seen from the bare soil when the topsoil (2–3 cm) was thawing and then a few weeks later after snowmelt from the soils under snow. In late May and early June the CO_2 emissions from the soil which had been under snow were higher than those from the bare soil. This could be a result from higher availability of plant derived easily available carbon (root material and root exudates) and higher respiration in soil with snow than in soil without snow—on the bare plots almost all plants had died as a result of a severe frost.

4.3. N_2O and CO_2 concentrations in soil

During the coldest months the emissions of N_2O and CO_2 were low from all plots. This was a result of an ice barrier in the top of the soil limiting the gas diffusion from the soil (van Bochove et al., 2001). The early winter in December and January was mild and there were several rain showers in periods when the top soil was already frozen, which promoted formation of an ice layer. The difference in the accumulation of N_2O and CO_2 in the soil indicates that the decrease in temperature resulting from the snow removal favours more the production of N_2O than that of CO_2 (the conclusion on the production can be done from the gas accumulation because both of the gases were efficiently blocked in soil with only minor release to the atmosphere). Koponen et al. (2004) showed from laboratory experiments that the low temperature conditions favour more the production of N_2O (denitrification) than the microbial respiration. Denitrifying microbes can be active even at temperatures as low as –4°C (Röver et al., 1998; Öquist et al., 2004; Schmidt and Lipson, 2004; Phillips, 2007) resulting from the unfrozen liquid contained in soil microsites (Teepe et al., 2001; Sparrman et al., 2004).

Concentrations of N_2O and CO_2 in frozen soil were high, but close to those reported by van Bochove et al. (2001). Most of the N_2O was accumulated in the bare plots within 2 weeks after the soil freezing. Mean temperature at 5 cm depth was –0.88 °C during that period. N_2O concentrations increased only slowly after that period until mid-March. When soil temperature dropped down to –15 °C, there was a decrease in the N_2O concentration. This can be a result of lower N_2O production in soil with less unfrozen water and physical release of N_2O via cracks in the soil. Concentration of CO_2 had similar trend as that of N_2O. We do not know why concentration of N_2O and CO_2 decreased in late winter when the frost was still developing. There was no evidence of gas release to the atmosphere during that period. The gases were released from soil just after the frost was disappearing. It has to be noted that in soil with snow there was a continuous accumulation of N_2O and CO_2 gases until thawing even the concentrations in soil were lower than in bare soil. Under snow the soil temperature was at the range where even 30% of soil water can remain unfrozen (Edwards and Cresser, 1992) allowing microbial activity.

4.4. CH_4 fluxes and concentrations

There were no changes in the CH_4 fluxes after removal of snow in contrast to the results of Groffman et al. (2006) or Borken et al. (2006). However, the CH_4 uptake rates in our study were low when compared to the forest soils. Therefore, the possible minor effect of the snow removal on the low fluxes here could be difficult to verify. Methane concentration in soil was below the atmospheric CH_4 concentration also during the winter indicating CH_4 oxidation even during the coldest period of the year.

5. Conclusions

The results here show how the possible reduction in snow cover thickness with global warming would affect the greenhouse gas dynamics of boreal agricultural soil, for example, the timing and magnitude of the high emissions can be changed. It is important that the thinner snow pack with lower soil temperatures can enhance the N_2O production during the cold periods of the year. The results stress the importance of the N_2O production at low soil temperatures, also below 0 °C. Furthermore, the N_2O production in winter does not correlate well with the N_2O emissions as a result of the low gas diffusion rate in frozen soil. Therefore, the production of N_2O during winter cannot be estimated only by measuring N_2O release to the atmosphere.

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