1. Introduction

Nitrous oxide (N\textsubscript{2}O) is a greenhouse gas with a global warming potential 298 times higher than carbon dioxide over a 100-year time horizon (Solomon et al., 2007). Soils contribute 70% to the global emissions of N\textsubscript{2}O and agricultural soil, in particular, is the major source of N\textsubscript{2}O, accounting for about 35% of the global annual emissions (Kroeze et al., 1999). N\textsubscript{2}O is produced in soils mainly in microbial denitrification and nitrification (Granli and Beckman, 1994). Several environmental factors, including soil characteristics (soil drainage, soil texture, content of organic matter, soil pH), crop type, climatic factors and N input, regulate the production of N\textsubscript{2}O (Scanlon and Kiely, 2003; Regina et al., 2004). The emissions of N\textsubscript{2}O have high spatial, seasonal and diurnal variation (e.g., Bouwman, 1990; Williams et al., 1999).

On pasture soils, a large quantity of nitrogen (N) is returned to the soil since about 60–80% of the N ingested by the cows is deposited as dung and urine (Haynes and Williams, 1993). This N is highly concentrated and the N load under urine patches can be equivalent to 470 kg N ha\textsuperscript{-1} and under dung pats it is 1130 kg N ha\textsuperscript{-1} (Saarijärvi et al., 2006). This amount is far higher than the plants can use, especially if the deposition occurs late in the autumn. The excess N can be lost via leaching, nitrification, denitrification and ammonia volatilization. The N dynamics of dung and urine differ since in dung the N is mostly in solid organic form, whereas in urine it is in soluble form. The excreta are an important source of N\textsubscript{2}O and can contribute up to 22% of the total N\textsubscript{2}O emissions from grassland in the temperate region (Yamulki et al., 1998). Added organic matter in dung and urine enhances microbial activity. The associated oxygen consumption may lead to the development of anaerobic micro-sites in soil, which favours denitrification.

There are many studies concerning N\textsubscript{2}O emissions from pastures and excreta in the temperate climate region (e.g., Calanca et al., 2007; Wachendorf et al., 2008). However, much less is known about boreal pastures with snow cover and soil frost periods of up to 5–6 months followed by a rapid thaw in spring. Especially, in the northern regions, N\textsubscript{2}O emissions outside the growing season can contribute significantly to the annual emissions (e.g., Regina et al., 2004). In boreal arable soil freezing and thawing events greatly increase the N\textsubscript{2}O emissions (Regina et al., 2004; Koponen et al.,...
Due to the large amount of N recycling on pasture, freezing and thawing events might cause even higher emission on boreal pasture. Furthermore, it can be argued that the later in the season excreta are deposited on pasture the less the vegetation can utilize it, and consequently, the more N would be vulnerable to losses such as leaching and N$_2$O emissions.

The vegetation of pasture soils itself may also affect the N$_2$O emission rates. White clover (*Trifolium repens* L.) is a N$_2$-fixing species and could thus favour the N$_2$O emissions via N input to the system. However, it has been shown that the down regulation of N fixing in the presence of mineral N has decreased N leaching from clover swards compared to grass swards (Saarijärvi et al., 2007). Whether this is true for N$_2$O emissions in the boreal climate, too, is still unclear.

Based on factors above, it is difficult to estimate N$_2$O emissions from boreal pasture soils including winter emissions that may be a significant part of the annual emissions. Therefore an experiment was conducted at MTT Maaninka, Finland in 2002–2004.

The aims of the study were

1. To quantify the annual N$_2$O emissions and emission dynamics from a boreal pasture
2. To test whether the time of deposition of dung and urine has any effect on the N$_2$O emissions
3. To test whether there is any difference in the annual N$_2$O emission between white clover-dominated pasture receiving no nitrogen fertilization and grass pasture with a conventional rate of added mineral N.

## 2. Methods

### 2.1. Study site

The study site is located in Eastern Finland (63°09’N, 27°20’E). The soil type according to FAO classification is medium-textured (clay and silt 20.4%, finer sand 70.4%, coarse sand 9.2%) Dystric Regosol. The content of total N is 0.12% and total P 1.73%. The organic matter content is 5.7% and soil pH$_{H_2}O$ 6.0. The mean annual temperature (1971–2000) in the region is 2.8°C and the mean annual precipitation 609 mm, of which approximately 50% falls as snow (Drebts et al., 2002). The grass sward was established in spring 2000 as a mixture of timothy, *Poa Pratensis* L. (seeding rate 7 kg ha$^{-1}$) and meadow fescue, *Festuca pratensis* Huds. (9.5 kg ha$^{-1}$) and was fertilized at an annual rate of 220 kg ha$^{-1}$ N N as NH$_4$NO$_3$. The fertilization was divided into three applications (90, 80 and 50 kg ha$^{-1}$ N) using commercial granulate fertilizers. The grass–clover sward was initially a mixture of white clover (4.5 kg ha$^{-1}$), alsike clover (*P. hybridium* 1.3 kg ha$^{-1}$), timothy (6.6 kg ha$^{-1}$), meadow fescue (8.2 kg ha$^{-1}$) and smooth meadow grass (*Poa Pratensis*; 3.3 kg ha$^{-1}$). However, the alsike clover and smooth meadow grass disappeared from the mixture rapidly so the white clover-dominated sward is later referred to as a grass–clover sward. It did not receive any mineral N fertilization. The plots were not grazed and they were harvested manually five times per grazing season to simulate the normal grazing practice in Finland.

### 2.2. Experimental design

N$_2$O emissions were measured from experimental dung and urine patches of dairy cattle on the grass sward or the grass–clover sward. Measurements were carried out during the grazing season and throughout the following year after the experimental excreta patches were applied.

On 10 June 2002, six experimental control, six urine (2.37 kg plot$^{-1}$, equals 59 g N m$^{-2}$, size 0.36 m$^2$) and six dung (2.47 kg plot$^{-1}$, equals 113 g N m$^{-2}$, size 0.075 m$^2$) plots (referred to as I urine or I dung) were established on a grass sward in a complete randomised design. The control plots received only mineral fertilizer and no excreta during the experiment, but they had been in grass–pasture rotation in the previous years. Three extra urine and three dung plots were made to permit soil sampling. The dung and the urine used in the experimental patches were collected directly from the dairy cows. The cows grazed with a herbage allowance of 25 kg dry matter d$^{-1}$. In addition, the cows were fed 6 kg grain-based concentrates per day. The total N in the dung and urine was analyzed by the Kjeldahl method (Kempainen, 1989). Collected urine and dung were pooled and weighed for each dung or urine plot and were applied to the soil within 2 h. Dung pats for soil sampling were placed over pieces of plastic net (mesh size 1.3 mm × 1.3 mm) which were removed with the dung during soil sampling.

On 26 August 2002, new patches (referred to as II dung or II urine) were established similarly on the same site with six replicates for urine and six replicates for dung. Six control plots were left without excreta and three extra replicate plots were established for soil sampling. The next growing season patches III were applied on 10 June 2003 and patches IV on 26 August 2003 on the grass sward (three replicate treatment plots) as described above and on the grass–clover sward (three replicate treatment plots). The between plot variation was judged to be small enough (coefficient of variation ranging from 3 to 8% depending on the treatment) to decrease the number of replicates from six to three and add a new treatment level (grass–clover) instead. The grass plots were fertilized with mineral fertilizers as described above. In 2004, no new experimental patches were applied. Instead, the last patches (IV) on both the grass sward and the grass–clover sward were observed for after-effects until June 2005.

### 2.3. Environmental variables

Soil frost was measured using a frost depth gauge filled with methylene blue (Gandahl, 1957). Air temperature, soil temperature at a depth of 5 cm and daily precipitation were recorded at a weather station about 100 m from the study site.

Soil samples for the analysis of NO$_3^-$ and NH$_4^+$ were collected at a depth of 0–10 cm at intervals of 3 weeks from unfrozen soil and less frequently from frozen soil. NO$_3^-$ was extracted with distilled water and NH$_4^+$ with 1 M KCl solution. NO$_3^-$ was analyzed with an ion chromatograph (DX120, Dionex Corporation, USA) and NH$_4^+$ with a spectrophotometer (Ultrospec 3000 pro, Biochrom Ltd, UK) according to Fawcett and Scott (1960). Soil electrical conductivity and K content were measured from soils sampled from IV control, IV urine and IV dung plots on the grass sward from September 2003 to August 2004. For the electrical conductivity measurements, 50 ml of distilled water and a sample of air-dried soil (20 ml) were mixed and soil electrical conductivity was then measured from the water phase after 24 h (WTW TetraCon$^{®}$325). K was extracted with acidic ammonium acetate (pH 4.65; Vuorinen and Mäkitie, 1955) and analysed with an ICP (Thermo Jarrel Ash Iris (II) Advantage ICP spectrometer, USA).

### 2.4. Gas flux measurements

Gas flux measurements were started in April 2002 and continued weekly or biweekly until early June 2005. N$_2$O flux rates were measured with a static chamber method using aluminium chambers (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 syringe at intervals of 5, 10, 15 and 25 min from the headspace of the chamber. Gas concentrations were analysed...
within 24 h from sampling with a gas chromatograph (Shimadzu GC-14B, Shimadzu Corp., Japan) equipped with an electron capture (EC) detector. N\textsubscript{2} (33 ml min\textsuperscript{-1}) was used as a carrier gas for the EC detector. A mixture of CH\textsubscript{4}/Ar (5\%) was added to the N\textsubscript{2} carrier gas flow (2 ml min\textsuperscript{-1}) before the detector to increase the sensitivity of EC. Compressed air containing 0.389 ll\textsuperscript{-1} N\textsubscript{2}O was used for hourly calibration. The linearity of EC was tested with N\textsubscript{2}O standards from 0.389 to 3 ll\textsuperscript{-1}. The N\textsubscript{2}O emission rates were calculated from the linear increase or decrease of the gas concentrations in the headspace of the chamber.

The N\textsubscript{2}O emission rates from the snow-covered soil were determined by measuring the gas concentration gradients in the snow pack and by calculating the associated diffusion rates in the snow (Sommerfeld et al., 1993; Maljanen et al., 2003). 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 surface and inside the snow 2 cm above the soil surface. The linearity of the gas gradient in the snow pack was checked during each sampling time by taking samples every 10 cm from the snow. Simultaneously with the gas sampling, samples of snow were collected for porosity measurements with a PVC tube (Ø 10.2 cm, h 55 cm). The intact samples were weighed for calculation of the average pore volume of the snow using the density of pure ice (0.9168 g cm\textsuperscript{-3}).

2.5. N\textsubscript{2}O concentration in soil

The N\textsubscript{2}O concentration in the soil air was measured from the grass sward after application of IV urine and dung patches from August 2003 to June 2005. Samples of 30 ml for the concentration measurement were taken with syringes from silicon tubes (Ø 1.0 cm, wall thickness 0.3 cm, length 110 cm, V = 86 cm\textsuperscript{3}, Kammann et al., 2001) inserted horizontally at a depth of 5 cm in control soil and under additional urine and dung patches outside the collars. Gas samples were analyzed as described above.

2.6. Statistical analyses

The sum variables for N\textsubscript{2}O emissions (kg N\textsubscript{2}O collar\textsuperscript{-1} or per ha\textsuperscript{-1} yr\textsuperscript{-1}) from different sources (control, urine and dung) were subjected to analysis of variance (ANOVA, SAS statistical software). Each sampling plot (collar) was treated as an experimental unit. The urine application covered the whole area of the collars, but the dung pats covered only 22\% of the collar area. Therefore, the emissions from the dung were calculated by first subtracting the emissions of bare soil inside each collar from the total emission of each collar using the measured emission rates of the control plots and then multiplying the dung emission for m\textsuperscript{2}. Finally, the emissions per hectare were calculated using the coverage values given by Saarijärvi et al. (2006) for Finnish pastures. Due to a slight skewness of that data, a LN \((x + 1)\) transformation was used before ANOVA. The ANOVA LS means obtained were then back-transformed to the original scale for biological interpretation.

The data were split into three subsets. First, the effect of treatments (control, urine and dung) and application time (June or August) on the grass sward were analyzed over 2 years (2002–2003). The statistical model included treatment, application time and year and their interactions. Each treatment \(\times\) time \(\times\) year combination had six collars in 2002 and three in 2003. The second step was the comparison of treatments (control, dung and urine) on two different application times (June or August) on swards of different species composition (grass and grass–clover sward) during 2003. Each treatment \(\times\) time \(\times\) species combination had three collars. The statistical model included treatment, application time and sward composition and their interactions. The third step was to analyse the after-effect of the treatments applied in the previous August. The corresponding model included treatment (control, dung and urine), sward composition (grass and grass–clover sward) and their interactions. The number of observations was three collars for each treatment \(\times\) sward composition combination.

As the dynamics of the N\textsubscript{2}O emissions are presented in figures, only the treatment LS means of sum variables are presented in tables despite the significant interactions observed between the treatments and time. The soil analysis of electrical conductivity and K originated from bulked samples over replicates on six occasions. Therefore, only the mean and standard deviation of each treatment are presented.

Correlations between soil parameters and not normally distributed N\textsubscript{2}O emission data were tested with non-parametric Spearman correlation (SPSS 14.0, SPSS Inc.)

3. Results

3.1. Weather conditions

The mean annual air temperature was 17.2 °C in 2002, 15.7 °C in 2003 and 14.9 °C in 2004, corresponding to the long-term average (Drebs et al., 2002). However, the mean annual air temperature during the first study period (from May 2002 to April 2003) was 0.6 °C lower than the long-term average (2.8 °C) due to the cold winter (Fig. 1). In the second and third year (from May to April) the mean air temperature was 1.1 °C and 0.9 °C higher than the long-term average.

![Fig. 1. Air temperature (solid line) and soil temperature at a depth of 5 cm (open circles) are shown in the top graph. Snow depth (dark solid line) and depth of soil frost (thinner solid line) at the study site are shown in the middle and daily precipitation (bars) at the bottom.](image-url)
In autumn 2002 the topsoil froze in mid-October and the thaw occurred in early May 2003 (Fig. 1). In autumn 2003, soil frost appeared in early December and the soil thawed in late April 2004. In 2004, the soil was frozen from early November to late April 2005, but during a warm period between December and January the soil frost almost disappeared (Fig. 1).

The grazing seasons 2002 and 2003 were slightly drier than the long-term average with a precipitation sum of 224 mm, but the grazing season 2004 was rainy, with a precipitation sum of 269 mm. The maximum daily precipitation, 82 mm, was measured in August 2004 (Fig. 1).

3.2. Soil chemical properties

Urine application on the grass sward (IV patches) increased the soil electrical conductivity \((220 \pm 87 \, \mu\text{s cm}^{-1} \text{; mean } \pm \text{ standard deviation})\) compared to the control soil \((75 \pm 47 \, \mu\text{s cm}^{-1})\). In the dung plots it was \(167 \pm 122 \, \mu\text{s cm}^{-1}\). The soil K content was also higher in the urine plots \((520 \pm 118 \, \text{mg l}^{-1}\) compared to the control \((163 \pm 59 \, \text{mg l}^{-1}\) or dung plots \((194 \pm 78 \, \text{mg l}^{-1}\). The difference was still obvious 12 months after application.

3.3. Mineral nitrogen and \(N_2O\) dynamics in grass sward

During the first study period, \(N_2O\) emissions from the control soil were low, from 6 to 56 \(\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}\), but increased during the spring thaw, up to 480 \(\mu\text{g N}_2\text{O m}^{-2} \text{ h}^{-1}\). The \(\text{NO}_3^-\) concentration in the control soil was highest in July at 40 \(\mu\text{g N g}^{-1}\), but decreased thereafter and remained low over the winter. The \(\text{NH}_4^+\) concentration in the control soil was low during the first year (Fig. 2a). The soil \(\text{NO}_3^-\) or \(\text{NH}_4^+\) concentrations did not correlate with the \(N_2O\) emission rates.

The application of the first urine patches enhanced \(N_2O\) emissions immediately (up to 840 \(\mu\text{g m}^{-2} \text{ h}^{-1}\)). The emissions decreased during the following day but increased again 3 weeks after application, when the maximum emission was 1140 \(\mu\text{g m}^{-2} \text{ h}^{-1}\). The \(N_2O\) emissions from the first dung pats had dynamics similar to the urine patches, but without the first
rapid emission peak (Fig. 2a). In August 2002, when the II urine and dung patches were applied, there was only a slight increase in the N2O emission rates from the treated soils. However, when the topsoil froze in November, emissions increased again. From January to March emissions were low, but peaked again during the thaw similarly to the control soils. The NO3− and NH4+ concentrations in the soil peaked after urine applications up to 60 μg NO3−-N·g−1 and 350 μg NH4+-N·g−1, respectively. There was a slight increase in the NO3− concentration after application of dung, but the NH4+ concentration did not change. Similarly as with the control soil, the soil NO3− or NH4+ concentrations did not correlate with the N2O emission rates.

During the second year, the N2O emission dynamics were rather similar to those in the first year; the III dung and urine patches applied in June resulted in higher N2O emission peaks than those (IV) applied in August 2003 (Fig. 2b). Enhanced but variable emissions were seen again from October to March after freezing of the soil. Thaw-related high N2O emissions were observed in all the soils in April–May 2004. Five weeks after the application of the urine III plots, there was a high concentration of NO3−, 120 μg N·g−1, but thereafter the concentration decreased unlike in the urine IV plots, where the NO3− concentration remained high (about 60 μg N·g−1) from the application of urine until soil thawing in May (Fig. 2b). The NO3− concentration in the control soil remained lower than in the treated soils. During the second year there was a significant (p = 0.012, r = 0.70) positive correlation between soil NO3− concentration and N2O emission rates. During the growing season the N2O emission rates from grass sward correlated also with soil moisture (p < 0.001, r = 0.19). However, the high daily rainfall, 82 mm d−1, at the end of July resulted in only a low increase in the N2O emissions.

In winter 2004/2005 (the after-effect period), N2O emissions remained low in all treatments. In spring 2005, smaller thaw-related N2O peaks were seen as in the previous years. The soil NO3− and NH4+ concentrations were not measured during winter 2004/2005 and spring 2005.

3.4. Mineral nitrogen and N2O dynamics in grass/clover sward

At the beginning of the grass–clover experiment the N2O emissions from the control plots were similar to those from the grass sward (Fig. 2c). During soil freezing in November–December, emissions increased but in February–April they were minimal. In the treatment plots after the urine III and dung III applications N2O emissions peaked up to 750 μg m−2 h−1 with urine and to 2000 μg m−2 h−1 with dung. The high emissions levelled off within a few weeks, but between November and April, some emission peaks were seen in the urine plots (Fig. 2c). All the plots emitted high amounts of N2O during soil thawing in May (up to 2850 μg N2O m−2 h−1). At this point, the grass–clover sward emitted more than the grass swards. During the growing season, N2O emission rates correlated with soil moisture (p < 0.001, r = 0.32). During the following winter the N2O emissions from all the plots remained low, less than 100 μg m−2 h−1.

The NO3− and NH4+ concentrations reached their maximum values, 140 μg NO3−-N·g−1 and 70 μg NH4+-N·g−1, after the urine III and IV treatments, respectively (Fig. 2c). With the dung III and IV treatments the increase was lower except in May 2004, when the NH4+ concentration reached a maximum of 55 μg N·g−1 in the dung plots. There were no significant correlations between soil NO3− or NH4+ concentrations and N2O emissions if all data were analyzed, but if only the control plots were included, there was a positive correlation between soil NH4+ and N2O fluxes (p < 0.001, r = 0.782).

3.5. Soil N2O concentration in the grass sward

Measurements of the soil N2O concentration in the grass sward started in August 2003, after application of the urine IV and dung IV patches. Before the application of urine and dung the N2O concentration in the soil was close to ambient (0.3 μl l−1), but increased up to 1.5 μl l−1 between August and November 2003, whereas in the untreated plots the soil N2O concentration remained close to ambient (Fig. 3). When the topsoil started to
freeze in December 2003, the N\textsubscript{2}O concentration increased rapidly in all the plots, reaching maximums of 33, 1760 and 66 \textmu g l\textsuperscript{-1} in the control, urine and dung soils, respectively. During the thaw, the soil N\textsubscript{2}O concentration decreased in 2 weeks to close to the ambient concentration and remained low during the growing season 2004. The following autumn, the N\textsubscript{2}O concentration increased again rapidly during soil freezing and continued to increase until the thaw in April. However, the maximum concentration (13 \textmu g l\textsuperscript{-1}) from the urine plots was much lower than during the previous winter and there were no differences in the N\textsubscript{2}O concentrations between the treatments and the control. When the measurements ended in June 2005, the soil concentrations were close to the ambient (Fig. 3). Soil N\textsubscript{2}O concentration correlated well with the depth of soil frost (\textit{r} = 0.56). The N\textsubscript{2}O concentration in the urine soils increased faster with increasing frost depth than in the untreated soil (Fig. 4).

3.6. Annual emissions

The emission rates measured from the collars were summed over 1 year after each treatment. The emissions from the dung pats were highest regardless of the application time or the botanical composition of the sward with the exception of the grass sward in June 2003 when the difference was not statistically significant (Table 1). On the grass swards the emissions from the urine-treated soils were higher than those from the untreated soil with the exception of the June 2003 application where the difference was not statistically significant. On the grass–clover sward this trend was also true in August 2003, but not for June 2003 application.

On the grass sward the N\textsubscript{2}O emissions in 2002 were not dependent on the application time, but in 2003 the August application (IV) tended to produce more N\textsubscript{2}O emissions than the June application (III) (\textit{P} = 0.083). It was evident that in the June application the N\textsubscript{2}O emission rates were similar for both sward types (grass vs. grass–clover, \textit{P} = 0.64). However, the treatment \times species interaction (\textit{P} = 0.022) revealed that the control area of grass–clover had higher emission rates than the grass sward, but in the urine-treated soil the opposite was true. For the August applications the N\textsubscript{2}O emissions were in general higher for the grass–clover than for the grass sward (\textit{P} = 0.014).

The next step was to calculate the N\textsubscript{2}O emission adjusted for typical pasture area by the coverage percentages of dung (4%) and urine patches (17%) (Saarial\textsuperscript{e}rvi et al., 2006). Due to its high proportion of the pasture area the untreated soil (control) formed the most significant source of N\textsubscript{2}O emissions (58–62% of total) for grass swards. On grass–clover sward the effect was even more pronounced since from 74 to 88% of the emissions originated from untreated soil. The only exception was on the grass swards in June 2002, when the dung pats made the highest contribution to the emissions (61%) and the contribution of the untreated area was only 25% of the total.

In 2002, the June applications (I) on grass sward produced slightly more N\textsubscript{2}O than the August application (II) (\textit{P} = 0.003), but the effect was very much dependent on the treatment (treatment \times season interaction \textit{P} < 0.001). In 2003, the season had no effect on the N\textsubscript{2}O emissions per hectare. There was no general difference between the sward type, i.e. grass vs. grass–clover sward, when the applications were made in June, but in the August application the grass–clover had much higher N\textsubscript{2}O emissions (\textit{P} < 0.001). However, the emissions from the control area were higher from the grass–clover sward than those from the grass sward, whereas for the urine- and dung-treated areas the difference was not clear. Winter-time N\textsubscript{2}O emissions ranged between 25 and 78% of the annual emissions in both swards.

The residual effect of the treatments IV, applied in August 2003, i.e. the N\textsubscript{2}O emissions in the 2nd year from August 2004 to July 2005, is presented in Table 1. The N\textsubscript{2}O emissions from the grass–clover sward were low compared to the grass sward (\textit{P} < 0.001). The actual residual effect of dung and urine was not significant on the grass–clover swards. On the grass swards the dung pats had the highest emission rates, but the difference was not significant.

### Table 1

<table>
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<th>Species and application time</th>
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<tr>
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<tr>
<td>Grass, August 2002</td>
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<tr>
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<tr>
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<td>Grass, August 2003</td>
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</table>

Numbers on the same line with a common superscript do not differ statistically (\textit{P} > 0.05; Tukey’s procedure).
4. Discussion

4.1. N₂O dynamics after excreta application

In early summer, immediately after the applications of urine, there was a rapid N₂O emission peak followed by a decrease and then after several days another increase in the emissions, as reported also by, e.g. Williams et al. (1999) and Yamulki et al. (1998). The first emission peak could be instant denitrification favoured by high nitrate availability and soil water content, but after the nitrate is consumed there is a delay until the soil moisture is low enough to allow nitrification to produce more nitrate (van Groenigen et al., 2005). This was not seen in the late summer urine applications. The maximum emission peaks from dung pats appeared later than those from urine, in agreement with Yamulki et al. (1998).

4.2. N₂O dynamics—environmental variables

The N₂O emissions here showed great temporal variation as reported in several studies (e.g. Anger et al., 2003; Yamulki et al., 1998; Williams et al., 1999). The N₂O in the soil probably originates from nitrification/denitrification and several factors can control the production (Firestone and Davidson, 1989). In our study, when the soil was unfrozen, soil moisture seemed to control the N₂O emissions, because in all untreated soils the N₂O emissions increased with increasing soil moisture content (p < 0.001, r = 41). Similarly, rain events have been reported to cause enhanced N₂O emissions (e.g. Mosier et al., 1991; Bronson et al., 1999; Saggar et al., 2004). However, in this study the very heavy rain event in August 2004 had no effect on the N₂O emissions.

When the soil is frozen, the main sources of N₂O may still be microbiological processes (Röver et al., 1998), but the physical properties of the soil control the emissions, e.g. by creating a diffusive barrier by ice on the soil surface (van Bochove et al., 2001). Furthermore, at low temperatures the soil N₂O is not reduced to N₂ during soil thawing before it reached the atmosphere (Wagner-Riddle et al., 2008; Ryan et al., 2000). Therefore, the depth of soil frost or N₂O concentration alone in frozen soil cannot be used to predict N₂O emissions in the pasture soil. It has to be pointed out that the long sampling interval (once a week here) during the thawing periods may also lead to biased emissions, if the highest emission peaks during thawing are missed.

4.3. Annual N₂O emissions

The total annual emission of typical pastures can be calculated as the sum of the direct and residual effects of dung and urine. However, when measuring the residual effects, the treatments based on both N₂O emission rates and accumulation of N₂O in soil (grass only) did not differ here from the control (untreated). Therefore, we conclude that the adjusted values of N₂O-N ha⁻¹ yr⁻¹ for typical pasture from each 365-day measurement period can be used directly. The estimated annual N₂O losses from grass sward varied between 3.2 and 4.1 kg ha⁻¹ yr⁻¹ and from grass–clover sward from 6.4 to 7.6 kg ha⁻¹ yr⁻¹. These values are similar or slightly higher compared to those in other studies with similarly long measurement periods on intensive pastures in temperate climates (from 0.05 to 3.7 kg N ha⁻¹ yr⁻¹ in Europe, Calanca et al., 2007; from 1.3 to 5.3 kg N ha⁻¹ yr⁻¹ in New Zealand, Ruz-Jerez et al., 1994; from 3.6 to 5.1 kg N ha⁻¹ yr⁻¹ in Germany, Anger et al., 2003 and Flessa et al., 2002). However, Saggar et al. (2004) reported emissions as high as 9.5 to 12 kg N ha⁻¹ yr⁻¹ in New Zealand.

Our results stress the importance of the cold period in the annual N₂O budget in boreal soils. Here the emissions during the winter months (from October to April) were up to 75% of the annual emission. The increase in the N₂O concentration in the soil immediately after the first sub-zero temperatures were measured from the soil, the negative correlation between the N₂O emissions and soil temperature, as well as the positive correlation between soil frost depth and soil N₂O concentration in addition to the high spring thaw emissions underline the importance of low temperatures in the N₂O production.

The N₂O-N emission from grass pastures expressed as a proportion of applied N was 0.6–1.4% for control plots, which is close to the emission factor in the IPCC Guidelines 2006, 1.25% of applied fertilizer N (IPCC, 2006). Additional N₂O-N emission from animal excreta N (0.3–0.9% of excreta N) was less than the default emission factor given by the IPCC (2% of excreta N) in most of the cases but for dung in June 2003 the proportion was clearly higher, 5.2% of excreta N.

The calculated proportions for urine (0.39–0.85%) during 1 year were slightly lower compared to the values reported in literature (1.4% for urea, Clayton et al., 1997). In experiments with shorter measurement periods (Anger et al., 2003; Flessa et al., 1996; Koops et al., 1997; Yamulki et al., 1998; Williams et al., 1999; Wachendorf et al., 2008) there is a great variation between studies, from 0.05 (Wachendorf et al., 2008) to 7% of given total N (Williams et al., 1999). The calculated proportions for dung on three occasions out of four (0.7–0.9%) were slightly higher than reported elsewhere (0.3–0.5%) (Flessa et al., 1996; Yamulki et al., 1998; Wachendorf et al., 2008). On one occasion (June 2003) the proportion was as high as 4.5% of total N given (or 5.2% of given excreta N), which is an extreme value for dung. However, as noted by Oenema et al. (1997), estimates from dung vary greatly due to strong influence of climatic variables on the physical properties of dung, e.g. crust formation.

To summarize, the most striking result in our study was that despite large differences in climate and N₂O emission dynamics...
between temperate and boreal pastures, the magnitude of annual emissions was rather similar.

4.4. Effect of sward type and application time

The \( \text{N}_2\text{O} \) emissions adjusted for unfertilized grass–clover sward were 64–91% higher in 2003 than for fertilized grass pasture receiving 220 kg N ha\(^{-1}\). This difference originated mainly from the untreated soil where the grass–clover soil had much higher \( \text{N}_2\text{O} \) emissions than the soil without \( \text{N}_2\text{O} \)-fixing vegetation. The contribution of the urine- and dung-treated areas to the difference was much less. However, the following year when the after-effect was measured, the emissions from the untreated grass–clover sward were clearly lower than in the previous year. The most probable reason for the difference between years was the lower clover content in the vegetation inside the collars during the after effect year. It was evident (Fig. 2) that high emission peaks occurred in the grass–clover sward in spring 2004. In the following spring, 2005, emissions during the thaw remained low. Our results suggest that most of the difference between the grass–clover and grass swards is a result of spring-time emissions caused by the release of both accumulated and newly formed \( \text{N}_2\text{O} \) (e.g. Wagner-Riddle et al., 2008). High \( \text{N} \) releases from grass–clover in the winter and spring before the growing season were found also by Müller and Sundman (1988). Furthermore, Müller (1987) suggested that clover \( \text{N} \) is not susceptible to leaching and much of the \( \text{N} \) escapes in gaseous form, e.g. as \( \text{N}_2\text{O} \). In general, the effects of legumes on 2004 emissions have been inconsistent (Granli and Beckman, 1994; Andrews et al., 2007).

Direct, long-term comparisons between grazed grass pastures with artificial \( \text{N} \) fertilizer and unfertilized–grass–clover mixtures are scarce and even lacking for the boreal climate. According to Ruz-Jerez et al. (1994), the annual \( \text{N}_2\text{O} \) emissions from grass–clover mixtures were clearly lower than those of perennial ryegrass pastures fertilized with 400 kg \( \text{N} \) ha\(^{-1}\), 1.3 kg vs. 5.2 kg \( \text{N}_2\text{O}-\text{N} \) ha\(^{-1}\), when grazed by sheep in a 3-year study at temperatures above 0 °C. Our results emphasize the large fluctuations in measured \( \text{N}_2\text{O} \) emissions from legume-containing canopies, especially when periods of sub-zero temperatures are present. Carter and Ambus (2006) showed with the \( ^{15}\text{N} \) technique that biologically fixed \( \text{N} \) does not contribute much to the \( \text{N}_2\text{O} \) emissions in short term. They postulated that legumes contribute more in the long run through their \( \text{N} \)-rich crop residues in soil. This hypothesis is supported by Kettunen et al. (2007) working with red clover–timothy mixtures, as well as by Baggs et al. (2003) and Niklaus et al. (2006). It is well known that the proportion of legumes varies in time in a grazed plant community (e.g. Loiseau et al., 2001). Therefore it is not surprising that great variation is measured for small plots containing a mixture of clover and grass. In conclusion, the use of legumes instead of mineral \( \text{N} \) seems not to be a way to diminish \( \text{N}_2\text{O} \) emissions from boreal pasture in contrast to temperate climate. Anger et al. (2003) found that \( \text{N}_2\text{O} \) emissions from urine were much greater during summer than in the autumn/winter period. In contrast, we found no consistent effect of excreta application time (June vs. August) on direct \( \text{N}_2\text{O} \) losses from soil. Especially in June 2002 the cumulative \( \text{N}_2\text{O} \) emission was exceptionally high from the dung plots. Furthermore, when the \( \text{N}_2\text{O} \) emissions were calculated for a typical pasture area, we found no substantial effect of the application times of excreta.

5. Conclusions

(1) Despite such large differences in climate and \( \text{N}_2\text{O} \) emission dynamics between temperate and boreal pastures, the magnitude of the annual emissions was rather similar. The annual \( \text{N}_2\text{O}-\text{N} \) emissions from boreal grass sward without excreta were close to the emission factor in the IPCC Guidelines 2006, 1.25% of applied fertilizer \( \text{N} \) (IPCC, 2006). The additional \( \text{N}_2\text{O}-\text{N} \) emission from animal excreta was lower than the default emission factor given by the IPCC (2% of excreta \( \text{N} \)) on most occasions although also higher proportions were detected.

(2) The deposition time of urine and dung had only a slight effect on the annual \( \text{N}_2\text{O} \) emissions.

(3) The \( \text{N}_2\text{O} \) emissions from grass–clover pasture were 60–90% higher than from \( \text{N} \)-fertilized grass pasture, but exhibited great variations between years mostly during the peak emission in spring.

(4) There was continuous production of \( \text{N}_2\text{O} \) in the frozen soil during winter. The addition of urine enhanced the production of \( \text{N}_2\text{O} \) also during winter. \( \text{N}_2\text{O} \) flux measurements year round are therefore essential in boreal ecosystems.

(5) The emission directly from excreta patches was higher for urine than for dung but, when adjusted to represent a typical pasture, the fertilized pasture without excreta contributed most to the annual emissions. The residual effects (>365 days) of the excreta were negligible.

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References


Anger, M., Hoffmann, C., Küchbach, W., 2003. Nitrous oxide emissions from artificial urine patches applied to different N-fertilized swards and estimated annual N2O emissions for differently fertilized pastures in an upland location in Germany. Soil Use Manage. 19, 104–111.


Bouwman, A.F., 1990. Exchange of greenhouse gases between terrestrial ecosys-


