

Emissions and dynamics of N₂O in a buffer wetland receiving water flows from a forested peatland

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Forestry operations can cause disturbances in nutrient cycling. Protection of watercourses by trapping the leached solids and nutrients in sedimentation ponds and buffer zones may create a new greenhouse gases (GHG) source. We measured *in situ* nitrous oxide (N₂O) fluxes in different parts of a spruce swamp buffer zone, N₂O emissions from intact peat columns after fertilization with different ammonium nitrate (NH₄NO₃) levels, and the rate and volume of *in vivo* N₂O accumulation. N₂O-producing micro-organisms existed throughout the buffer zone. The rate of N₂O formation was highest at depths close to the prevailing water table within the buffer zone. Groundwater level and the vicinity of bypass water flows at the soil surface regulated the spatial and temporal variation in the rate of N₂O efflux in the field. Nitrogen (N) addition rapidly increased *in vivo* N₂O release. Microbial activity in the laboratory incubations under optimal conditions was high, but the *in situ* N₂O efflux in the field was low. The actual leaching of mineral N from forestry areas was low and the inorganic N concentration in the buffer zone inflow was no higher than is typical for humic brooks or lakes in Finland. The low N₂O fluxes indicated that forestry operations in the catchment did not result in significant N enrichment of the buffer zone. This study does not support the postulate that peatland buffer zones may become significant sources of N₂O.

Introduction

Forest management operations, such as clear-cutting and soil preparation prior to replanting, have been reported to increase the leaching of dissolved organic nitrogen (DON), nitrate (NO₃⁻) or ammonium (NH₄⁺) from both peatland forestry areas (e.g. Nieminen 1998) and from mineral soils (e.g. Piirainen *et al.* 2007). Leaching of N may occur immediately after the cessa-

tion of forestry operations or may occur several years after the operations (Kubin 1998, Nieminen 1998, Mannerkoski *et al.* 2005, Piirainen *et al.* 2007). In order to protect watercourses, solids and nutrients should be retained in buffer wetland zones established between the forest management areas and the watercourses. Surplus NO₃⁻ or NH₄⁺ may be immobilized by micro-organisms (Silvan *et al.* 2003), vegetation (Silvan *et al.* 2004) and chemical adsorption

by the peat (Heikkinen *et al.* 1995), or may be released in gaseous form, e.g. dinitrogen (N_2) or nitrous oxide (N_2O). Experiments with a high rate of nutrient supply have shown that the peatland buffers retain nutrients as intended (e.g. Silvan *et al.* 2003, Silvan *et al.* 2004, Vikman *et al.* 2008). However, N fertilization in the catchment above the buffer may result in increased N_2O emissions (Duxbury *et al.* 1982, Mosier *et al.* 1991, Silvan *et al.* 2002), which suggests that the buffer zone may be a hot spot of N_2O emissions (Silvan *et al.* 2002).

N_2O is produced as a by-product in microbial N cycling both under oxic and anoxic conditions. In nitrification, NH_3 is oxidized to NO_3^- and in denitrification NO_3^- is further reduced to N_2 (e.g. Wrage *et al.* 2001). Fluxes of N_2O in peatlands are strongly controlled by the water-table level and additionally by soil temperature, soil pH and organic matter mineralization (Maljanen *et al.* 2003). A strong response in the rate of N_2O release is found in nutrient rich peatlands, where in general, the fluxes of N_2O increase after a lowering of the water table (Martikainen *et al.* 1993, Regina *et al.* 1996, Alm *et al.* 1999, Regina *et al.* 1999, Pihlatie *et al.* 2004, Chapuis-Lardy *et al.* 2007). In nutrient-poor peatlands, a low mineral N content in some cases actually favors N_2O consumption (as reviewed by Chapuis-Lardy *et al.* 2007). However, extreme drought may increase N_2O emissions even from nutrient poor peat (Dowrick *et al.* 1999). According to Freeman *et al.* (1993) and Regina *et al.* (1999), rewetting rapidly reduces N_2O fluxes in drained fens to levels similar to those that preceded drainage. In contrast, Silvan *et al.* (2002) measured high N_2O emissions in a peatland buffer zone with a high water table following considerable N additions.

In natural peatlands, the water-table level is high and nitrification is often limited by oxygen availability. However, in peatland buffer zones nitrification is not necessarily the sole precursor for denitrification, especially if there is an external load of NO_3^- or NO_2^- from forestry areas. Nitrification is regulated by the availability of NH_4^+ or NH_3 (e.g. Wrage *et al.* 2001), which depend on the mineralization rate of organic matter, its quality and the external load of NH_3 or organic N (Papen *et al.* 1989, Wrage *et al.* 2001). In peatlands, organic N is available from

peat decomposition, but inorganic N may be the restrictive nutrient (Baum *et al.* 2003, Silvan *et al.* 2003). Flooding modulates the oxygen and nutrient availability in the buffer soil. Both N influx and a raised water table may affect the rates of N immobilization and denitrification. It is also unclear as to how a buffer maintains its N retention capacity in the long term after forestry operations.

We studied N_2O efflux and production dynamics in a spruce swamp buffer over a four-year period. The buffer zone was constructed six years prior to the start of this study when forestry operations, which included thinning, fertilization, and clear-cutting, commenced in the catchment area. We assumed that in the aftermath of the forestry operations, N_2O efflux from the buffer zone would be high (cf. Silvan *et al.* 2002). N_2O efflux and production rates in the peat were expected to be highest in the areas nearest to the water inflow due to the higher accumulation of N from the catchment. The main objectives were (1) to verify high N_2O effluxes in the peatland buffers after forestry operations, and (2) to estimate the significance of N load to the magnitude of N_2O flow. In order to verify whether the peat in the buffer zone contained active microbial populations that would be able to utilize the added mineral N and produce N_2O in the process, we sampled peat from different parts of the buffer zone, which were exposed to inflow waters that varied both spatially and depthwise. The capacity of peat microorganisms to process inorganic N input under laboratory conditions was tested by fertilizing the buffer zone samples with a wide range of ammonium nitrate (NH_4NO_3) concentrations.

Material and methods

Study site

In 1997, a peatland buffer zone was established on a spruce swamp ($63^{\circ}38'N$, $29^{\circ}25'E$, 192 m a.s.l.) in Nurmes, eastern Finland (Fig. 1a). The buffer zone system (0.5% of the total 72 ha forest catchment area) consisted of a sedimentation pond to trap solids and a dam to guide the incoming surface waters onto the buffer zone. Typical

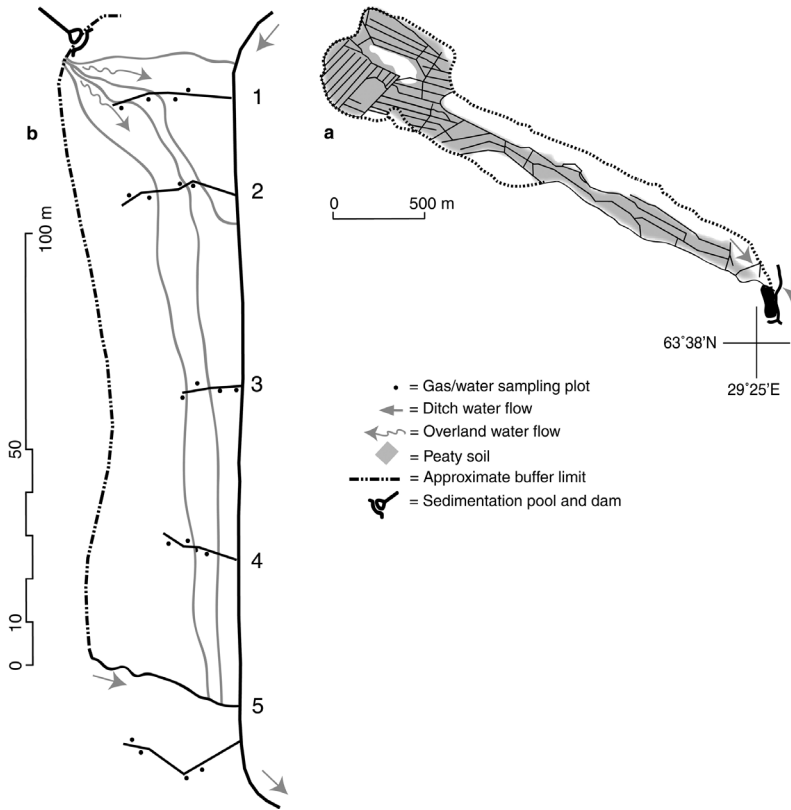


Fig. 1. (a) Catchment consisting mostly of diked and drained peatland forests (grey). A buffer and transect 5 are located in the lower, right corner. (b) A spruce swamp peatland buffer zone and transect 5 outside the buffer zone. Gas sampling plots are used in summer. During winter, the snow gradient samples were taken outside the permanent summer sampling plots.

forestry operations in Finland, which include ditch cleaning, phosphorus (P) and potassium (K) fertilization, thinning, and harvesting, were carried out within the catchment area (Table 1). All forestry operations, in addition to underlying natural processes, may contribute to the leaching of N to the buffer zone (e.g. Harriman 1978, Nieminen 1998, Nieminen 2003, Piirainen *et al.* 2002, Piirainen *et al.* 2007). The annual mean temperature was 3.0 °C and the average annual precipitation in the Nurmes area for the period of the study was 533 mm with over 30% falling in the form of snow (data contributed by the Finnish Meteorological Institute). Snowmelt occurred in April–May. In July, the water table is typically below the soil surface although the autumn rains tend to raise the water table even above the soil surface.

Prior to the start of measurements, boardwalks were constructed to prevent disturbance to the soil during the measurements and during sampling of gas fluxes and vadose water quality in the buffer zone. Transects 1–4 were estab-

lished in order to examine the impact of the nutrient load at different distances from the pond and the buffer water inflow (Fig. 1b). Transect 5 was located in the original spruce swamp and separated from the flooded buffer zone by a ditch. Along each transect, there were four fixed sampling points, equipped with 50-cm deep vadose water wells, which were used during vadose water sampling and to monitor the water table depth when the soil was unfrozen. At each four sampling points within every transect, a

Table 1. The time and area of forest management operations in the catchment of the spruce swamp study site (Lyytikäinen *et al.* 2003; S. M. Heikkinen pers. comm.).

Forest management	Year	Area (ha)
Ditching	1960s	3
Clear-cutting	1995	3
Thinning	1998	22
Ditch cleaning	1998	13
PK fertilizer (450 kg ha ⁻¹)	1998	15
Clear-cutting	2006	5

round steel plate collar, made from a air ventilation tube 30 cm in diameter, was inserted in the peat to a depth of about 15 cm. The collars were used to facilitate gas measurements during the snow-free season. In winter, gas was sampled from areas of undisturbed snowpack at five locations adjacent to each transect. The locations were selected so that the permanent collars were avoided.

Average peat depth in the spruce swamp was 0.6 m within the buffer zone (transects 1–4) and 0.3 m at transect 5. Near the water inflow (transects 1–3), the peat was mainly composed of *Sphagna*, whereas at transects 4–5, the peat was composed mainly of decomposed vascular plant remains. The ground vegetation in the buffer zone had partly changed due to flooding and was characterized by grasses and herbs, such as *Calamagrostis purpurea*, *Carex canescens* and *Trientalis europaea* and mosses, e.g. *Sphagnum riparium* and *S. girgensohnii*, which represented a continuum from an oligo-mesotrophic *Myrtillus* spruce mire type (Eurola *et al.* 1995) to a meso-eutrophic herb-grass spruce mire. Transect 5, which was located outside the buffer zone, was a mesotrophic fern spruce mire with grasses and herbs, such as *Dryopteris expansa*, *Equisetum sylvaticum*, *Gymnocarpium dryopteris*, *Vaccinium myrtillus* and mosses *Pleurozium schreberi*, *Brachythecium* sp. and *S. girgensohnii*.

N₂O measurements

Gas fluxes were measured during the summers of 2003, 2004 and 2005 and during the winter periods of 2005 and 2006. Samples were taken 1–5 times per month in the summer and 1–3 times per month in the winter. The total number of calculated fluxes was 935 in summer and 291 in winter. In the winter, N₂O fluxes were determined using the snow gradient method and in the summer using static chambers.

Chamber techniques

The chambers were made from the same air ventilation steel-plate tube as the collars. The diam-

eter and height of the chambers was 30 cm and the volume 21 dm³. Rubber gaskets were glued onto the edges of both collar and chamber. At the start of each measurement, the chamber was gently placed on the collar and interlocked using adjustable clips. The clips pulled the gaskets of the collar and chamber together thus ensuring an air tight seal with minimal disturbance to the soil. Compensation air was let into the chamber through a 1.5-m-long, 2-mm inner diameter silicon tube. The rationale for the compensation air inlet was that the soil pore space may contain extremely high gas concentrations as compared with the ambient air, which could markedly exaggerate the flux estimates even with the relatively small underpressures generated by the sampling. This is known to be true for CO₂, and was applied here for N₂O as a precaution. The small overhead of ambient air flowing into the headspace would not generate a similar potential error in the flux rate.

For each sample, a volume of 30 ml was drawn from the chamber headspace into a 50-ml polypropylene syringe equipped with a 3-way stopcock. The period of chamber closure was 20 min in summer, but in colder conditions with lower microbial activity before the spring thaw, the chamber was kept closed for 40 min. Four samples were taken every 5 (summer) or 10 min (winter), following closure of the chamber. Chamber air temperature was measured using a multi thermometer or a digital thermometer (Suomen lämpömittari Oy) in conjunction with each sampling. The average of all four temperature measurements was used in the flux calculation. As the chambers were opaque and had a reflecting metal color, the headspace temperature during chamber closure did not change by more than 0.18 ± 0.1 °C (mean \pm SE). The temperature of the soil profile (soil surface, –2, –5, –10, –15, –20, –25, –30, –40 and –50 cm) was measured using a Fluke 52 K/J thermometer (Everett, USA).

Gradient measurements

The gas fluxes through the snowpack were determined by drawing 30 ml of gas from close to the soil surface below the snowpack and from the air

above the snow (Sommerfeld *et al.* 1993, Alm *et al.* 1999). The samples were taken into 50-ml polypropylene syringes closed with a 3-way stopcock, through a 4 mm diameter metal pipe that was long enough to penetrate the snowpack. The pipe was flushed with ambient air before each sampling. Gas samples were also taken from different depths in the snowpack to examine the linearity of the gas concentration gradient in the snow profile.

During the sampling campaign, snow samples were taken 1–3 times per month each winter from 5–10 locations on each transect. The snow depth was measured from 5 to 10 volumetric profiles taken through the snowpack using a 54-mm inside diameter plastic tube. The snow samples were weighed and the average porosity of the profiles calculated using the assumption that the snow consisted of only ice and air, with reference to the density of solid ice (0.9168 g cm^{-3}). The gas flux was then calculated using Fick's first law of diffusion through a porous medium using coefficient $0.139 \text{ cm}^2 \text{ s}^{-1}$ for N_2O (Sommerfeld *et al.* 1993).

The depth of ground frost was measured from four locations using pipes drilled into the soil and filled with methylthioninium chloride. The color of the inner pipe content was blue at temperatures above 0°C and turned colorless at depths where the soil temperature was below 0°C . The inner pipe was taken out and the height of clear region of the pipe (ground frost depth) was measured.

N_2O accumulation rate, bulk density and particle density of peat

Volumetric peat samples were collected from transects 1, 3, 4, and 5 using a $6 \times 6 \text{ cm}^2$ box corer during the autumn and spring flooding periods, on 5 October 2005 and on 10 May 2006. The rate and volume of N_2O accumulation at different depths of the peat profile were measured in the laboratory as follows. The peat samples were cut into 5-cm-thick slices and each sub-sample (8 cm^3 in volume, altogether 47 sub-samples) was cut and incubated in glass bottles ($V = 590$ or 612 ml) under controlled conditions (water saturated, temperature $21.7 \pm 1.0^\circ\text{C}$, with

N_2 atmosphere and potassium nitrate (KNO_3) addition). Anoxic conditions were initially created in the bottles by flushing the bottles with 99.95% quality N_2 . Chemically inert N_2 was used, because it is the end product of denitrification and does not disturb the process. We did not measure the accumulation rate of N_2 .

The first 30 ml samples from the bottle headspace were taken immediately after the N_2 flushing. Consecutively, more samples were taken 2–4 times a day, depending on the observed rate of N_2O production. Samples were taken more frequently from bottles that displayed a higher and a more rapid increase in N_2O production. Each time after a sample was drawn from the headspace, a similar amount of N_2 was returned in order to maintain the headspace pressure. The sampling was stopped when three consecutive analyses showed a decreasing trend in the headspace N_2O concentration, indicating the cessation of N_2O accumulation in the soil sample. On average, 14 gas samples (range = 5–28) were taken from each sample bottle. Wet weight of the peat sample was measured before the incubation and dry weight after 2 days drying at 105°C .

Peat bulk density and particle density were determined from the samples used in the N_2O accumulation rate experiment. Particle density was obtained by dividing soil particle mass by soil particle volume. The particle volume was determined by boiling the dried and weighed soil sample in a pycnometer, in order to remove air from the soil, after which the particle volume was indirectly obtained by filling the pycnometer with water and subtracting the known water volume from the volume of the vessel.

Nitrogen addition experiment

Peat samples (diameter and height 15 cm) were cored in October 2007 from the uppermost part of the soil profile. Green parts of the vegetation were cut off and the samples were kept in plastic pails in laboratory greenhouse cabins under controlled conditions of temperature ($19.8 \pm 0.5^\circ\text{C}$) and moisture (the water table level was maintained at 2 cm below the peat surface by the addition of deionized water as needed). The peat samples were fertilized using NH_4NO_3

at 1.25, 2.5, 5.0, 10.0, 65.0 kg N ha⁻¹ ($n = 5$ for each addition level) and 130.0 kg N ha⁻¹ ($n = 6$). Ten of the samples received no fertilization to act as controls. The highest N addition level corresponds to N fertilization recommendations (about 100 kg N ha⁻¹, Päivänen 2007: 256) for peatland forests. The pails were enclosed in a 4.2 dm³ chamber with an air-tight gasket for N₂O flux measurements. Four 30 ml samples were drawn into syringes at 5 min intervals. Compensation air was let into the chamber through a 2 mm inner diameter silicon tube from plastic bags of ambient air. The headspace temperature was measured using a Fluke 52 K/J thermometer (Everett, USA). At least one N₂O flux measurement per peat sample was performed prior to the fertilizer treatment.

Gas analysis

Gas concentrations were determined in the laboratory within two days of sampling using a gas chromatograph (Shimadzu GC-14-A, Kyoto, Japan) equipped with an electron capture detector (ECD). The precision limit of the detector was 20 ppb for N₂O. The gas fluxes were calculated from the linear change in gas concentration in the combined airspace of the chamber and the collar over time. The airspace volume within the collars was measured every summer. Concentration data that showed an apparent chamber leakage or the gas chromatograph failure were discarded.

Measurements of N and pH from the buffer inflow and outflow water

Water samples for the analysis of total N (N_{tot}), ammonium (NH₄⁺), and nitrite + nitrate (NO₂⁻ + NO₃⁻) were taken from the sedimentation pond and from the water that outflowed from the buffer zone beyond transect 4. Concentrations of N_{tot}, NO₂ + NO₃ and NH₄⁺ were measured using standard methods of SFS-EN ISO 11905-1, SFS-EN ISO 13395 and SFS 3032, respectively. pH (H₂O) was measured from the filtered vadose water samples in the laboratory using a PHM 92 Radiometer (Copenhagen).

Statistical analyses

Field measurements of N₂O in the peatland buffer

The statistical package SPSS ver. 15 was used for calculations. Pearson's correlation was computed to explore possible relationships between pH or soil temperature and N₂O. For the relationships with water table, Spearman's correlation was chosen. Differences in N₂O fluxes or the water table level between the different parts of the study site were tested using a linear mixed model. The statistical model for y_{ijklms} , the ln-transformed measured N₂O during snow-free period [$\ln(N_2O + 5)$], was

$$y_{ijklmr} = c_0 + T_i + D_j + Q_k + T_i Q_k + Y_l + S_m + c_1 W + e_{ijklmr}, \quad (1)$$

where c_0 is the constant; T_i ($i = 1-5$) denotes the study transect effect; D_j ($j = 1-4$) denotes the effect of relative distance to the ditch delineating the buffer from one side, $j = 1$ when the collar is closest to the ditch as compared with other collars on the same transect, and $j = 4$ when it is farthest from the ditch; Q_k ($k = 1$ or 2) stands for the influence of an overland flow path, Q_1 is for the measurement collars that are within the influence of an overland flow path, and Q_2 is for the other collars; Y_l ($l = 2003-2006$) stands for a study year; S_m ($m = 1$ or 2) is the season effect, S_1 is for the season from April to August and S_2 for the season from September to December; c_1 is a regression coefficient and W is the water table depth (cm); and e_{ijklr} is the error term for the r th repeated measurement of the collar ijk within season l .

In addition to the variation in the N₂O flux, the variation in the water-table depth was analysed using a similar model, but with untransformed values and without any continuous covariate.

The observations were correlated in space and time. The spatial correlation was taken into account in the model by fixed spatial terms transect (T_i), distance to the ditch (D_j), vicinity of an overland flow path (Q_k), and depth of the water table (W). The time correlation was taken into account by fixed year and season effects. In addition the correlations of the residuals were modelled by a first order autoregressive cov-

ariance structure for the residuals of the consecutive measurements of a random season within year within collar subjects. The normality of the marginal distribution of the residuals and the homogeneity of the variance of the residuals were checked graphically, and selection of the covariance structure was based on Akaike's information criteria.

N₂O accumulation experiment

We observed differences both in the total amount and rate of N₂O formation in the bottles. We therefore described the N₂O accumulation rate kinetics with the formula sigmoid:

$$F_{\text{N}_2\text{O}} = a \left(1 + e^{\left[\frac{-(n-x_0)}{b} \right]} \right)^{-1} \quad (2)$$

where $F_{\text{N}_2\text{O}}$ is the N₂O accumulation rate; a is the parameter denoting the maximal N₂O concentration predicted by the model for each bottle; n is the time in hours from the bottle closure to the maximal N₂O concentration in the bottle; b determines the shape of the sigmoid, i.e. relates to the rate of N₂O formation; and x_0 is the turning point of the sigmoid projected on abscissa corresponding to $a/2$ on the ordinate. The differences between the different peat layers and locations within the buffer zone in respective parameter values a and b were tested using ANOVA. The parameter estimates of each separate sigmoid were downweighted by $1/\text{SE}$ (standard error of the parameter estimate) in order to reduce the impact of uncertainty in some estimates, e.g. due to the smaller number of accepted measurements during the incubation period. Differences in the amount and the rate of N₂O accumulation were tested between profiles and seasons (autumn 2005 and spring 2006).

Nitrogen addition experiment

The values of N₂O fluxes were ln-transformed with a linear shift [$\ln(\text{N}_2\text{O} + 4)$]. ANOVA was used for testing the differences in N₂O emissions between the different fertilization levels and controls, or the distance of the sample from the

cooling fan in the greenhouse cabin. Interactions between the parameters were also tested. SPSS uses the Satterthwaite formula to approximate degrees of freedom for F in the analyses.

Results

Field measurements of N₂O in the peatland buffer

In the spruce swamp, N₂O fluxes differed with changing water-table levels and between the transects (ANOVA: $F_{1,528} = 26.6$, and $F_{4,285} = 7.8$, respectively, $p < 0.0005$, Figs. 1 and 2). Transect 3 with high N₂O emissions (mean = $1.27 \text{ mg m}^{-2} \text{ d}^{-1}$, 95%CL = 0.95–1.59) differed from the other transects. The highest N₂O efflux rates were observed at a low water-table level (Fig. 2 and Table 2). N₂O fluxes were higher ($F_{1,274} = 16.2$, $p < 0.0005$) in collars near the surface-water flow paths (mean = $1.03 \text{ mg m}^{-2} \text{ d}^{-1}$, 95%CL = 0.78–1.29; Fig. 3) than in the collars not affected by such water flows (mean = $0.38 \text{ mg m}^{-2} \text{ d}^{-1}$, 95%CL = 0.21–0.55). As such, the surface-water flows influenced the N₂O emissions irrespective of the distance from the water inlet. With the exception of the continuously wet transect 1, the N₂O flux rate correlated negatively and significantly with water-table depth variations: low water table conditions were associated with high N₂O emissions (Table 2). Emissions of N₂O increased when the water-table

Table 2. Significant ($p < 0.05$) Spearman correlations between the depth of water table and fluxes of N₂O by transect, calculated separately for sampling points close to (OWF) or far from (N-OWF) overland water flow paths. Non-significant correlations are indicated by ns, n.a. denotes that OWFs did not occur in the reference transect 5.

Water table level with transect	N ₂ O, OWT	N ₂ O, N-OWT
1	ns	ns
2	-0.498 ($p < 0.001$)	-0.279 ($p = 0.019$)
3	-0.591 ($p < 0.001$)	ns
4	-0.310 ($p = 0.008$)	ns
5	n.a.	-0.213 ($p = 0.015$)

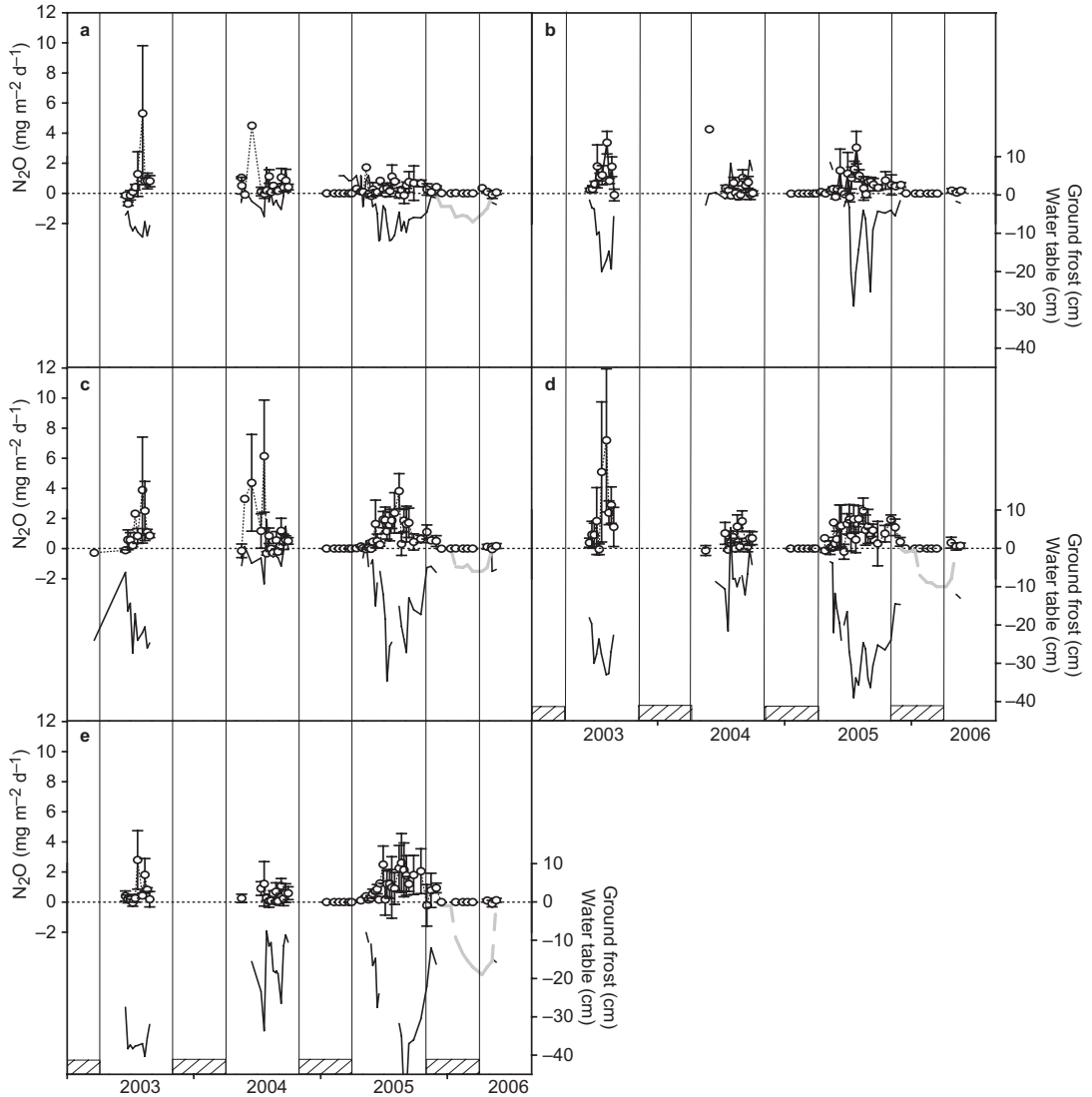


Fig. 2. The daily mean \pm SE nitrous oxide (N_2O , mg m⁻² d⁻¹) flux, water tables (solid lines, cm) and ground frost (grey lines, cm) at different distances from the sedimentation pond (transects 1–4, a–d, respectively) and transect 5 (e). Winter periods are shown as the hatched areas.

level dropped below -20 cm, and persisted until the water-table level increased again. However, this correlation was obvious only at the measurement points that were close to the overland water flow-paths. A similar, but weaker correlation was found for transects 2 and 5, which were not influenced by overland flow. In both cases, the correlation was due to a single measurement point out of four points on the transect. In winter, N_2O fluxes differed among the years (ANOVA: $F_{1,112} = 10.5$, $p = 0.002$) and between positions

in respect to the water inlet (sedimentation pond, $F_{4,112} = 2.8$, $p = 0.029$). Emissions of N_2O correlated positively with soil temperature at all measured depths.

N_{tot} in surface and subsurface waters was mainly in an organic form. Only low concentrations of NH_4^+ and $NO_2 + NO_3$ were found in the incoming and outflowing waters of the buffer zone (Fig. 4). The concentrations of N_{tot} and $NO_2 + NO_3$ were higher in the outflow than in the inflow. Assuming that the inflow and the outflow

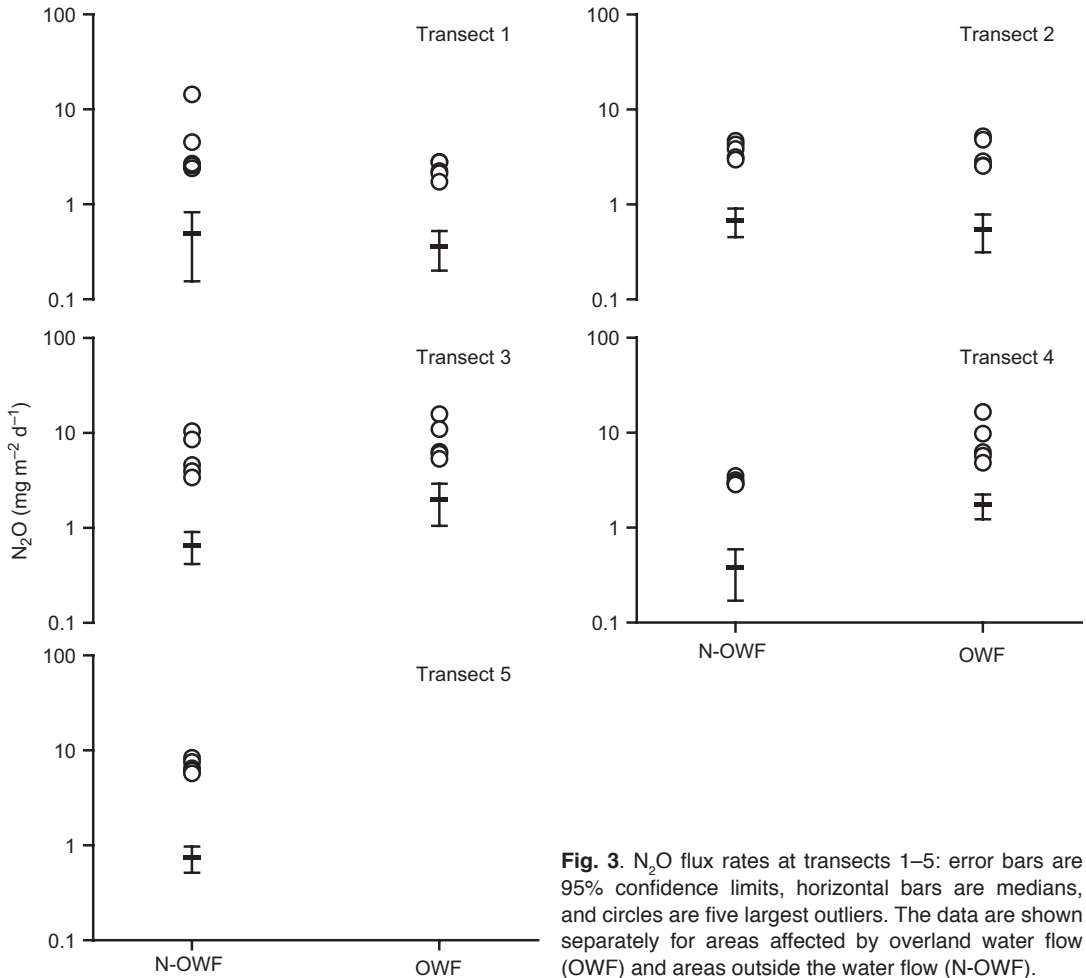


Fig. 3. N_2O flux rates at transects 1–5: error bars are 95% confidence limits, horizontal bars are medians, and circles are five largest outliers. The data are shown separately for areas affected by overland water flow (OWF) and areas outside the water flow (N-OWF).

rates were relatively similar, the retention of N in the buffer zone was not complete.

The pH of vadose water followed the peat quality pattern in that low values were associated with the *Sphagnum* peat area (Table 3). The dynamics of pH were similar in all transects, showing high variability in spring. The highest values were observed after midsummer, and the lowest values in winter.

Averaged water-table levels over the snow-free season differed among transects and years ($F_{1,528} = 26.6$, $p < 0.0005$), in all transects with the exception of transects 1 and 2, both located near the inflow of the buffer zone. At transects 1 and 2, the water table remained above -20 cm for most of the study period (Fig. 2), whereas at transects 3 and 4 water tables deeper than

-20 cm were observed. The driest years 2003 and 2005 caused significantly lower water tables in comparison with the other years. An interaction was observed between the location in respect to the water inflow area (denoted by “transect” in Eq. 1) and the presence of surface water bypass flow (denoted by “overland flow”, respectively) close to the collar ($F_{3,273} = 11.5$, $p < 0.0005$, Fig. 3). Ground frost extended to the deepest soil profiles at transects 4 and 5 with the lowest water table (Fig. 2).

N_2O accumulation experiment

N_2O accumulation (g/g peat dry mass) was highest at the peat depths close to the water-table level

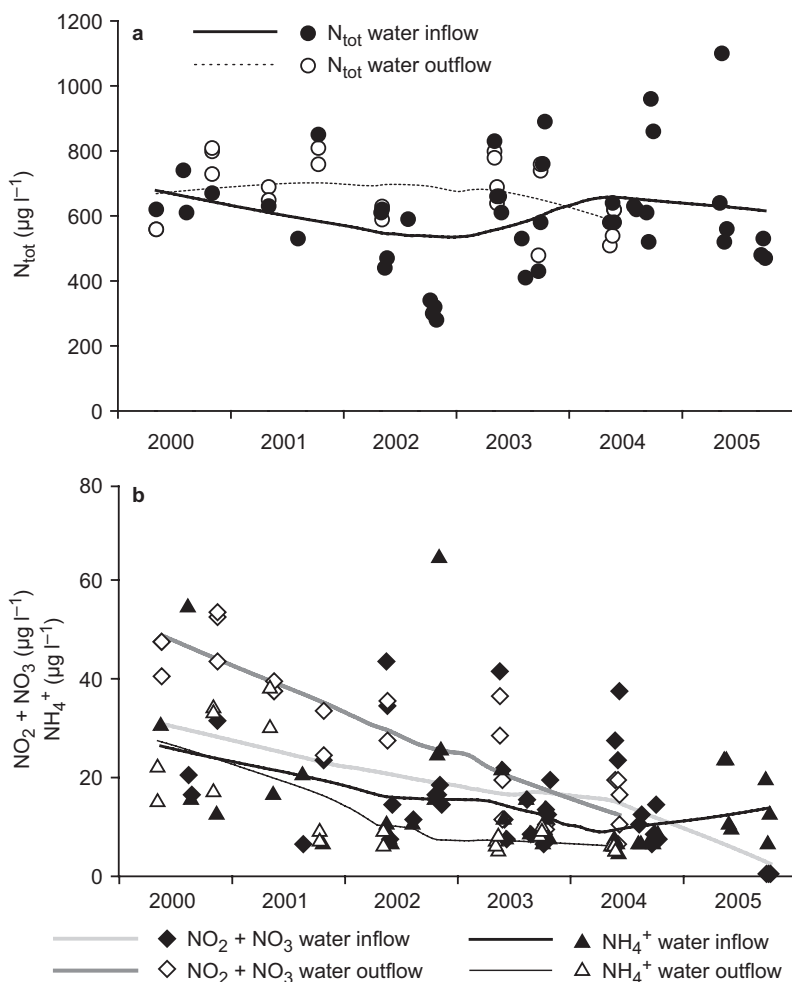


Fig. 4. Concentrations of (a) total nitrogen (N_{tot}), and (b) nitrite + nitrate ($\text{NO}_2 + \text{NO}_3$) and ammonium (NH_4^+) in the water inlet and outlet from spring 2000 to autumn 2005.

during the coring except at transect 4 in autumn and at transect 5, where the water-table level was below the cored peat layer (Fig. 5). The rates of N_2O accumulation were lower in the deeper-peat horizons than those near the soil surface. The rate of N_2O accumulation was slightly slower in spring than in autumn ($F_{1,2} = 9.1, p = 0.083$), and

Table 3. The median values of pH in vadose water with minimum and maximum at different distances from the sedimentation pond (transects 1–5).

Transect	Median	Min–max
1	5.15	4.52–5.99
2	5.05	4.58–6.53
3	4.79	4.33–6.39
4	5.75	4.74–6.60
5	5.84	4.54–6.56

accumulation commenced more rapidly along transects 1 and 3 than along 4 and 5 ($F_{3,9} = 19.1, p < 0.0005$ between profiles). The production potential at transect 5 differed significantly from that at transects 1, 3, and 4. The rate of N_2O accumulation correlated positively with the maximum concentration in the bottle. ANOVA also revealed an interaction between sample depth in the peat profile and season ($F_{2,21} = 4.8, p = 0.019$), indicating that the accumulation was higher at different depths in spring than in autumn.

Bulk density explained over 70% of the variance in the N_2O accumulation of the peat samples ($F_{1,45} = 35.6, p < 0.0005$, Fig. 6). The apparently nonlinear relationship between bulk density and N_2O indicated that the highest N_2O accumulation rates occurred in the loose surface peat layers while the densest, deeper peats showed lower

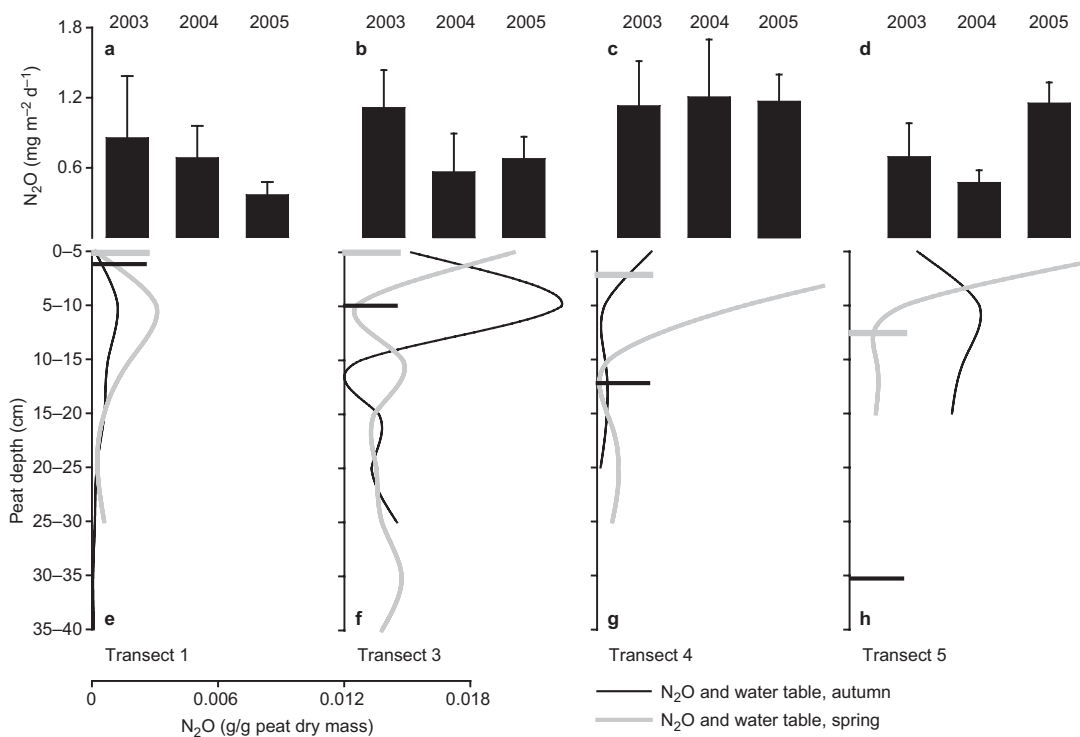


Fig. 5. (a–d) Mean \pm SE N_2O emissions during the non-frost period in the years 2003–2005. (e–h) Peat depth profiles (0–40 cm) of maximum N_2O accumulation. The curves (black and grey) represent the spring and autumn measurements of N_2O accumulation. Horizontal bars show the water table level (cm) in sampling points during the peat sampling.

rates. The absolute distance of the sample depth above or below the water table level at coring time explained over 25% of the variance in the potential N_2O accumulation inside the buffer zone ($F_{1,37} = 12.6, p = 0.001$).

Nitrogen addition experiment

N_2O effluxes differed from those of the control at all fertilization levels, except at the lowest level of $1.25 \text{ kg N ha}^{-1}$ (Fig. 7). Clear differences were noted in headspace temperatures close to or farther away from the cooling fan of the incubation cabin. However, this did not significantly affect N_2O emissions. A high proportion of the added N was released as N_2O (Fig. 8), and the highest proportion (over 50%) corresponded to an addition of 10 kg N ha^{-1} . The lowest and the highest additions produced proportionally the lowest amounts of N_2O .

Discussion

Field measurements

Most of the field measurements of N_2O showed a low rate of net emissions or consumption. However, some higher episodic fluxes were measured (Fig. 3). The highest emissions occurred when the water table was deep (Fig. 2), a condition typical for drained peatland forests (*see e.g. Martikainen et al. 1993, Wolf and Brumme 2002, Maljanen et al. 2010*). The temporally most covering data set was collected from July 2005 until June 2006. Similar to the findings of Wolf and Brumme (2002), N_2O fluxes in the buffer zone were highest in summer and lowest in winter. From April to May, the buffer zone N_2O emissions varied from -1.0 to $4.3 \text{ mg m}^{-2} \text{d}^{-1}$, from June to September from -2.7 to $16.5 \text{ mg m}^{-2} \text{d}^{-1}$, and from October to March -0.5 to $2.9 \text{ mg m}^{-2} \text{d}^{-1}$. Average N_2O emission during the snow free period, $0.83 \text{ mg m}^{-2} \text{d}^{-1}$, is compa-

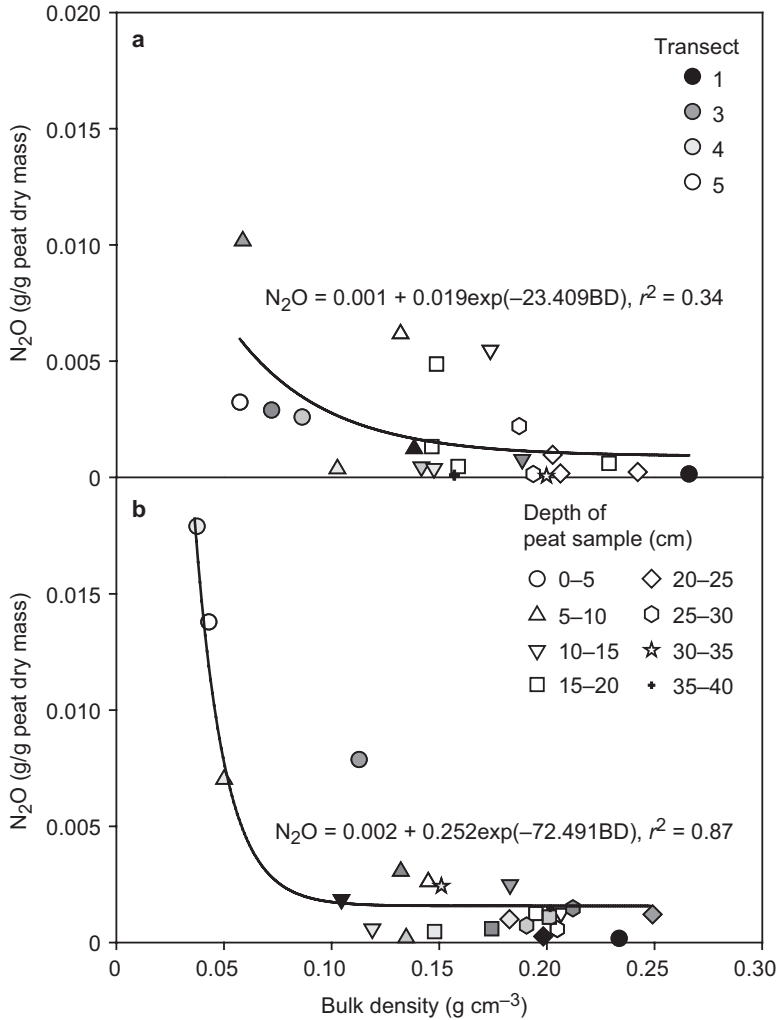
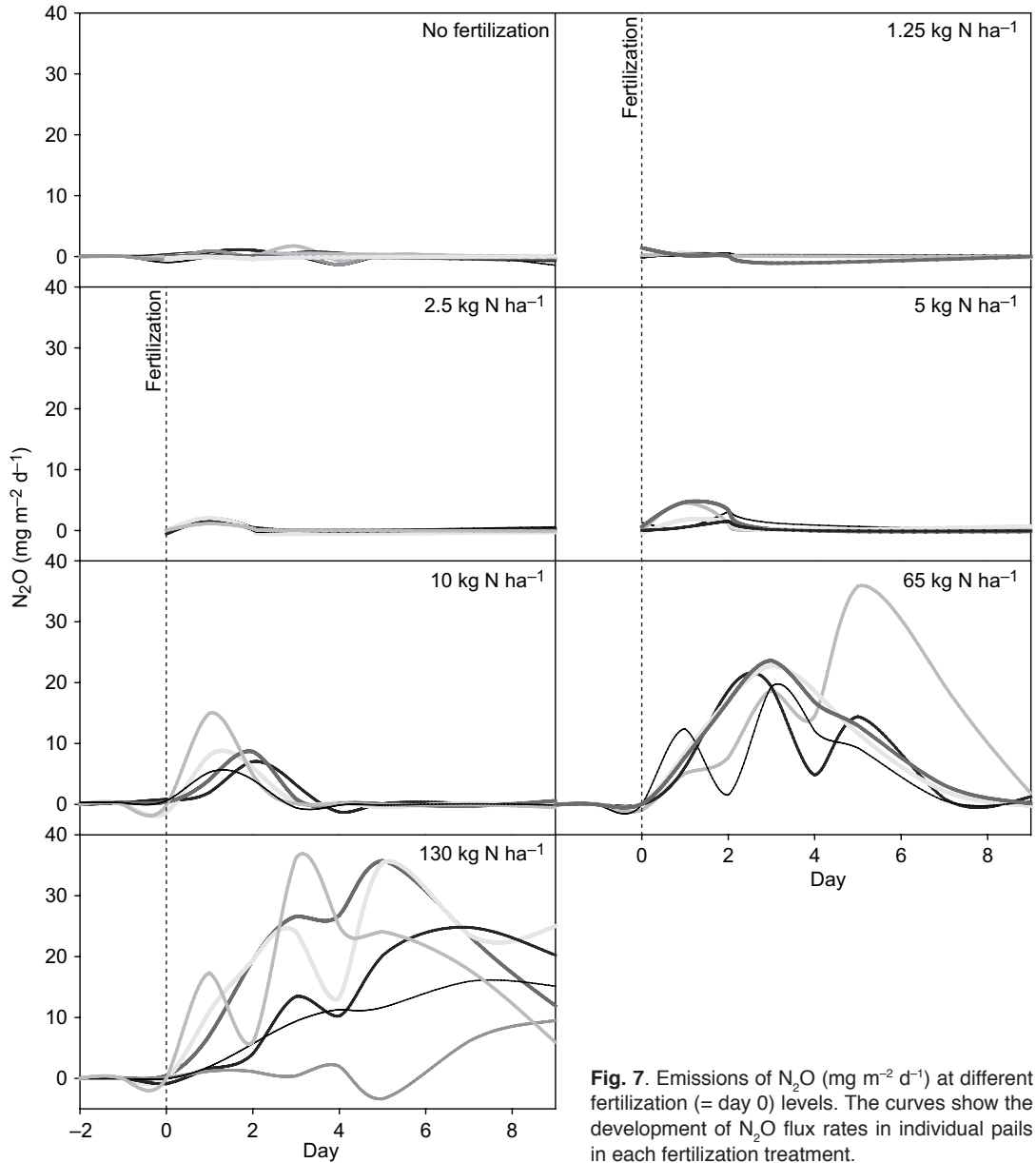


Fig. 6. Correlations of maximal N₂O accumulation and bulk density of the peat sample (g cm⁻³) in (a) autumn 2005, and (b) spring 2006. The regression curves fitted to the autumn and spring data sets should be considered indicative only.

rable to those reported earlier by Martikainen *et al.* (1993) and Ojanen *et al.* (2010). For forest land in Fennoscandia, our fluxes were typical or near the lower range of reported values; e.g. Ernfors *et al.* (2007) calculated an annual average efflux of 0.85 mg N₂O m⁻² d⁻¹ (from 0.03 to 12.08 mg N₂O m⁻² d⁻¹) for drained organic forest soils, and Alm *et al.* (2007) gave a range of 0.82 to 2.22 mg N₂O m⁻² d⁻¹ for spruce mires. No annual net N₂O consumption was reported either by Ernfors *et al.* (2007) or Alm *et al.* (2007).

We expected that field emissions would be higher as buffer zones are reported to have been enriched by nutrients and solids received from the catchment as a result of forestry operations (see e.g. Kubin 1998, Nieminen 1998, Nieminen 2004, Palviainen *et al.* 2004, Mannerkoski *et al.*

2005, Piirainen *et al.* 2007). The main reason for the low N₂O efflux was probably due to the low availability of substrates coming from the managed catchment. Incoming N was mainly in an organic form and the concentrations of NO₃⁻ and NH₄⁺ in the inflow to the buffer zone were low during the 2–8 year period after forestry operations (Table 1 and Fig. 4). Piirainen *et al.* (2007) reported an average N leaching rate of 0.5 kg ha⁻¹ a⁻¹ from managed upland forests that are comparable to the catchment in this study and such a value is clearly not high enough to support high N₂O production in the buffer zone. Nevertheless, under some conditions, ditch cleaning, N fertilization or clear-cutting on the upper catchment may release higher concentrations of inorganic N to the buffer zone and N₂O



emissions may be higher than we have measured and reported here.

Successful rewetting normally results in a rapid suppression of N_2O efflux to a level similar to undrained peatland forests (Freeman *et al.* 1993, Regina *et al.* 1999). Similarly in our study, the average N_2O efflux in the center of the buffer zone (transect 3) was higher than that from near the water inlet (the wettest transects 1 and 2). Therefore, the rate and volume of N_2O accumu-

lation for the continuously water-saturated peat layers were low (Fig. 5). Similar observations have been published for riparian wetlands and for agricultural sand, silt and clay fields (Clément *et al.* 2002, D'Haene *et al.* 2003).

Unlike flooded wetlands constructed for municipal waste water treatment, buffers receive only a weather-dependent water input from the catchment and both higher and lower water tables may be found throughout the year (Fig. 2).

The dynamics in the water level and peat oxygen conditions may influence N removal as reviewed by Lee *et al.* (2009). The significant interaction of surface flow pattern and water table depth, visualized in Fig. 3, might be interpreted as follows: During higher inflow periods the buffer zone was more enriched by N near the surface water channels in comparison to areas with a slower, predominantly subsurface level water movement. When the water flow diminished during drier periods, more oxygen penetrated the “nitrogen charged” soil, and caused a moderate “discharge” of N_2O (transects 3 and 4 in Fig. 3). Similar, but stronger episodic N_2O emissions may occur in constructed wetlands used for water purification (reviewed by Mander *et al.* 2008: table 1). These results reflect the complex origin of N_2O from different processes that typically produce N_2O as a by-product, especially when conditions are unfavorable, i.e. too wet for complete nitrification or too dry for complete denitrification.

Laboratory measurements

Fertilization levels higher than 10 kg N ha⁻¹ tended to cause two or multiple peaks in the headspace N_2O concentrations during the measurement period (Fig. 7). One explanation to those increasing and decreasing N_2O concentrations that eventually were followed by a gradual N_2O depletion in the headspace, may be the fact that the headspace samples repeatedly drawn to syringe were compensated by pure N_2 , and the N_2O formation just temporarily decreased or stopped. Another explanation may be a relative rise of N_2O reducing microbial activity, but we have no direct evidence. Even with these uncertainties concerning the processes in the bottles, our interpretations on the initial rise of the concentration are not compromised.

The highest N_2O accumulation was measured in peat samples that originated from a depth close to the water-table level at the time of coring (Fig. 5). In the field, N_2O in the uppermost oxic peat profile may be produced by nitrification that produces NO_3^- from NH_3 and NO_3^- may subsequently leach downwards to the increasingly hypoxic peat layers, and potentially support den-

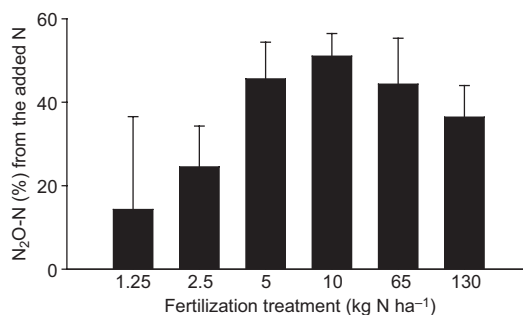


Fig. 8. Proportion (+ SE) of added N released as N_2O-N in the laboratory experiment.

itrification and N_2O production there (Regina *et al.* 1996). Hence, the most optimal conditions for denitrifying organisms are found near the oxic-anoxic interface. Our bulk density data (Fig. 6a) suggest that the most effective N_2O production occurs in the loose surface peat layers from 0 to 15 cm below the soil surface. In contrast, the deeper, more dense peat layers below the water table show a consistently lower N_2O production capacity. The laboratory potentials seem to peak at or above the prevailing water-table depth at the time of peat sampling in the field in spring or autumn (Fig. 5). At transects 3 and 4 (Fig. 3), the highest flux rates also occurred in buffer areas directly affected by overland flow water paths. Similarly, the maxima of N_2O concentrations in the accumulation experiment were usually achieved more rapidly during the incubation experiment in the cores taken near the wet areas of the buffer (data not shown). Such reactions suggests that the N_2O forming microbial population is larger or in a more active state in the flooded areas. The microbial activity may be maintained through a small but persistent flow of mineral N in the inflow water, or by other conditions, e.g. hypoxia in the surface peat layers.

Comparison of field and laboratory measurements

Despite the high responsiveness to N addition (Fig. 8) and high rate of N_2O accumulation under controlled and optimal conditions (Fig. 5), the bulk of N_2O emissions in the field were typically low for the studied peatland (Fig. 2). Peat soils are potential sources of N_2O because of their

high N content (Regina *et al.* 1996). However, N is mainly in an organic form (Fig. 4) and not usable for denitrification. A high water table level does not allow nitrification, which could modify organic N to an inorganic form and a suitable reactant for denitrification.

High inflows of N, such as those reported by Silvan *et al.* (2002), could result in N₂O emissions comparable to those observed in the nutrient-addition experiments at optimal temperatures. As the buffer-zone peat in the laboratory incubations showed a high potential for N₂O production, minor inorganic N additions should increase N₂O emissions significantly in summer time making buffers potential hot spots (Fig. 7). However, areas used as buffers are small in Finland. If all peatland forests in Finland (ca. 5.7 Mha) were equipped with buffer zones, the total area of those buffers would be about 57 000 ha. However, in reality the area remains much smaller, a few thousand ha only, since most of the buffer zones created tend to become very small. N₂O emissions from such a small area would have to be exceptionally high to have a considerable climate impact. Instead, high emissions may appear in the catchments above the buffer zone particularly if peatland forests are fertilized according to forestry guidelines (approximately 100 kg N ha⁻¹ is proposed). In most cases, N fertilization is not put into practice and, therefore, the risk of peatland forests becoming N₂O hot spots is negligible.

The nutrient addition experiment indicated high N₂O emissions even at low inorganic N additions and supported our hypothesis that peatland buffers may become N₂O hot spots, as reported by Silvan *et al.* (2002). However, the laboratory measurements were made under a temperature regime and artificial anoxia conditions that were different from conditions in the field. Although the laboratory data indicated a high potential for N₂O production, the low inorganic N availability did not result in the creation of N₂O hot spots in the peatland buffer zone, even near the water inlet.

Conclusions

N₂O efflux in the field was relatively low throughout the years of this study. This con-

firms that the low leaching of mineral N from our forestry catchment areas ensured that the inorganic N concentrations in the buffer zone inflow remained low and typical of humic waters in general in Finland. The low observed N₂O fluxes indicated that forestry operations (clear-cutting, thinning, fertilization and ditch cleaning) in the catchment did not enrich the buffer zone with N over a period of nine years. Instead, the laboratory incubation results of the peat samples showed that N₂O producing microorganisms existed throughout the buffer zone and had a high potential to process both minor and major loads of added inorganic N under optimal conditions. This study does not support the postulate that peatland buffer zones may become a significant source of N₂O due to the N load from the applied forestry operations in the catchment, but emphasizes the fact that the microorganisms are present and ready for any high mineral N inputs.

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