

Gas concentration driven fluxes of nitrous oxide and carbon dioxide in boreal forest soil

By M. PIHLATIE^{1*}, J. PUMPANEN², J. RINNE¹, H. ILVESNIEMI^{2,3}, A. SIMOJOKI⁴, P. HARI² and T. VESALA¹, *Department of Physical Sciences, University of Helsinki, P.O. Box 64, 00014, Finland*
Department of Forest Ecology, University of Helsinki, P.O. Box 27, 00014, Finland
Finnish Forest Research Institute, Vantaa Research Unit, P.O. Box 18, 01301 Vantaa, Finland
Department of Applied Chemistry and Microbiology, University of Helsinki, P.O. Box 27, 00014, Finland

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ABSTRACT

Nitrous oxide (N₂O) and carbon dioxide (CO₂) fluxes were measured in a boreal forest during two growing seasons with soil gradient and chamber methods. N₂O fluxes obtained by these two techniques varied from small emission to small uptake. N₂O fluxes were of the same order of magnitude, however, the fluxes measured by the soil gradient method were higher and more variable than the fluxes measured with chambers. The highest soil gradient N₂O fluxes were measured in the late summer and the lowest in the autumn and spring. In the autumn, litter fall induced a peak in N₂O concentration in the organic O-horizon, whereas in the spring N₂O was consumed in the O-horizon. Overall, the uppermost soil layer was responsible for most of the N₂O production and consumption. Soil gradient and chamber methods agreed well with CO₂ fluxes. Due to the very small N₂O fluxes and the sensitivity of the flux to small concentration difference between the soil and the ambient air, the flux calculations from the O-horizon to the atmosphere were considered unreliable. N₂O fluxes calculated between the soil A- and O-horizons agreed relatively well with the chamber measurements.

1. Introduction

Boreal forest zone is the largest forested region in the world covering approximately 11% of the total land area (Archibold, 1995). This zone plays an important role in the global balance of atmospheric trace gases such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O). Soil CO₂ flux has been intensively studied in the boreal forest region during the last decade (Widén and Majdi, 2001; Shibistova et al., 2002; Pumpanen et al., 2003; Niinistö et al., 2004; Kolari et al., 2004 and 2006). Research on N₂O emissions has concentrated on managed environments, such as fertilized or drained, boreal forest ecosystems (e.g. Martikainen, 1985; Sitaula et al., 1995; Priha and Smolander, 1999; Maljanen et al., 2003) and very little is known on N₂O fluxes from natural forest ecosystems.

CO₂ and N₂O are produced by the metabolism of soil organisms: CO₂ via microbial and root respiration (Gaudinski et al., 2000; Chapin and Ruess, 2001) and N₂O via microbial nitrification and denitrification (e.g. Robertson and Kuenen, 1991). Major factors regulating soil CO₂ production are the amount

and quality of organic matter in the soil, soil temperature and soil moisture, and photosynthetic activity of leaves (Kirschbaum, 1995; Davidson et al., 1998; Prescott et al., 2000; Högberg et al., 2001). The same factors affect the production of N₂O in the soil (Schindlbacher et al., 2004), however, the availability of ammonium (NH₄⁺) and nitrate (NO₃⁻) are the key regulators of N₂O production, as NH₄⁺ is the precursor for nitrification and NO₃⁻ that for denitrification.

According to Ambus et al. (2006) the N₂O production in European forest ecosystems is mostly driven by nitrification since that is the sole source of NO₃⁻ for denitrification. Non-fertilized forest ecosystems receive nitrogen (N) only from the atmosphere and hence regions with low N deposition, such as boreal forests in Finland, are largely N limited. In the boreal upland forest soils, the mineral N is predominantly ammonium, and the soil nitrate content and nitrification activity are very low (Priha and Smolander, 1999; Priha et al., 1999). Hence, N₂O emissions from boreal upland forest soils are expected to be small.

Fluxes of N₂O and CO₂ in soil are examples of biophysical phenomena, where the biological gas production creates spatial concentration gradients that are dissipated by physical transport mechanisms (Stepniewski et al., 2002). Molecular diffusion is the most important gas transport mechanism in the soil. Its

*Corresponding author.
e-mail: mari.pihlatie@helsinki.fi
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magnitude depends on the total porosity, the pore-size distribution and the amount and continuity of air-filled pores in the soil (e.g. Glinski and Stepniewski, 1985; Sijmojoki, 2001; Stepniewski et al., 2005). As the rate of molecular diffusion in air is 10 000-fold compared to that in water, the amount of water critically determines the rate of diffusion within the soil. If the gas transport characteristics and concentrations in the soil are known, the transport of gases from the soil to the atmosphere can be calculated.

The soil gradient method, the calculation of gas fluxes based on concentration differences between the soil layers or between the top-soil layer and the atmosphere, has recently become increasingly popular in studying CO₂ emissions (Šimůnek and Suarez, 1993; Fang and Moncrieff, 1999; Pumpanen et al., 2003; Jassal et al., 2004; Tang et al., 2005). The soil gradient method agrees relatively well with the fluxes determined by conventional chamber techniques for CO₂ (e.g. Tang et al., 2005). Only a few studies report soil N₂O concentration measurements (Nefitel et al., 2000; Flechard et al., 2005) and comparisons of fluxes calculated from soil gas profiles to fluxes measured with enclosure techniques (Hosen et al., 2000; Kim and Tanaka, 2002).

The aim of our study was to quantify the soil N₂O fluxes in a boreal forest and to assess the factors regulating the N₂O production or consumption. We estimated the fluxes using soil gradient and chamber methods. We hypothesize that the soil gradient method can be used for determining fluxes of N₂O between the soil and the atmosphere. To test our hypothesis we tested the applicability of the soil gradient calculation with CO₂ that has large concentration gradients and therefore high fluxes between the soil and the atmosphere. Then we applied the same model for N₂O that has the same molecular weight as CO₂. The fluxes determined by the soil gradient method for both trace gases were then compared to those measured by chambers. We also identified the soil layers responsible for N₂O production or consumption from the concentration gradients.

2. Methods and site description

2.1. Measurement site

The measurements were conducted at Station for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) measuring station in a 40-yr-old Scots pine (*Pinus sylvestris* L.) forest in Southern Finland (61° 51'N, 24° 17'E) (Hari and Kulmala, 2005). The site is located on a hill approximately 180 m a.s.l.. According to the FAO-Unesco soil classification system, the soil is a Haplic Podsol on glacial till (FAO-Unesco, 1990). The soil is characterized by an organic O-horizon and subsequent eluvial (A-) and illuvial (B-) horizons and parent material (C-horizon). The O-horizon comprises of an approximately 4-cm-thick litter layer and an approximately 1-cm-thick humus layers. The chemical and physical characteristics of the soil are presented in Table 1.

Scots pine (*Pinus sylvestris* L.) is the dominant tree species in the forest with a few scattered Alder (*Alnus incana* (L.) Moench) and Aspen (*Populus tremula* L.) trees. The herb-layer vegetation is dominated by *Vaccinium myrtillus* L. and *Vaccinium vitis-idaea* L. and the ground vegetation consists of mosses *Dicranum polysetum* Sw., *Hylocomium splendens* (Hedw.) B.S.G., and *Pleurozium schreberi* (Brid.) Mitt. The annual mean temperature during 1961–1990 in the area was +2.9 °C, January the coldest month (mean –8.9 °C) and July the warmest (mean +15.3 °C). The 30-yr mean annual precipitation at the site was 709 mm (Drebs et al., 2002). The year 2002 was exceptionally dry with an annual precipitation of 535 mm at the weather station of the Finnish Meteorological Institute in Hyytiälä. The atmospheric nitrogen deposition on the site is approximately 5 kg N ha⁻¹ yr⁻¹ (Kulmala et al., 1998).

2.2. Static chamber measurements of N₂O fluxes

The N₂O fluxes were measured with static chambers in six plots (1–6). Plots 2, 3 and 4 were collocated with soil gas collection pits

Table 1. Soil extractable ammonium (NH₄⁺) and nitrate (NO₃⁻), total carbon and total nitrogen contents, carbon to nitrogen ratio, soil acidity and soil texture in different soil horizons at Hyytiälä

Horizon	NH ₄ -N	NO ₃ -N mg N kg ⁻¹ soil ^a	C % ^b	N % ^b	C:N ^b	pH ^b CaCl ₂	Texture ^b		
							Clay%	Silt%	Sand%
O	10.2	1.4	33.0	1.1	30.6	3.2	n.d.	n.d.	n.d.
A	4.5	1.5	4.1	0.11	34.3	3.8	9.4	17.5	60.5
B	–	–	0.34	0.004	85.7	4.5	7.0	13.4	51.6
C	–	–	0.23	0.01	23.0	4.5	7.8	17.4	55.0

^aAverage of measurements on 3 June 2002, 1 November 2002, and 4 June 2003. The concentrations of NH₄⁺ and NO₃⁻ in the O-horizon are averages from litter and humus layers.

^bHaataja and Vesala (eds.) (1997)

and are later referred to as pit 160, 130 and 70, respectively. One rectangular 0.29 m × 0.40 m stainless steel collar was installed in each plot 1 month before starting the flux measurements. The fluxes were measured weekly or fortnightly during the snow free period between 6 June 2002 and 31 July 2003, and once per month in the winter. The measurements (June 2002–June 2003) were started by closing the collars with a 0.20 m high stainless steel chamber fitted with a rubber septa, cellular rubber sealing and a battery powered fan. In June–July 2003, the collars were closed with a polyethylene plate to make the chamber headspace smaller and improve the sensitivity of the measurement. Four 20 ml gas samples were drawn from the chamber at 2, 20, 40 and 60 min after closing the chambers. In addition, air temperatures inside and outside the chamber were recorded at the time of gas sampling.

During the snow-covered period N₂O fluxes were measured twice (14 February 2003 and 27 March 2003) with the closed chamber technique and once (20 February 2003) with the snow gradient technique (Sommerfeld et al., 1993). Before the chamber measurements the snow was removed from the soil surface and the chamber was placed on the ground and made gas-tight by compacting the edges of the chamber with snow. Four gas samples were collected during a 2-hr enclosure with the same procedure as described above.

2.3. Dynamic chamber measurements of CO₂ fluxes

Soil CO₂ fluxes were measured with two (2002) or three (2003) automatic flow-through soil chambers (Pumpanen et al., 2001). The chambers were operated throughout the year; however, here we present data only from the snow free periods. Two chambers were located within a distance of 1–3 m from the soil gas collection pits 70 and 160 (in 2003), and one adjacent to the N₂O chamber in plot 1. The chambers were transparent (inner diameter 20 cm, height 20 cm) and operated once an hour. During one measurement the chambers were closed for 240 s and the chamber air was drawn through heated polytetrafluoroethylene (PTFE) tubing to the infrared CO₂ analyser ('URAS 4', Manesmann, Hartman and Braun, Frankfurt am Main, Germany). Compensation air of known CO₂ concentration was pumped into the chamber at the same flow rate as the chamber air was pumped to the CO₂ analyser. The flow rates were adjusted with mass flow controllers (5850E, Brooks Instrument, Veenendaal, the Netherlands).

Plants were not removed from the chamber. Thus night-time flux values resulted from the respiration of ground vegetation and soil only, whereas daytime values are additionally influenced by the photosynthesis of ground vegetation. According to Kolari et al. (2006) the respiration of ground vegetation is very small compared to soil respiration. Therefore, we estimated the bulk soil surface respiration during the snow-free period by fitting the night time CO₂ flux values between hours 23 and 04 to the respective temperatures of the A-horizon with an exponential

function

$$r = \alpha e^{\beta T}, \quad (1)$$

where r is the CO₂ flux rate (g m⁻² s⁻¹), T is the temperature of soil in the A-horizon and α and β are parameters. The hourly measured temperatures in the A-horizon were then used to determine the actual soil CO₂ flux in the daytime. The chamber-type-specific measurement error in CO₂ fluxes was corrected using the correction factor according to Pumpanen et al. (2004).

2.4. Soil gas concentration measurements

Soil N₂O and CO₂ concentrations were measured once or twice per month in four pits, each at four soil depths. The gas collectors had been installed in pits 70, pit 100, pit 130 and pit 160 in 1995, with pit number indicating the total soil depth above bedrock (cm). Mean thicknesses of the soil O-, A-, B- and C-horizons are given in Table 2. Soil gas samplers were perforated and hollow nylon bars covered with a Gore-Tex PTFE 0.45- μ m membrane (W.L. Gore & Associates (UK) Ltd., Coating Division, Dundee, Scotland). The samplers were in the middle of each soil horizon at approximate soil depths of 3, 8, 19 and 54 cm from the topsoil in the O-, A-, B- and C-horizon, respectively.

Gas samples were drawn with a syringe connected to the sampler with a nylon tube. At each gas sampling, the gas sample was taken after first discarding a volume of air corresponding to that inside the nylon tube. Ambient air was sampled between June 2002 and March 2003 manually in four replicates at the approximate height of 50 cm above the soil surface. From March 2003 onwards the ambient air was collected at the height of 2 m, through a 22-m-long PTFE Teflon tube, to a 10-l glass bottle at a flow rate of 0.4 l min⁻¹. The air was sampled for 30 min after which the pump was stopped and the gas samples were drawn from the bottle through a septum.

When measuring the gradient in the snow, the gas samples were drawn from the pore space of snow with polypropylene syringes connected to a stainless steel tube with an inner diameter of 3 mm. Gas samples were taken by inserting the tube vertically through the snow pack and drawing the sample first from the soil surface (beneath the snow) and then from the snow surface.

Table 2. Parameters used in the calculation of gas transport functions (eqs. 6,7)

Horizon	u^a	h^a	l^b	E_{tot}^c
O	0	1.1	0.050	0.70
A	0	1.4	0.054	0.61
B	0	1.4	0.17	0.58
C	0	1.4	0.54	0.50

^aEmpirical parameters from Glinski and Stepniewski (1985).

^bSoil layer thickness (m).

^cSoil total porosity (m³ m⁻³), Source: Mecke and Ilvesniemi (1999).

Volumetric snow samples, adjacent to each measurement location, were taken and weighed in order to estimate the porosity of the snow. The porosity was calculated from the weight and volume of the snow assuming the density of pure ice (0.92 g cm⁻³).

2.5. Gas collection, storage and analysis

The gas samples from static soil chambers, soil gas samplers and from snow profiles were taken in polypropylene syringes (BD Plastipak 20, Drogheda, Ireland) equipped with three-way valves (BD Connecta Stopcock, Beckton Dickinson, Helsingborg, Sweden). Immediately after the sampling, the gas samples were transferred into pre-evacuated 12 ml glass vials (Labco Ltd., UK). The concentrations of N₂O and CO₂ were analyzed with a gas chromatograph equipped with an electron capture detector and a flame ionization detector (Hewlett Packard 6890) as described by Syväsalo et al. (2004). A set of five reference gases with increasing N₂O and CO₂ concentrations were analysed before and after the gas sample analysis.

2.6. Soil and litter measurements

Soil temperatures and moistures were measured in the same four pits and at the same soil depths as the soil gas concentrations. Soil temperatures were monitored at 15-min time intervals with silicon temperature sensors (Philips KTY81-110, Philips Semiconductors, Eindhoven, the Netherlands). Hourly mean soil temperatures were calculated from the raw data. Soil volumetric water content adjacent to the soil temperature sensors was measured at 1-hr intervals with a time-domain reflectometer (TDR, Tektronix 1502 C cable radar, Tektronix Inc., Redmond, WA). These soil moisture values were expressed as percentages of water-filled pore space (wfps%).

Extractable mineral nitrogen (NO₃-N and NH₄-N) was determined from litter, humus and mineral soil samples collected in June and November 2002 and June 2003. Fresh soil samples were extracted with 2 M KCl for 1 hr on a reciprocating shaker. Soil-to-solution ratios (SSR) for mineral soil, humus and litter layers were 1:10, 0.5:10 and 0.25:10, respectively. The extracts were filtered through Whatman 42 filter papers and stored at 4 °C for 1–3 days until analysis. Dissolved NH₄⁺ and NO₃⁻ in the extracts were analysed by flow-injection spectrometry (QuikChem8000 autoanalyser, Lachat Instruments, Milwaukee, USA).

Net N mineralization in the field was analysed from litter, humus and mineral soil samples collected from each chamber plot in 13 June 2005. In each plot, eight 2.5 cm diameter core samples were pooled to make 1 l, humus and mineral soil sample from each plot. Half of the pooled soil samples from each layer were taken to the laboratory (initial soil samples) for extraction and analysis. The other half was incubated for 4 weeks in the field in aerated plastic cylinders (105 cm³) in the soil (Potila and

Sarjala, 2004). In the laboratory, the initial soil samples and the field-exposed soil samples were extracted for 2 hr with 0.5 M K₂SO₄ (SSR 1:10 for humus and 2:10 for mineral soil). The extracts were filtered through a filter paper and frozen until analysis. Total dissolved N, NH₄⁺ and NO₃⁻ in the extracts were analyzed at the Finnish Forest Research Institute by flow-injection spectrometry (FIA Star 5020, Tecator). Net N mineralization rates of NO₃⁻ and NH₄⁺ were calculated from the difference between the N concentrations in the initial and incubated samples.

The litter fall from the tree canopy was collected with 21 funnels placed systematically on the measurement site. The funnels were 500 mm in diameter and 600 mm in height. The funnels were emptied every 3 months in 2002 and 2003 and fortnightly to monthly in 2005. The litter was dried at 70 °C for 24 hr and weighed. Different litter fractions were separated and weighed.

2.7. Emission calculations

2.7.1. Closed static chambers. Chamber fluxes of N₂O were calculated from the mass balance of the static chamber enclosure where the derivative was obtained from a linear fit of gas concentrations during the enclosure,

$$F_c = \frac{dC}{dt}h, \quad (2)$$

where F_c is the flux of N₂O (g m⁻² s⁻¹), C is the N₂O concentration in the chamber air (g m⁻³), t is time (s) and h the height of the chamber (m). As CO₂ concentration was analysed from the same chamber closure, measurements with a coefficient of determination (R^2) below 0.7 for the regression line of CO₂ concentration were discarded as poor quality data.

The detection limit of closed static chambers was estimated for a typical chamber enclosure. First, we calculated the 95% confidence interval (β) for the regression coefficient as

$$\beta = b \pm 4 SE, \quad (3)$$

where b is the regression coefficient and SE the standard error of the regression coefficient. As the regression was based on four data points (concentrations) the degrees of freedom was 2 ($n-2$). The 95% confidence band for the N₂O fluxes was calculated using the estimates for the upper and lower limit regression coefficients. In a typical chamber enclosure, when the N₂O flux was 0.4 μg N m⁻² h⁻¹ the 95% confidence band for the fluxes was -0.2 to 0.9 μg N m⁻² h⁻¹.

2.7.2. Dynamic chambers. The CO₂ fluxes from dynamic chambers were calculated based on the mass balance equation,

$$F_d = \frac{dC_i}{dt}h - \frac{q_1 C_0}{A} + \frac{q_2 C_i}{A}, \quad (4)$$

where F_d is the soil CO₂ flux (g m⁻² s⁻¹), h is the height of the chamber (m), A is the cross-sectional area of the chamber (m²), C_i the CO₂ concentration in the chamber (g m⁻³), t time (s), q_1 the flow of the compensation air (m³ s⁻¹), q_2 the air

flow to the analyser ($\text{m}^3 \text{s}^{-1}$), and C_0 the CO_2 concentration in the compensation air (g m^{-3}). The flux F_d was calculated at 5-s intervals during the first minute of chamber closure and expressed as the mean flux during the 1-min period.

2.7.3. *Snow and soil gas profiles.* The fluxes measured by the snow gradient method were calculated by the Fick's law of diffusion through porous media as

$$F_s = -D_0 E_g \frac{\Delta C}{\Delta z}, \quad (5)$$

where F_s is the gas flux ($\text{g m}^{-2} \text{s}^{-1}$), D_0 is the diffusion coefficient of the gas in air ($\text{m}^2 \text{s}^{-1}$), E_g the air-filled porosity of snow ($\text{m}^3 \text{m}^{-3}$), ΔC is the concentration difference between the bottom and the top of the snow pack (g m^{-3}) and Δz the depth of the snow pack (m). The value for diffusion coefficient in air (D_0) of $1.39 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ for N_2O and CO_2 was taken from Sommerfeld et al. (1993).

CO_2 and N_2O transport from the soil gas profiles was calculated based on the diffusion model adapted from Pumpanen et al. (2003). The model uses the measured CO_2 and N_2O concentrations in each soil layer, the diffusion coefficients for the gases in the soil, and soil porosity values for each soil layer as input variables. The gas fluxes between soil layers were calculated as follows,

$$F_i = -D_i \frac{C_{i+1} - C_i}{(l_i + l_{i+1})/2}, \quad (6)$$

where F_i is the flux from the soil layer i to the soil layer above it $i + 1$ ($\text{g m}^{-2} \text{ s}^{-1}$) ($i = 1, 2, 3$), D_i is the diffusion coefficient of the gas in the soil layer i ($\text{m}^2 \text{ s}^{-1}$), C_{i+1} is the gas concentration (g m^{-3}) in the layer $i + 1$ and C_i the gas concentration in the soil layer i , respectively and l_i and l_{i+1} are the thicknesses of soil layers (m), respectively. The soil layer pairs can be O-horizon–the atmosphere, A–O-horizon, B–A-horizon, C–B-horizon, respectively. In the case of the O-horizon – the atmosphere we assume that most of the resistance to the transport occurs in the soil: in this case D_i is that of the O-horizon and the distance $(l_i + l_{i+1})/2$ is simply the depth of the O-horizon divided by 2. We thus assume ambient atmospheric gas concentrations at the surface of the O-horizon. This is due to the rapid diffusion and partly turbulent flow regime of gases in the atmospheric air close to the ground.

The gaseous diffusion coefficients (D) in the soil were calculated from the diffusion coefficients in the air (D_0) according to Troeh et al. (1982),

$$\frac{D}{D_0} = \left(\frac{E_g - u}{1 - u} \right)^h, \quad (7)$$

where E_g is the air filled porosity of soil ($\text{m}^3 \text{m}^{-3}$) and u and h are empirical parameters obtained from the literature (Glinski and Stepniewski, 1985). D was determined separately for each layer and an average D of subsequent soil layers i and $i + 1$ weighed by the thicknesses of the layers was used as D_i in eq. (6). E_g was obtained by subtracting the volumetric water content from the

total porosity (E_{tot}) of the soil. The parameter values used in eqs. (6) and (6) are presented in Table 2.

The diffusion coefficient of CO_2 in the air (D_0) was estimated as a function of temperature by a non-linear function after Armstrong (1979),

$$\log(D_0) = 1.9975 \log(T) - 9.7273, \quad (8)$$

where T is the temperature of the soil layer (K). The same D_0 value was used for N_2O .

2.7.4. *Model sensitivity analysis.* The flux between two layers is generally proportional to the transport coefficient and the concentration difference (driving force). The sensitivity of the flux to the concentration difference ΔC can be analysed by writing ΔC in the form (see eq. 6)

$$\Delta C = C_i \left(\frac{C_{i+1}}{C_i} - 1 \right). \quad (9)$$

It can be seen that the relative sensitivity of flux estimate $(\frac{C_{i+1}}{C_i} - 1)$ depends on the ratio of concentrations in the respective layers. Namely, if the ratio of concentrations C_{i+1}/C_i is of the order of 0.5, then the increase of 1% in C_{i+1} decreases the driving force of flux similarly by 1%, or $-0.495/-0.5 = 0.99$. Instead, if C_{i+1}/C_i is of the order of 0.99, then the increase of 1% in C_{i+1} decreases the driving force of flux by 99%, or $-0.0001/-0.01 = 0.01$.

The former example corresponds to the typical CO_2 concentration ratios in the O-horizon and in the atmospheric air close to the ground. The latter is typical for N_2O . Since the concentration in the ambient air (C_{i+1} in the above examples) is fluctuating much more than that in the soil due to turbulence, the sampling procedure used in this study does not necessarily give a reliable enough estimate for $C_{\text{air}}/C_{\text{O-horizon}}$, particularly, during the period when the ambient air was sampled instantaneously with syringes. The concentration differences between the soil layers are more reliable, since no turbulent fluctuations exist, although soil ratios C_{i+1}/C_i are much closer to 1 for N_2O than for CO_2 .

To test the sensitivity of soil gradient fluxes of N_2O and CO_2 to variations in soil moisture we calculated the fluxes with 10% higher and 10% lower soil water contents. The 10% decrease in the soil water content increased the soil N_2O and CO_2 fluxes on average 6, 7, 13 and 29% from the O-, A-, B- and C-horizon, respectively. Similarly, the 10% increase in soil water content decreased the fluxes from the same layers by 6, 7, 13 and 25%, respectively. The changes in the fluxes were symmetrical and rather small for the first three soil layers. The largest changes in the gas fluxes were calculated for the deepest layers, especially during the periods when soil moisture contents were generally high, such as in the spring (see Fig. 1).

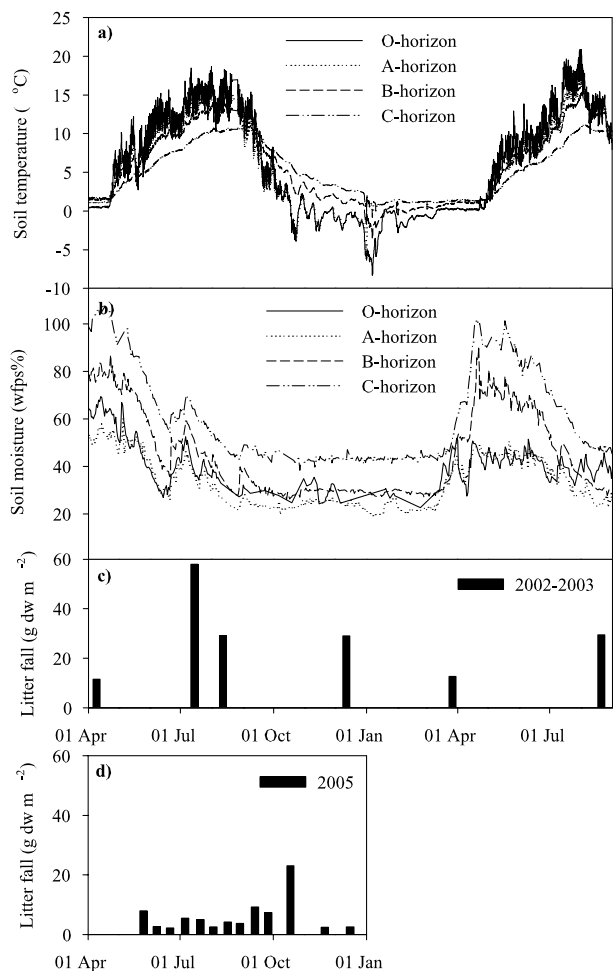


Fig. 1. Soil temperature, soil moisture and total litter fall at Hyytiälä measurement site: (a) soil temperature; (b) soil moisture in different soil horizons; (c) total litter fall in 2002–2003 and (d) 2005. Soil temperatures expressed as 6-hr averages and soil moistures as daily averages.

3. Results

3.1. Variation in soil temperature, moisture and litter fall

Soil temperature had a seasonal pattern typical for boreal soil (Fig. 1a). In the summer, the O-horizon was warmest reaching a daily maximum of 15–20°C in July–August. The temperature decreased with soil depth to the C-horizon, which reached the maximum of 10–12°C in late July. When the soil was not covered with snow, a diurnal pattern in soil CO₂ flux followed daily changes in the soil temperatures (data not shown). In the winter, the temperature profile was inverse; the deepest soil horizons being the warmest. The soil temperature dropped only occasionally below 0°C under the O-horizon.

The year 2002 was exceptionally dry compared to average years (Fig. 1b). The water content in the deepest soil horizon

dropped from 100% water filled pore space (wfps) in the spring to 45% wfps during the summer. Soil moisture in the main rooting zone (at 0–30 cm depth) was only 20% wfps in the summer. The summer drought in 2002 probably induced exceptionally high litter fall between August and October 2002 (Fig. 1c). More frequent litter collections in 2005 show a more typical seasonal variation (Fig. 1d). In 2005 the amount of litter fall increased during the autumn and peaked in October.

3.2. Nitrous oxide fluxes

The chamber N₂O fluxes varied from a small uptake to a small emission (Fig. 2). The mean N₂O emission (\pm standard error) during the whole measurement period was $0.35 \pm 0.11 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$, and the annual mean (July 2002–June 2003) emission was $0.32 \pm 0.11 \mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$. Fluxes in individual chambers ranged from an uptake of $7.7 \mu\text{g N m}^{-2} \text{ h}^{-1}$ to an emission of $4.5 \mu\text{g N m}^{-2} \text{ h}^{-1}$. The mean fluxes during the snow-free period ($0.41 \mu\text{g N m}^{-2} \text{ h}^{-1}$) were higher than the winter time emissions ($0.06 \mu\text{g N m}^{-2} \text{ h}^{-1}$). Occasional uptake of N₂O occurred throughout the year. Annual cumulative N₂O emission from the chambers was $0.0030 \text{ g N m}^{-2}$.

Soil N₂O concentrations were on average higher than the ambient atmospheric N₂O concentrations resulting in, on average, positive, however, highly variable N₂O fluxes. Figure 2 shows the comparison of the fluxes measured by the chambers and calculated from soil and snow gradients. The N₂O fluxes by the soil gradient method were higher than those by the chambers. This was most evident when calculating the fluxes from the O-horizon to the atmosphere (Fig. 2). Mean N₂O fluxes over the measurement period were 3.0, 0.70, 0.24 and $0.04 \mu\text{g N m}^{-2} \text{ h}^{-1}$ from the layer pairs O-horizon to atmosphere, A- to O-horizon, B- to A-horizon and C- to B-horizon, respectively. Annual cumulative N₂O emissions from the O-horizon to the atmosphere and from

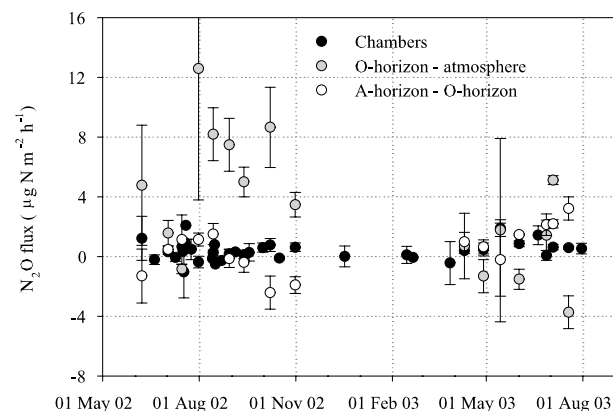


Fig. 2. Mean N₂O fluxes measured by six soil chambers and calculated by snow/soil concentration gradient method in four replicate pits from O-horizon to the atmosphere and A- to O-horizon. Error bars represent the standard errors of the mean.

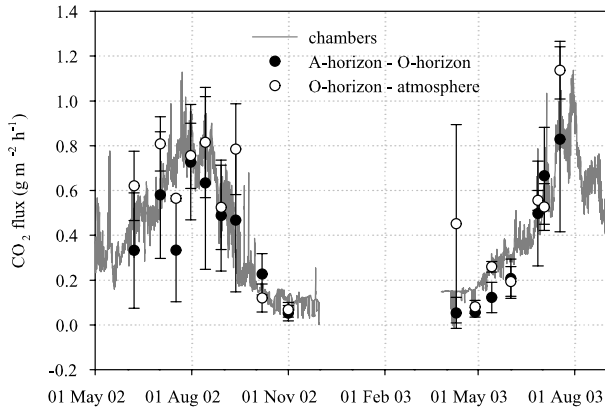


Fig. 3. Fluxes of CO_2 measured by automatic soil chambers and calculated from soil gas concentrations. Chamber fluxes are an average from two automatic chambers and soil gradient fluxes are averages over four locations (pits). Black circles give the soil gradient CO_2 fluxes from O-horizon to the atmosphere and open circles modelled CO_2 fluxes from the soil A- to the O-horizon. Error bars are the standard errors of the mean between four flux calculations.

the A-horizon to the O-horizon as averages over all the pits were 0.027 and 0.0057 g N m^{-2} , respectively.

3.3. Soil CO_2 fluxes

Soil CO_2 fluxes had a clear annual pattern with a maximum during summer and a minimum during winter. The CO_2 fluxes calculated with the gradient method agreed well with the fluxes measured by the chambers (Fig. 3). The CO_2 fluxes from the O-horizon to the atmosphere fitted best to the CO_2 fluxes from the chambers.

Soil air CO_2 concentrations increased with soil depth (Fig. 4). This pattern was clear throughout the measurement period and independent of the time of year. The concentration ranged from 420 ppmv in the O-horizon to 14700 ppmv in the C-horizon in the summer. There was a clear seasonal pattern in the soil CO_2 concentrations (data not shown). The concentrations increased rapidly in the spring and early summer and peaked in July–August. The increase followed the same pattern as that of the soil CO_2 flux and soil temperature. The highest concentration gradients were measured during late summer and the lowest in the spring.

3.4. Variation in soil N_2O concentration profile

N_2O concentrations in the soil air were usually higher than the concentrations in the atmosphere, especially in the summer and autumn indicating an upward flux from the soil to the atmosphere. The concentrations ranged from 0.325 ppmv in the O-horizon to 0.393 ppmv in the C-horizon the gradient being several orders of magnitude lower than that of CO_2 concentration. The largest concentration gradient between the O-horizon

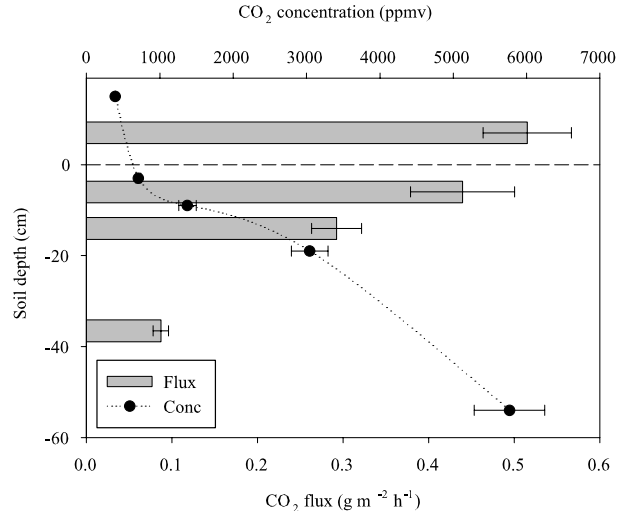


Fig. 4. Mean soil CO_2 concentrations and CO_2 fluxes from each soil layer over all four pits and the whole measurement period 7 June 2002–31 July 2003. Error bars represent the standard errors of mean ($n = 57$). Dotted line between the concentration measurements is drawn to guide the eye of the reader.

and the atmosphere was measured in the end of July 2002. Soil gas concentrations and N_2O fluxes were highest in the pit 160. This pit is located next to a group of alder trees [*Alnus incana* (L.) Moench], which are known for their symbiotic N fixing actinomycetes *Frankia* in the root system.

Overall, there was a clear trend in soil N_2O concentration over time. In the summer and most of the spring, the N_2O concentrations increased with soil depth (Fig. 5). In the autumn, the N_2O concentrations peaked in the O-horizon (Fig. 6). This autumn peak was observed in all pits between late August and November.

In the spring the N_2O fluxes from the O-horizon to the atmosphere were often negative (Fig. 7). This N_2O uptake occurred only in the O-horizon, whereas the deeper soil layers produced N_2O . In the spring, the N_2O concentrations decreased in the deepest soil layers (Fig. 7). This decrease occurred during a period when the C-horizon was drying up from water saturation and was around 80–90% wfps.

3.5. Soil N mineralization

Net mineralization experiment showed that during a 1-month period (June–July 2005) soil N mineralization was dominated by ammonifying bacteria. The net mineralization equalled to the net ammonification and no measurable nitrate was detected either at the start or in the end of the experiment. Net mineralization was markedly higher in the O-horizon than in the mineral soil. Mineralization rates in the O-horizon ranged from 1.5 to 10.3 mg N kg^{-1} of dry soil and in the mineral soil from 0.2 to 1.8 mg N kg^{-1} of dry soil.

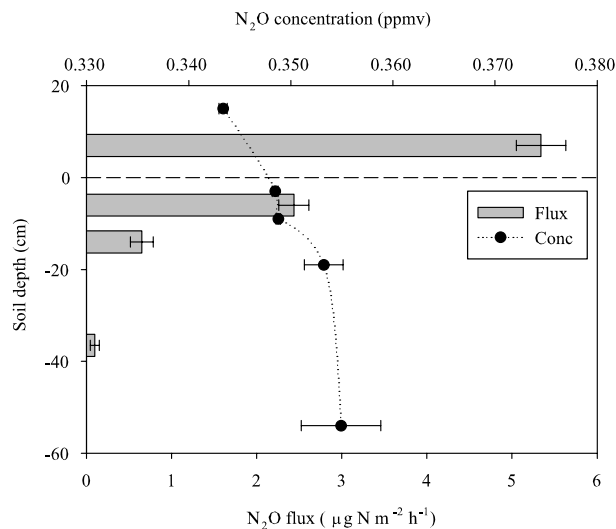


Fig. 5. Example of summer time (3 July 2003) soil N₂O concentration profile and N₂O fluxes as an average from the pits 100, 130 and 160. Error bars represent the standard errors of the mean between the pits and between the ambient air samples ($n = 4$), respectively. A dotted line between the concentration measurements is drawn to guide the eye of the reader.

4. Discussion

The low N₂O emissions and the variability between uptake and emission from the Hyytiälä upland forest soil are in line with earlier measurements from upland boreal forest soils (Schiller and Hastie, 1996; Saari et al., 1997; Simpson et al., 1999). The N₂O emissions, however, were markedly lower than those measured from organic boreal forest soils (Maljanen et al., 2003) or from temperate and tropical forest ecosystems (Butterbach-Bahl et al., 2002; Kiese et al., 2005).

The chamber measurements indicated negligible seasonal variation in N₂O production. The soil gas concentration measurements, however, revealed clear seasonal variation in the N₂O production. In the summer and most of the time in the spring the soil N₂O concentrations increased with depth of the soil. The highest N₂O emissions calculated from the soil profiles occurred in July–August 2002 when the soil temperatures were high and the soil moisture was intermediate. In the autumn, the N₂O concentration profile changed and the highest N₂O concentrations were measured in the O-horizon.

As the N₂O source in each soil layer is directly related to the difference of N₂O flux at lower and upper boundary of the layer, the flux profiles can be interpreted to yield sink and source horizons. At our site, the O-horizon acted as a source of N₂O in the autumn but as a sink in the spring, whereas, the A-horizon acted as a sink during most of the autumn and as a source in the spring. In the autumn, the peak in N₂O concentration and production in the O-horizon occurred after a litter fall, which in 2002 was exceptionally high due to the summer drought. It

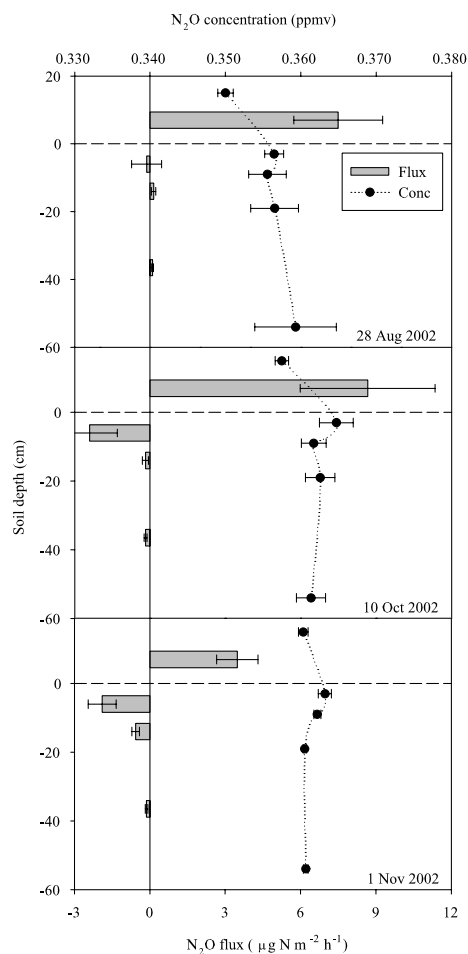


Fig. 6. Mean soil N₂O concentrations and N₂O fluxes in the autumn 2002. The error bars for the soil concentrations and fluxes are the standard errors of the mean between the four locations (pits). For the ambient air values the error bars express the standard errors of the mean between four replicate air samples. A dotted line between the concentration measurements is drawn to guide the eye of the reader.

seems that the litter fall may have stimulated N₂O production in this layer. This may be explained by an increased organic matter mineralization in the litter and humus layer and a consequent release of mineral N into the soil. In the N limited soil system the newly available mineral N may then be utilized by nitrifying and denitrifying bacteria to produce N₂O.

Consumption of atmospheric N₂O has previously been reported in some N limited temperate and Mediterranean forest ecosystems (Butterbach-Bahl et al., 1998; Goossens et al., 2001; Rosenkranz et al., 2006). However, to our knowledge, this is the first study to show that boreal forest soils may act as sinks for atmospheric N₂O. Similar to our study, Rosenkranz et al. (2006) found that the organic soil layer was responsible for most of the N₂O consumption in a Mediterranean pine forest. The only biological process currently known to consume N₂O is

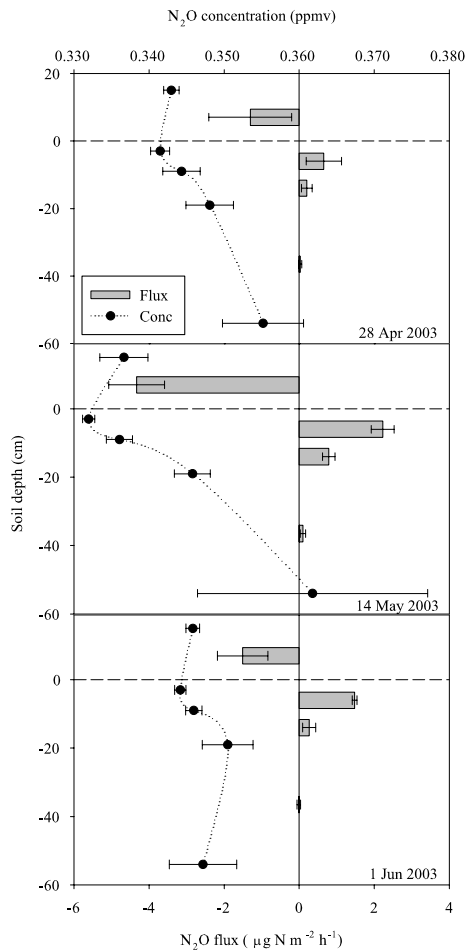


Fig. 7. Mean soil N_2O concentrations and N_2O fluxes in the spring 2003. The error bars for the soil concentrations and fluxes are the standard errors of the mean between the four locations (pits). For ambient air values the error bars express the standard error of the mean between four replicate air samples. A dotted line between the concentration measurements is drawn to guide the eye of the reader.

denitrification (Conrad, 1996). Other processes hypothesized to consume N_2O are aerobic denitrification by heterotrophic nitrifiers, and nitrifier denitrification (Wrage et al., 2001; Rosenkranz et al., 2006). As the nitrifier denitrification favours high soil N content, low organic C content, and low O_2 concentration (Wrage et al., 2001), we neglect it as a possible process in Hyttiälä. From the remaining processes, both the anaerobic N_2O reduction by denitrifiers and aerobic N_2O reduction by heterotrophic nitrifiers may have taken place since the environmental conditions such as low soil N content and high soil C content in the O-horizon favour both processes (Wrage et al., 2001).

The reason for the markedly higher variability in the soil gradient N_2O fluxes as compared to the chamber N_2O fluxes remains partly unknown. Particularly, the fluxes from the O-horizon to the atmosphere were higher than those measured by the chambers. As the gas samplers were installed in the middle of the

O-horizon, some consumption of N_2O may have taken place in the soil above the sampler. As we have seen from the gas concentration measurements, the O-horizon acts as a source of N_2O and occasionally as a sink for N_2O . Since the flux calculation does not account for consumption processes, the fluxes from the O-horizon to the atmosphere may therefore be overestimated.

As the soil chambers and the soil gas concentration pits in our study were not collocated, the comparison of the gas fluxes between the individual chamber and pit pairs was not possible. Hence, when comparing the mean fluxes the differences in the N_2O fluxes between the two methods may also have resulted from small scale variation in the factors regulating N_2O production or consumption in the soil. The soil at Hyttiälä site is spatially very heterogeneous, partly because of the site history and partly because of the distribution of trees and stones on the site. The soil was exposed to prescribed burning and ploughing in 1962 upon the clear-cut and regeneration, which affected the soil layers in the soil surface.

Klemmedtsson et al. (2005) suggested recently that N_2O emissions from forested histosols depend on soil C:N ratio in a way that the smaller the C:N ratio the higher the N_2O emissions. They concluded that soil emissions are very small from forest ecosystems with C:N ratios higher than 25. The C:N ratio in the O-horizon in Hyttiälä was approximately 30, which is above this C:N ratio limit and also higher than the limit of 22 suggested for the onset of nitrification (Ollinger et al., 2002; Aber et al., 2003). Our results support their findings and suggest that the relation between C:N ratio and N_2O emissions may also be applicable to upland forest ecosystems. Also, the relationship between nitrification activity and C:N ratio seem relevant here since both the soil mineral N analysis and the net mineralization experiment indicated that this forest ecosystem is largely ammonium-dominated. In addition, in a separate study the nitrification and denitrification activities to produce N_2O in Hyttiälä forest soil were found to be very low (Ambus et al., 2006).

When soil gradient gas fluxes are calculated based on very small changes in gas concentrations, such as those of N_2O in our study, the estimates are sensitive to any disturbance in the concentration measurement. The gas concentrations in the soil develop over a period of hours to days and the gas sample represents an average over the equilibration time. The ambient air sample, in contrast, gives a concentration at a given moment and hence the timescale for the soil and the ambient air samples are different. Due to the turbulent mixing of ambient air and to some extent the topmost O-horizon there is always some variation in the gas concentrations. This may become important when sampling gases with very low concentration differences in the soil and the atmosphere. As the fluxes between the uppermost soil layer (O-horizon) and the atmosphere are calculated from the difference in soil and ambient air concentrations, even a small error in the gas sample may change the flux direction. This does not seem as critical when measuring gases that have high concentration differences between the soil and the atmosphere,

such as CO₂ in our study. The flux estimates for N₂O are much more sensitive to the accurate determination of the concentration ratios of adjacent layers since the fluxes are small. To improve the reliability of the ambient air sampling we changed the sampling from an instantaneous to a 30-min averaging in March 2003. Although, this change in the procedure did not lower the standard deviation between the four replicate ambient gas samples, we consider the 30-min sampling more reliable. Hence, the flux estimates from the O-horizon to the atmosphere prior to this change in the ambient sampling have a much higher uncertainty than those calculated after the change in the ambient air sampling.

The chamber type and the measurement protocol used in the chamber measurement substantially affect the flux values. The comparisons carried out between different types of chambers have indicated relatively large differences between chamber types (Raich et al., 1990; Norman et al., 1997; Janssens et al., 2000; Pumpanen et al., 2004) or showed chamber-specific limitations (Fang and Moncrieff, 1998; Gao and Yates, 1998). In general, most chamber types tend to underestimate trace gas fluxes from the soil by slowing down the gas diffusion from the soil to the chamber headspace during the measurement (Norman et al., 1997; Conen and Smith, 2000; Rayment, 2000; Pumpanen et al., 2004; Livingston et al., 2005). The dynamic chambers used in this study for CO₂ were tested in a calibration campaign and the underestimation of this chamber type was corrected according to Pumpanen et al. (2004). The static chambers used for N₂O flux measurements were tested in the same calibration campaign for CO₂, however, we did not correct for the possible underestimation of N₂O fluxes since the enclosure time and sampling procedures for the two gases were not the same.

In conclusion, we measured N₂O fluxes ranging from small emissions to small soil uptake with both soil chamber and soil gradient techniques. The fluxes obtained by these two techniques were of the same order of magnitude, however, the N₂O fluxes measured by the soil gradient method were more variable than the fluxes measured by the chambers. The topmost soil layer, O-horizon, was responsible for most of the N₂O production or consumption. As for CO₂ fluxes, the chamber and soil gradient techniques agreed better, which we considered to result from a much higher concentration differences between the soil and the atmosphere.

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change and its Interactions with the Climate System (NECC), and Helsinki University Environmental Research Centre (HERC).

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