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Greenhouse gas fluxes in a drained peatland forest during spring frost-thaw event

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Abstract

Fluxes of greenhouse gases (GHG) carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) were measured during a two month campaign at a drained peatland forest in Finland by the eddy covariance (EC) technique (CO₂ and N₂O), and automatic and manual chambers (CO₂, CH₄ and N₂O). In addition, GHG concentrations and soil parameters (mineral nitrogen, temperature, moisture content) in the peat profile were measured. The aim of the measurement campaign was to quantify the GHG fluxes before, during and after thawing of the peat soil, a time period with potentially high GHG fluxes, and to compare different flux measurement methods. The forest was a net CO₂ sink during the two months and the fluxes of CO₂ dominated the GHG exchange. The peat soil was a small sink of atmospheric CH₄ but a small source of N₂O. Both CH₄ oxidation and N₂O production took place in the top-soil whereas CH₄ was produced in the deeper layers of the peat. During the thawing of the peat distinct peaks in CO₂ and N₂O emissions were observed. The CO₂ peak followed tightly the increase in soil temperature, whereas the N₂O peak occurred with an approx. one week delay after soil thawing. CH₄ fluxes did not respond to the thawing of the peat soil. The CO₂ and N₂O emission peaks were not captured by the manual chambers and hence we conclude that automatic chamber measurements or EC are necessary to quantify fluxes during peak emission periods. Sub-canopy EC measurements and chamber-based fluxes of CO₂ and N₂O were comparable, although the fluxes of N₂O measured by EC were close to the detection limit of the EC system. We conclude that if fluxes are high enough, i.e. greater than 5–10 μg N m⁻² h⁻¹, the EC method is a good alternative to measure N₂O and CO₂ fluxes at ecosystem scale, thereby minimizing problems with chamber enclosures and spatial representativeness of the measurements.

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1 Introduction

Drainage of peatlands for forestry has been a common practice in Fennoscandia during the past 100 years. In Finland, more than half of the original peatland area has been drained for forestry or agricultural use since the 1920s (Paavilainen and Päivänen, 1995; Joosten and Clarke, 2002). Drainage lowers the groundwater table and improves the aeration of the peat, which increases the growth of trees. Thereby, drainage also changes greenhouse gas dynamics of the peatland, as a large part of the decomposition of the peat switches from anaerobic to aerobic conditions with a shift from methane (CH₄) to carbon dioxide (CO₂) as the end-product of decomposition (Moore and Dalva, 1993; Silvola et al., 1996; Minkinen et al., 2002; Roulet et al., 1993; Martikainen et al., 1995; Nykänen et al., 1998). Stimulated aerobic decomposition of the peat releases nutrients, especially nitrogen, to the soil, which may lead to elevated emissions of nitrous oxide (N₂O) (Martikainen et al., 1993; Silvola et al., 1996; Laine et al., 1996). However, the changes in N₂O emissions after drainage seem to depend on the fertility of the original peatland, i.e. its nitrogen content or the C:N ratio of the peat, and the level of the water table after the drainage (von Arnold et al., 2005a, b).

Drained peatlands with former agricultural history (afforested peat soils) are strong point sources of N₂O. The N₂O emissions are of the same order of magnitude as the emissions from cultivated peat soils (Maljanen et al., 2001; Regina et al., 2004; Mäkiranta et al., 2007). Drained forested peatlands cover 25% of forest area in Finland making these ecosystems potentially important sources of greenhouse gases. During the last two decades there has been debate whether the drainage of peatlands for forestry turns them from net sinks of carbon into net sources, and whether N₂O makes up an important part of the total greenhouse gas balance.

Intensive measurements of GHG emissions from drained peatland forests are scarce. Also, comparisons of different measurement techniques in these ecosystems are almost non-existent. Most of the studies have been conducted with chamber techniques using weekly to monthly measuring intervals. This measurement frequency

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may severely miss important emission events, so called “hot moments”, related especially to N₂O emissions from soils (see e.g. Matzner and Borken, 2008; Papen and Butterbach-Bahl, 1999), such as frost-thaw periods which could be substantial in boreal environments (see e.g. Koponen et al., 2004, 2006). As a result, calculations of seasonal or annual budgets of greenhouse gases may be biased and potentially underestimated if the frequency of measurements or spatial coverage is not sufficient to cover variations.

We report results of greenhouse gas emissions (CO₂, CH₄ and N₂O) from a drained peatland forest in Kalevansuo, southern Finland. The measurement campaign lasted two months from the end of April until the end of June 2007, and was run under the NitroEurope IP EU-project. The main aim was to quantify the total GHG balance during a potentially high peak season in the spring, where frost-thaw driven N₂O fluxes are likely to occur. We measured net CO₂ exchange above and below the forest canopy and N₂O exchange below the forest canopy by the eddy covariance (EC) method and compared these fluxes to soil CO₂, CH₄, and N₂O fluxes measured simultaneously with automated and manual chamber techniques.

Our aim was to estimate the net GHG exchange and the importance of different C and N flux components on the total GHG balance during the two-month measuring period. We hypothesise that N₂O is an important component of the ecosystem greenhouse gas exchange due to “hot moment” emissions such as frost-thaw events. Our second aim was to evaluate the suitability of sub-canopy EC-based N₂O measurements as a sophisticated alternative to traditionally used chamber methods in this environment. The quality control and flux error analysis of the EC N₂O measurements at the site are presented in this issue in Mammarella et al. (2009).

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2 Materials and methods

2.1 Site description

The measurements were conducted at a Kalevansuo drained peatland forest classified as an ombrotrophic dwarf-shrub pine bog. The site was located in southern Finland (60°39' N, 24°22' E), where the mean annual precipitation is 606 mm and the mean annual temperature is 4.3°C. The bog was drained for the first time in 1971 by open, about 1 m deep ditches dug with approximately 40 m spacing between the parallel ditches. In 1973 the site was fertilised with phosphorus and potassium, following the guideline practises for drained peatlands. Drainage resulted in a lowered water table down to approx. -40 cm from the peat surface, and a changed composition of ground vegetation from typical bog vegetation towards more of a forest understorey. However, some features such as the abundance of peatland dwarf shrubs and fairly high coverage of *Sphagnum* species still distinguish the site from upland forests. Currently the height of the tree stand is 15–18 m, the tree stand composition is uneven and consists mainly of Scots pine (*Pinus sylvestris* L.) with some small-sized Norway spruce (*Picea abies* L.) and downy birch (*Betula pubescens*) in the gaps near the ditches.

Forest floor vegetation consisted mainly of hummock dwarf shrubs (*Vaccinium vitis-idaea*, *Vaccinium myrtillus*, *Empetrum nigrum*, *Vaccinium uliginosum*, *Ledum palustre* and *Betula nana*), sedges like *Eriophorum vaginatum* and mosses (*Pleurozium schreberi*, *Dicranum polysetum*, *Sphagnum russowii*, *Sphagnum capillifolium* and *Sphagnum angustifolium*).

The depth of the well decomposed *Sphagnum* peat at the site is approximately 2.5 m with peat a pH of 5.0 and C/N ratio of 41 in the litter layer and 45 in the top 10 cm of the peat soil.

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2.2 Flux measurements

Intensive GHG measurements were carried out from 25 April to 27 June, 2007 within a homogenous and representative approx. 1 ha plot of the forest (total area of approx. 60 ha). The main measurements included micrometeorological eddy covariance (EC) measurements of CO₂ above and below the forest canopy and N₂O fluxes below the canopy, automated as well as manual chamber-based measurements of CO₂, CH₄ and N₂O fluxes. The locations of the different measurement systems are shown in Fig. 1.

The above canopy EC CO₂ flux measurement system (EC_{above}) included a METEK USA-1 ultra sonic anemometer (METEK GmbH, Elmshorn, Germany) mounted on the top of a 21.5 m telescopic mast and a LI-7000 CO₂/H₂O analyzer (Li-Cor, Inc., Lincoln, NE, USA) mounted at 6 m height in the tower. Air was drawn from the proximity of the sonic to the LI-7000 CO₂/H₂O analyzer using a bev-a-line tubing which has an inner diameter of 3.1 mm. The storage flux of CO₂ was calculated from the concentration data measured at heights of 21.5 m and 6 m, the latter being measured with a LI-820 CO₂ analyzer (Li-Cor Inc., Lincoln, NE, USA). The storage flux was added to the measured NEE, hereafter NEE referring to the sum of turbulent and storage fluxes. The mast was located at the centre of the measurement site (Fig. 1).

The sub-canopy EC measurements (EC_{sub}) were conducted at 4 m height. The sub-canopy mast was located approximately 100 m southwest of the tall mast, and approximately half way between the tall mast and the automatic soil chambers (see Fig. 1). The CO₂ fluxes were measured with a Li-7500 Open-Path Infrared CO₂/H₂O Gas Analyzer (Li-Cor, Inc., Lincoln, NE, USA) and a CSAT3 Sonic Anemometer (Campbell Scientific Inc., Logan, UT, USA). EC measurements of N₂O fluxes were conducted at the same mast using the same CSAT3 anemometer and a tunable diode laser spectrometer (TGA-100A, Campbell Scientific Inc., Logan, UT, USA). Details of the measurement setup are given in Mammarella et al. (2009).

Forest floor (soil and ground vegetation) fluxes of CO₂, N₂O and CH₄ were measured

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with the enclosure method using automatic (transparent) and manual (opaque) chambers. The automatic chamber system consisted of a valve-driven sampling system (custom-made by IMK-IFU) for nine soil chambers with dimensions of 50×50×15 cm (length × width × height). The automatic chambers were located approx. 170 m south-west of the tall EC mast, and approx. 100 m southwest from the sub-canopy EC mast (Fig. 1). The chambers were connected to a gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with an electron capture detector (ECD) for N₂O and a flame ionization detector (FID) for CH₄, and a GMD20D infrared CO₂ analyzer (Vaisala, Vantaa, Finland). The nine chambers were split into 3 sets of 3 chambers. One measuring cycle including 4 samplings per chamber, and simultaneous calibration with a reference gas resulted in an enclosure time of 48 min per chamber set and 144 min for sampling of all 3 chamber sets, respectively. The measurement system is described in more detail in Kiese and Butterbach-Bahl (2002) and Werner et al. (2007). The vegetation inside the automatic chambers was similar than in the peatland generally, however, tall dwarf shrubs were not present. Detailed vegetation survey was not conducted for the automatic chambers.

Manual chamber measurements were conducted once a week during April to June 2007, and fortnightly during July to September 2007. In total 16 circular metal collars were located in groups of four approx. 30–60 m from the tall EC mast in the four main directions, and 10–150 m north-east from the sub-canopy EC mast (Fig. 1). The collars were installed in 2004 at soil depth of 3–5 cm, on top of the root layer. During chamber measurements, a 30 cm high circular metal chamber was placed on the collar. Air inside the chamber was mixed with a fan, and the temperature inside the chamber was monitored with a thermometer in order to correct the fluxes. Gas samples (100 ml) were collected with a syringe at 2, 15, 25 and 35 min intervals and transferred immediately into 12-ml glass vials (Labco Exetainer, Labco Limited, Buckinghamshire, UK). Ninety ml of the gas sample was used to flush the air in the vial with two needles. The rest 10 ml of the gas sample was used to over-pressurize the vial after removing the flushing needle. Gas samples were analyzed within one week for N₂O and CH₄ by a

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gas chromatograph (Agilent 6890 GC, Agilent Technologies Finland, Espoo, Finland) equipped with an ECD for N₂O and an FID for CH₄.

2.3 Soil measurements

Soil concentrations of N₂O and CH₄ were measured in the peat profile at three locations below the litter layer at 5 cm, and at 22 and 45 cm peat depth. The three profiles were located approximately 40 m southwest of the tall EC mast. Gas collector cups were 100 ml in volume and made of stainless steel. The cups were installed upside down with an open end at the bottom in the soil and connected to the atmosphere via a 1/8" stainless steel tube. Gas samples were collected weekly during April to June from the depths 5 and 25 cm and fortnightly during July to September from all depths (5, 22 and 45 cm). At the time of gas sampling, the 5–10 ml gas volume inside the tubing was discarded after which a 100 ml gas sample was taken and transferred into 12-ml glass vials as described above. When a gas collector was below the groundwater table, a water sample of 50 ml was taken with the syringe. Then the gas dissolved in the water was equilibrated with 50 ml of ambient air by shaking the syringe rigorously for 10 min. After shaking, 20 ml of the gas sample was injected into a pre-evacuated 12-ml glass vial.

Soil volumetric water content and temperature were measured at two of the gas collection pits by ECH₂O-20 soil moisture sensors (Decagon Devices, Inc., Pullman, WA, USA) and RTD (Resistance Temperature Detector) sensors at the soil depths of 5, 22 and 45 cm. Soil temperature and volumetric water contents were also measured adjacent to the automatic chambers at 5 and 10 cm depths (Trime TDR IMKO and Pt-100, IMKO GmbH, Ettlingen, Germany). In addition, soil temperatures at 5 and at 30 cm depth were measured close to the tall EC mast by FMI (Finnish Meteorological Institute) The variation of the ground water level near the main EC mast was monitored by a PDCR 1830 level pressure sensor (Druck Inc., New Fairfield, CT, USA).

Soil ammonium (NH₄-N), nitrate (NO₃-N) and total dissolved nitrogen contents were analysed from samples collected weekly during April to June 2007, and monthly during

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July to September 2007. Soil samples from the litter layer and peat (0–10 cm) were collected in 5 replicates: four from close vicinity to the manual chambers (4 groups) and one from close vicinity of the automatic chambers. Fresh soil samples were stored at +4°C and extracted with 1M KCl the next day after the sampling. The extracts were frozen at –18°C until analysis by a flow injection analyzer (FIA 5012, Tecator) at the Finnish Forest Research Institute. Total carbon and nitrogen contents were analyzed from dried (40°C) soil samples using a vario MAX CN elemental analyser.

2.4 Data analysis

Flux rates of manual and automated chamber measurements were calculated with the following equation

$$F_c = \frac{dC}{dt}h, \quad (1)$$

where F_c is the flux of the target gas [$\text{g m}^{-2} \text{s}^{-1}$], C is the gas concentration in the chamber air [g m^{-3}], t is closure time [s] and h the height of the chamber [m]. The development of gas concentrations inside the chamber during an enclosure period was linear, hence the changes in the gas concentrations were calculated by linear regression analysis ($n=4$). Flux rates were corrected for pressure and temperature.

EC fluxes were calculated as 30 min average covariances between the scalars (CO_2 and N_2O) concentration and the vertical wind velocity according to the commonly accepted procedures (Aubinet et al., 2000). All signals were detrended for removing the average values and trends. A simple linear detrending procedure was used for calculating the CO_2 flux. The N_2O signal measured by the TDL gas analyzer was characterized by stronger trends, caused mainly by instrumental drift, which can give an extra contribution to the estimated flux in the case that the fluctuations of the concentration are correlated with the fluctuations of the vertical wind velocity. In order to remove the instrumental drift effect and to reduce the random flux variability, a running mean filter (McMillen, 1988) was performed prior to calculation of the N_2O flux. A more

detailed description of the data processing of N₂O EC signal is given in Mammarella et al. (2009).

A lag-time of 2.3 s was obtained for the above-canopy CO₂ signal, maximizing the cross-covariance function between the CO₂ concentration and the vertical wind velocity. The same procedure was applied to the sub-canopy N₂O signal, but because the N₂O emissions were very close to detection limit of the system, it was not possible to clearly determine experimentally the N₂O lag time. Then using a procedure similar to Pihlatie et al. (2005), we used a fix lag time of 1 s. The same value was obtained by using the sample flow and volumes of the inlet tubing and the sample cell, for estimating the theoretical N₂O lag time. The CO₂ flux was corrected for density fluctuations effect (WPL correction, Webb et al., 1980), while such correction was unnecessary for N₂O fluxes, because of the presence of high flow sample dryer in the system (PD1000 Nafion dryer, Campbell Scientific, Inc., Logan, UT, USA). Temperature fluctuations do not need to be corrected because they can be assumed to be damped in the sampling tube (Rannik et al., 1997). No Burba correction was used for the eddy covariance data from open path CO₂ analyzer even though the correction may slightly increase the flux levels (Burba et al., 2008). The EC fluxes were corrected for the high frequency flux underestimation according to Mammarella et al. (2009). For typical mean wind velocity in the sub-canopy layer, the flux loss was about 5% and less than 10% for CO₂ and N₂O, respectively.

Statistical tests (paired t-test) for the flux and soil measurement data was done with SPSS statistical program.

3 Results

3.1 Environmental conditions

At the start of the measurement campaign part of the peat was still frozen. The air temperatures varied from below 0°C in the end of April to a maximum of 27°C in the

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beginning of June (Fig. 2). Prior to the start of the measurement campaign the soil had melted and frozen several times. The first pronounced freeze-thaw cycle was recorded in the end of March, one month prior to the measurement campaign (data not shown). However, as indicated by temperature measurements of air and litter layer, the peat surface layer was still freezing and thawing during the measuring campaign in the end of April (Fig. 2). During the intensive measurement period (25 April–27 June) the soil temperature generally increased from around 0°C up to approx. 16°C in the upper part (5 cm depth) of the peat soil. Rainfall during April–June was low with low intensities except for two events in mid April and in the end of May, resulting in short increases in the soil water content (Max. 22 vol%) and water table (see Fig. 2). Despite these short increases, the water table and soil moisture decreased (–25 cm to –40 cm; 16 to <10 vol%) during the intensive measurement period.

3.2 Concentration of soil ammonium, nitrate and total dissolved nitrogen

Soil nitrate (NO_3^- -N) concentrations were close to zero throughout the whole measuring period, whereas soil ammonium (NH_4^+ -N) and total nitrogen (tot-N) concentrations were elevated at the beginning of the measurement period with a maximum during the frost-thaw event in May, and decreased towards the end of the measuring campaign (Fig. 6). The concentrations of NO_3^- -N, NH_4^+ -N and tot-N were always higher in the litter layer than in the peat at 0–10 cm depth (data not shown). Total dissolved nitrogen concentrations in the soil varied between 50–230 mg N kg⁻¹ dry soil, and were approximately one order of magnitude higher than the concentrations of NH_4^+ -N in the soil.

3.3 CO₂ fluxes

EC measurements above the forest canopy revealed that the site was on average a net sink for CO₂ during the measuring campaign, from late April to late June 2007 (see Fig. 3). The daily net ecosystem exchange (NEE) of CO₂ increased from approximately

–0.014 mg C m⁻² s⁻¹ during April to maximum of –0.064 mg C m⁻² s⁻¹ in the middle of June. The drained peatland forest was a weak source of carbon (0.02 mg C m⁻² s⁻¹) on few rainy days during the measurement period. Overall, the CO₂ exchange followed the changes in air and soil temperatures being higher (uptake) in warm and lower (up to emission) in cold days (see Fig. 3).

In contrast to the net CO₂ uptake of the whole forest ecosystem, soil and ground vegetation together (automatic chambers and sub-canopy eddy covariance) turned out to be a source of CO₂ to the atmosphere. Both, CO₂ fluxes below the forest canopy measured by the EC and by automatic chambers on the soil surface showed an increasing emission trend from April to June (Fig. 3). Forest floor CO₂ fluxes (automatic chambers) and sub-canopy fluxes (sub-canopy EC) increased from a minimum of 0.001 mg C m⁻² s⁻¹ in the end of April to a maximum of 0.013 mg C m⁻² s⁻¹ and 0.03 mg C m⁻² s⁻¹, respectively, in the end of May when also soil and air temperatures reached their maximum. In June a decrease in temperature was followed by a decrease in CO₂ fluxes, however, this was more pronounced in the sub-canopy EC fluxes. In the end of June forest floor and sub-canopy fluxes leveled around 0.01 mg C m⁻² s⁻¹, however still following changes in the air and soil temperatures (Fig. 3). Mean forest floor (0.008 mg C m⁻² s⁻¹) and sub-canopy CO₂ exchange (0.009 mg C m⁻² s⁻¹) over the measuring period were almost identical and a paired t-test analysis did not reveal any statistical differences (Table 1). Forest floor CO₂ and sub-canopy exchange correlated positively with air and soil temperatures. Thereby the soil temperature at 5 cm depth explained most of the variability of CO₂ flux rates ($r=0.96$, $p<0.01$). The correlation was less pronounced for sub-canopy EC based fluxes due to a more scattered temporal emission pattern also reflected in higher values of CV% (Table 1, Fig. 3). Furthermore, a negative correlation of forest floor CO₂ fluxes with soil moisture (-0.60 , $p<0.01$) and water table depth (-0.76 , $p<0.01$), which was not significant for the EC-based sub-canopy measurements. However, this was likely due to a negative correlation of soil moisture and water table depth with soil and air temperatures.

The measurement campaign can be divided into two distinct periods: a cold and a

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warm period. During the cold period (30 April–10 May) the net forest floor CO₂ fluxes, the sum of soil respiration and CO₂ photosynthesis of ground vegetation, and the CO₂ net ecosystem exchange (NEE) above the forest canopy were small (Fig. 4). During the warm period (5 June–15 June) both the net CO₂ emissions of the forest floor (Fig. 4c) and the net CO₂ uptake of the forest canopy (Fig. 4d) increased. During both cold and warm periods, the sub-canopy CO₂ fluxes followed a small but clear diurnal trend when the net CO₂ emission decreased during day-time and increased during night-time (Fig. 4a and c).

The comparison of the mean and median GHG exchange measured by above canopy EC and sub-canopy EC and by automatic forest floor chambers during the entire two-months measurement period is shown in Table 1. During the period of 25 April–21 June the cumulative CO₂ fluxes measured by sub-canopy EC (46 g C m⁻²) and forest floor chambers (41 g C m⁻²) did not statistically differ from each other, and accounted for 41 and 36% of the total NEE (−102 g C m⁻²), respectively (Table 1).

3.4 CH₄ fluxes

Kalevansuo peatland forest was a small sink for CH₄ during the measurement campaign (Fig. 5a). The CH₄ uptake measured with the automatic chambers increased from around −30 μg C m⁻² h⁻¹ to a approximately of −60 μg C m⁻² h⁻¹ in June. The CH₄ fluxes measured with manual chambers were constantly by at least a factor of two smaller than the CH₄ fluxes measured with the automatic chambers (Fig. 5). The fluxes of CH₄ were not affected by thawing of the soil but followed more closely the groundwater table and soil moisture content in the peat. CH₄ uptake correlated positively with soil water content ($r=0.38$, $p<0.01$) and water table depth ($r=0.44$, $p<0.01$), and negatively with soil temperatures at 5 cm and at 30 cm depth ($r=-0.50$, $p<0.01$; $r=-0.62$, $p<0.01$), respectively, and CO₂ fluxes measured by the automatic chambers ($r=-0.50$, $p<0.01$).

3.5 N₂O fluxes

Kalevansuo drained peatland forest was a small source of N₂O during the measurement period from April to June 2007. Mean emission rates varied between 3.2 μg N m⁻² h⁻¹ measured by the sub-canopy EC technique, 4.5 μg N m⁻² h⁻¹ by the automatic chambers, and 6.8 μg N m⁻² h⁻¹ by the manual chamber techniques (Fig. 6, Table 1). Independent of the measuring technique N₂O emissions hardly exceeded 10 μg N m⁻² h⁻¹ except for a short period at the beginning of the measuring campaign when elevated N₂O emissions could be detected at least with the temporally highly resolved EC and automatic chamber measurements (see Fig. 6). The elevated N₂O emissions coincide with the coldest period (air temp <0°C) within the measuring period and a rapid increase in air temperatures up to 15°C (Fig. 6). A significant uptake of atmospheric N₂O was never detected. In general, N₂O fluxes measured with the EC technique were more variable than chamber based N₂O fluxes which is indicated by a much higher CV% of 123 as compared to values of CV% of 62.3 and 42.8 by the automatic and manual chambers, respectively (Table 1). N₂O emissions measured by the automatic chambers correlated negatively with air temperature ($r = -0.50$, $p < 0.01$) and soil temperatures in the litter layer, at 5 cm and at 30 cm depths ($r = -0.48$, $p < 0.01$; $r = -0.47$, $p < 0.01$; $r = -0.46$, $p < 0.01$), respectively, soil moisture content ($r = -0.46$, $p < 0.01$), and CO₂ fluxes ($r = -0.48$, $p < 0.01$). Positive correlations were found with water table depth ($r = 0.40$, $p < 0.01$) and CH₄ uptake ($r = 0.30$, $p < 0.05$).

3.6 CH₄ and N₂O concentration in peat profile

During the intensive measuring campaign from April to June 2007 CH₄ and N₂O concentrations in the peat profile were close to ambient air concentrations of ~1.8 ppmv and ~0.35 ppmv, respectively (Figs. 4b and 5b). In general, during the intensive measurement campaign the CH₄ concentrations decreased (i.e. consumption) and N₂O concentration slightly increased (i.e. production) with peat depth in the top-soil. From July to September the concentrations of CH₄ in deeper peat layers (22 and 45 cm

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depth) increased markedly. The highest concentration of 1400 ppmv was measured at 45 cm depth in September. At the same time the CH₄ concentrations in the litter layer were close to the ambient air concentrations and the net fluxes measured by manual chambers showed that the soil was still a sink of CH₄ (Fig. 5a and b).

5 Nitrous oxide concentrations at 22 cm depth were most of the time higher than the concentration just below the litter layer at 5 cm (Fig. 4b). Concentrations at 45 cm depth measured during July to September varied between 0.210–0.240 ppmv and were much lower than at 5 or 22 cm depths and well below the atmospheric concentration.

4 Discussion

10 4.1 CO₂ fluxes

Eddy covariance (EC) measurements above the forest canopy revealed that the Kalevansuo drained peatland pine forest was a net sink of CO₂ during the measuring period from the end of April to the end of June. The measurements below the forest canopy by sub-canopy EC and automatic chambers showed that the forest floor was a net source of CO₂, however, only a small part of the net CO₂ uptake of the whole forest ecosystem. During few rainy days in the campaign (in total 5 days) the Kalevansuo peatland forest turned from a net sink of carbon to a net source. This finding is in line with the study by Lohila et al. (2007) where they found that an afforested boreal peatland turned from a net sink to a source of carbon during rainy days in the summer. Total NEE at the Kalevansuo drained peatland forest from spring to early summer (25 April–21 June, –102 g C m⁻²) is comparable to NEE values reported from boreal forests growing on mineral or peat soils (Sunı et al., 2003; Lohila et al., 2007).

15 In this study the diurnal variation in the CO₂ exchange of the soil and forest floor vegetation was very small measured by the sub-canopy EC and non-existent measured by the automatic soil chambers. Similarly small diurnal variation in the forest floor CO₂ exchange of a boreal forest ecosystem has been measured earlier by Launiainen et

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al. (2005) and Kulmala et al. (2008). However, much stronger diurnal variation in the CO₂ exchange of soil and forest floor vegetation has been measured in a temperate forest ecosystem on mineral soil (Subke and Tenhunen, 2004). In our study the lack of diurnal variation in the CO₂ exchange of the forest floor may result from 1) a small photosynthetic activity of the forest floor vegetation as compared to the soil and forest floor respiration, or 2) the possibility of high photosynthetic activity during day-time and a simultaneous increase in the soil respiration due to temperature dependency, which then compensates for the photosynthesis. The net forest floor CO₂ fluxes measured by sub-canopy EC during April–June period compare well with sub-canopy EC measurements carried out in a boreal pine forest (Launiainen et al., 2005), and chamber based measurements in other drained peatland forests (Martikainen et al., 1995; Alm et al., 1999).

Correlation of forest floor CO₂ fluxes was highest with soil temperatures in 5 cm depth. This shows that rather the topsoil, getting fresh litter input from vegetation, is the major source of CO₂ as compared to the peat body itself, thus, stimulated decomposition of the peat due to aeration by drainage has already diminished.

In contrast to N₂O emissions no increases in CO₂ emissions following thawing of the litter layer could be detected. The intermittent increase of CO₂ emissions in the end of April can be related to a significant increase in soil and air temperatures, however, in a period when temperatures were never below 0°C. As the measurements started after the first freeze-thaw cycles, it is unclear whether such freeze-thaw induced CO₂ peaks occurred at the site although the absence or less pronounced effect of frost-thaw cycles on in situ CO₂ emissions in forest ecosystems is also reported in the review of Matzner and Borken (2008).

4.2 CH₄ fluxes

Automatic and manual chamber based measurements revealed that the peatland forest was a sink for atmospheric CH₄ during the whole measuring period from end of April to end of June 2007. This means that the drainage was deep enough to change

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the aeration status and, thus, the conditions favourable for methanogenes to those favourable for methanotrophs. The high influence of the water table depth on the CH₄ exchange of peatlands has been observed in many other studies (Martikainen et al., 1993, 1995) and is further reflected by the significant positive correlation of CH₄ uptake rates with changes in water table depth during the observation period. Maximum uptake rates of >60 μg CH₄-C m⁻² h⁻¹ were significantly higher than observed by Martikainen et al. (1995) for a drained fen with comparable water table depths. In a large study combining data from drained and undrained peatland forests in Finland Minkkinen et al. (2007) found that in general, undrained sites functioned as CH₄ sources whereas drained sites functioned either as CH₄ sinks or still as small sources for CH₄. In their study the mean CH₄ uptake rates varied from 1 up to 90 μg CH₄-C m⁻² h⁻¹. For the Kalevansuo site they reported a mean uptake rate of 34 μg CH₄-C m⁻² h⁻¹, which is close to our value of 37 μg CH₄-C m⁻² h⁻¹ measured with the automatic chamber system. The extrapolated annual CH₄ sink of 3.2 kg CH₄-C ha⁻¹ yr⁻¹ is significant and even higher than the mean value (1.95 kg CH₄ ha⁻¹ yr⁻¹) for boreal forests reported by Dutaur and Verchot (2007) in their global inventory of soil CH₄ sinks. However, one has to stress that the value calculated from manual chamber measurements of 1.65 kg CH₄-C ha⁻¹ yr⁻¹ was significantly lower, which may be explained by differences in the water table depth and minerotrophic conditions between the manual and automatic chambers. The automatic chambers were located closer to the edge of the peatland area, where minerotrophic conditions were stronger and the drainage was more effective than in the middle of the measurement area, where manual chambers were located.

We found that CH₄ was produced throughout spring and summer at 22 and 25 cm depth in the peat profile. At the same time the net flux of CH₄ was negative, showing CH₄ uptake. This implies that the Kalevansuo site was well drained and the oxic top-layer of the peat was sufficient not only to oxidize the CH₄ produced in deeper layers, but also to oxidize additional atmospheric CH₄. This observation is in-line with observations at other sites, where also CH₄ concentrations well above atmospheric

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concentrations were detected in deeper soil layers, while soil was still functioning as a net sink for atmospheric CH₄ (Butterbach-Bahl and Papen, 2002). The concentration of CH₄ in the deep soil below the groundwater table (−45 cm) increased during the summer from July to September indicating an increase in the production of CH₄ in the peat profile. Unfortunately there were no CH₄ concentration measurements at −45 cm depth during April–June and, hence, it is unknown how the concentration developed at that depth during spring and early summer. At the same time the net CH₄ fluxes measured with the manual chambers showed nearly constant values during August and September. This reveals that, as the CH₄ production in deep soil increases, also the CH₄ oxidation rate in the aerobic peat layer increased during the summer.

The CH₄ fluxes measured with automatic and manual chambers differed by almost a factor of two. On average the manual chamber measurements resulted in significantly smaller CH₄ uptake values as compared to the automatic chamber measurements. The reason for this difference may be the locations of the chambers, as well as in the chamber design. The automatic chambers were located 170 m southwest of the EC mast, whereas the manual chambers were in all main directions of the mast at approx. 30–60 m distance. Despite this the vegetation around both manual and automated chambers was very similar. The manual chambers were dark, whereas the automatic chambers were transparent. It remains unclear whether ground vegetation influenced the net uptake of atmospheric methane, or whether the vegetation could participate in CH₄ production in the presence of light as suggested by Keppler et al. (2006).

When extrapolating the CH₄ fluxes measured with the automatic chambers during the two-month measurement period to a full year we get an annual cumulative CH₄ flux of −0.09 g C m^{−2} yr^{−1}, which is half of the annual sink estimate of −0.2 g C m^{−2} yr^{−1} for the same site during the years 2004–2005 (Minkkinen et al., 2007). The sink estimates can be considered as being relatively close to each other keeping in mind that we extrapolate measurements from two months of data to a full year.

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4.3 N₂O fluxes

In general, the N₂O emissions from the drained peatland forest were small and not exceeding 10 μg N m⁻² h⁻¹, except for a short period from the end of April to the beginning of May. During this spring-peak period the daily mean N₂O emissions measured by automatic chambers and sub-canopy EC peaked at approx. 11 and 20 μg N m⁻² h⁻¹, respectively. The peak in the EC measurements occurred approximately one week before the peak observed by the automatic chambers. Overall, these peak emissions occurred during a period when the air and litter layer temperatures fluctuated around zero and when the peat soil was finally fully melting. However, the peak in sub-canopy EC occurred at the same time as the peak in soil temperature and in CO₂ fluxes, whereas the peak measured by the automatic chambers occurred with a delay after the increase in soil temperature. This delayed emission peak took place during a period when air and litter layer temperatures again reached zero degrees, a night time minimum of -6.9°C and -2.2°C, respectively. In general, we interpreted that the N₂O emission peaks measured by both measurement techniques were most likely caused by freeze-thaw events in the soil and litter layer. The reason for different timing in these peak events remain unclear and may be explained by different soil conditions around the automatic chambers and the footprint of the sub-canopy eddy system. Similar to our measurements, Holst et al. (2008) related elevated springtime N₂O emissions in a steppe ecosystem to repeated night-to-day freezing-thawing cycles in the uppermost layer of the soil.

Freeze-thaw peaks in N₂O emissions have been well documented in laboratory and in field studies in boreal region (Koponen et al., 2004; Öquist et al., 2004; Regina et al., 2004; Koponen et al., 2006). Still most of the field measurements have been conducted with weekly to fortnightly manual chamber measurements, thus potentially missing or at least underestimating freeze-thaw driven N₂O pulses (Groffman et al., 2006). Matzner and Borken (2008) concluded in their review that freeze-thaw events have a high potential to cause gaseous N losses relevant at the annual time scale

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in all types of ecosystems. The freeze-thaw peaks measured at Kalevansuo peatland forest were relatively small as compared to thawing peaks measured in forest ecosystems in Central Europe experiencing high loads of N deposition, where freeze-thaw induced N₂O emissions have been found to contribute up to 73% to the annual N₂O emissions (Papen and Butterbach-Bahl, 1999). As the measured N₂O peaks at Kalevansuo drained peatland were relatively small the contribution of freezing-thawing induced emissions is most probably insignificant in this drained peatland forest. However, it has to be stressed that we most likely missed some freeze-thaw related N₂O emission pulses earlier in the season, as it was clear that the soil had been already partly thawing before the measurement campaign started. These emissions could be even higher than those that were measured since the intensity of freeze-thaw induced N₂O emission has been shown to decrease with time (Holst et al., 2008; Priemé and Christensen, 2001; Papen and Butterbach-Bahl, 1999).

Regarding the mean N₂O emission rate of 3.2 to 6.8 μg N m⁻² h⁻¹ over the study period similar values have been reported from natural and drained peatlands in Canada and Scandinavia (Martikainen et al., 1993; Regina et al., 1996; Schiller and Hastie, 1996; von Arnold et al., 2005a and b). The low fluxes at the Kalevansuo site can be explained by the high C:N ratio (40–45) of the litter layer and peat, indicating limited amounts of available nitrogen. Klemetsson et al. (2005) found a strong negative relationship between C:N ratios and N₂O emissions from drained forested peatlands mainly in Sweden and Finland. Klemetsson et al. (2005) used the C:N ratio as a scaling parameter for estimation of the annual source strength for N₂O (Ernfors et al., 2008). Our annual N₂O emission rate of 0.39 kg N ha⁻¹ yr⁻¹ extrapolated from our two-month measurement period fits well into the relationship found by Klemetsson et al. (2005). The importance of the soil C:N ratio as an indicator of the nutrient availability, and thus, the risk of potential ecosystem N losses could also be demonstrated for other ecosystems with low C:N ratios, e.g. nitrate leaching in European forests (MacDonald et al., 2002) or N₂O emission from tropical forests (Kiese and Butterbach-Bahl, 2002).

Regina et al. (1998) and Pihlatie et al. (2007) found that in nutrient poor peat soils

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and in upland boreal forest soils N_2O emissions originate from the litter layer rather than the peat or mineral soil body. In our study, we found that 1) the N_2O emissions correlated best with the air and litter layer temperature rather than the soil temperatures in deeper soil layers, 2) the concentrations of available nitrogen (NH_4^+-N , $NO_3^- -N$ and total N) in the litter layer were always higher than the concentrations in the peat, and 3) the C:N ratio of the litter layer was lower (approx. 40) than the C:N ratio in the peat body (approx. 45). All of these findings suggesting that most of the N turnover in this peatland forest takes place in the litter layer, and that the N_2O production is driven by the N release from the litter layer.

4.4 Comparison of the eddy covariance and chamber methods

The eddy covariance (EC) method is still relatively little used in measuring N_2O fluxes in terrestrial ecosystems (e.g. Wienhold et al., 1994; Christensen et al., 1996; Laville et al., 1997; Wagner-Riddle et al., 1997; Scanlon and Kiely, 2003; Pihlatie et al., 2005; Eugster et al., 2007). Much more data is available on the EC measurements of CO_2 fluxes in forest ecosystems, especially above forest canopies but also in the trunk-space (e.g. Baldocchi, 2003; Subke and Tenhunen, 2004; Launiainen et al., 2005). Among the studies available on the EC based N_2O studies only few have focused on method comparison between EC and chamber technique (Christensen et al., 1996; Pihlatie et al., 2005).

Despite measuring close to the detection limit of the N_2O EC system, the EC and chamber methods compared reasonably well with both N_2O and CO_2 fluxes. The difference between the two methods was that the EC fluxes of especially N_2O were smaller in magnitude and much noisier than the chamber measurements (see also Mammarella et al., 2009). Part of the variability and high noise level of the EC- N_2O fluxes was due to the fact that the fluxes were low and close to the detection limit of both the chamber and EC measurement systems. The reasons for the remaining noise in the EC N_2O measurements are discussed in more detail in Mammarella et al. (2009). Like in many other studies using the EC method for N_2O , we also ended up using daily averages of

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the N₂O fluxes. Reasons for doing so were that the fluxes were small and hence the only way to separate the signal out from the noise is averaging between subsequent flux values.

4.5 Greenhouse gas balance and the effect of freeze-thaw peaks

5 The measurements of GHG fluxes at the Kalevansuo site fits with the study of Minkkinen et al. (2002) stating that altered exchange rates due to drainage and afforestation have decreased the radiative forcing of peatlands in Finland. The negative radiative forcing was caused by increases in CO₂ sequestration in the tree stands and peat soil, decrease in CH₄ emissions from peat to the atmosphere and only a small increase in
10 N₂O emissions. To our knowledge there are no studies monitoring GHG exchange in the years after drainage, hence, high uncertainty is still associated with estimates of GHG exchange and balance of drained peatlands. As Martikainen et al. (1993) pointed out, the enhancement of the N₂O emission increase after drainage depends mainly on the nutrient status of the virgin peatland, thus, the overall negative contribution of enhanced N₂O emissions is potentially higher from nutrient-rich peatlands. Furthermore,
15 the contribution of frost-thaw driven N₂O emissions to the annual emission budget, which could be especially high in the years shortly after drainage is also unclear. Due to the high and short-term variability of fluxes we conclude that rather automatic chamber or EC method than manual chamber based measurements of N₂O emissions are
20 needed to further improve our scientific understanding in N₂O exchange of drained peatlands.

5 Conclusions

During the two-month measurement period the greenhouse gas (GHG) balance of the drained peatland forest at Kalevansuo was driven by CO₂. Fluxes of CH₄ and N₂O contributed only insignificantly to the GHG balance. The drained peatland forest (approx.
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after 40 years of drainage impact) was not a strong source of N₂O, but freeze-thaw driven N₂O emissions may contribute substantially to annual N₂O fluxes. Comparison between automatic and manual chamber methods, and eddy covariance (EC) method showed large differences, particularly with respect to the fluxes of CH₄ and N₂O measured by the automatic and manual chambers. As the chamber method is generally used for estimating annual GHG budgets of different ecosystems, it is crucial to pay attention to the locations and the number of chambers to cover the spatial variability of the site. Due to the combination of low N₂O emission levels the EC-TDL-based N₂O flux measurements were highly uncertain, whereas the EC-based CO₂ fluxes compared better with the fluxes measured by the automatic chambers.

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Table 1. Mean and median fluxes of CO₂, CH₄ and N₂O and coefficient of variation (CV%¹) measured by eddy covariance, and automatic and manual chambers in Kalevansuo peatland forest during 25 April–27 June 2007. EC_a and EC_s stand for eddy covariance above and below the canopy, respectively, and AC and MC stand for automatic and manual chambers, respectively.

	mg CO ₂ -C m ⁻² s ⁻¹			μg CH ₄ -C m ⁻² h ⁻¹		μg N ₂ O-N m ⁻² h ⁻¹		
	CO ₂ .EC _a	CO ₂ .EC _s	CO ₂ .AC	CH ₄ .AC	CH ₄ .MC	N ₂ O.EC _s	N ₂ O.AC	N ₂ O.MC ²
Mean ³	-0.031 ^a	0.009 ^b	0.008 ^b	-37.1 ^a	-18.5 ^b	3.2 ^a	4.5 ^b	6.8 ^c
Median	-0.026	0.008	0.008	-35.6	-15.4	2.5	3.9	6.8
CV%	180	75.7	45.3	40.2	144	123	62.3	42.8

¹ Coefficient of Variation was calculated as CV%=stdev of the flux/mean flux*100.

² Measurement period 25 April – 18 June 2007.

³ Different superscripts indicate significant differences between flux rates of one component measured with different methods.

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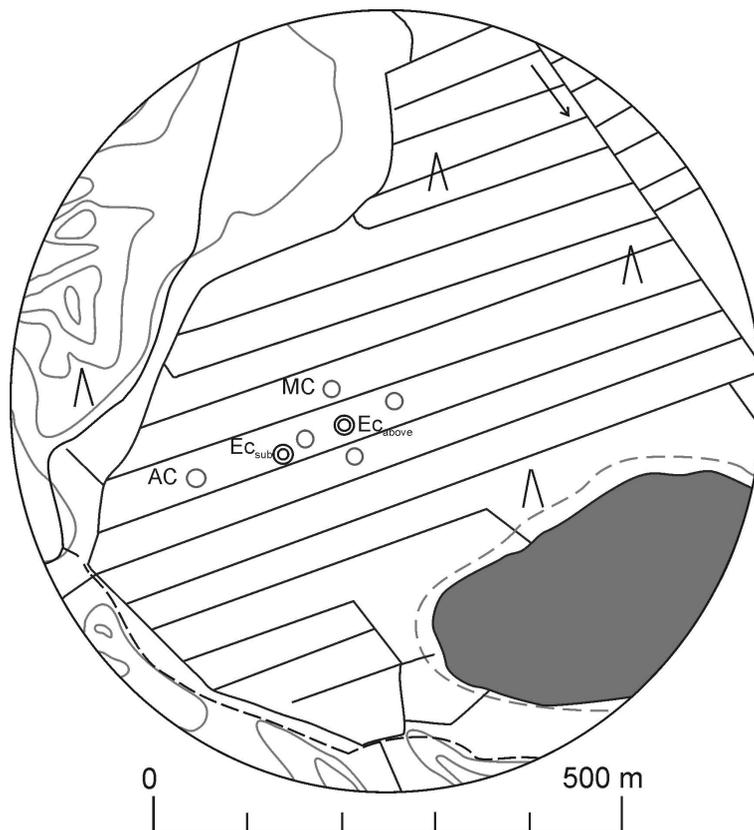


Fig. 1. Map of the measurement site showing the locations of tall eddy covariance (EC) mast (EC_{above}), sub-canopy EC mast (EC_{sub}), manual chambers (MC) and automatic chambers (AC).

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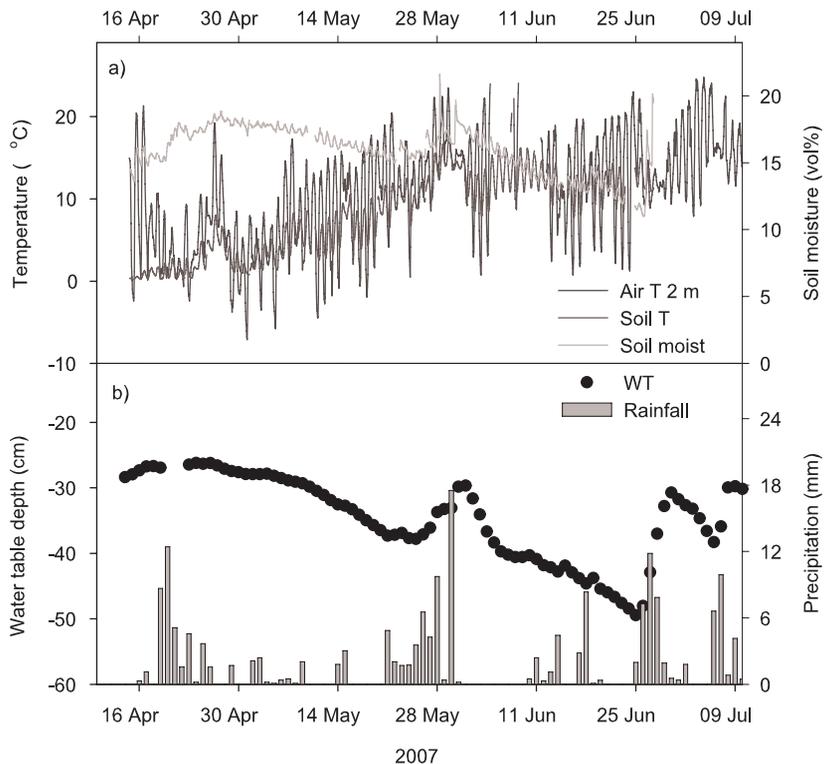


Fig. 2. (a) Soil and air temperatures, soil moisture, and **(b)** ground water table and precipitation at the drained peatland pine forest.

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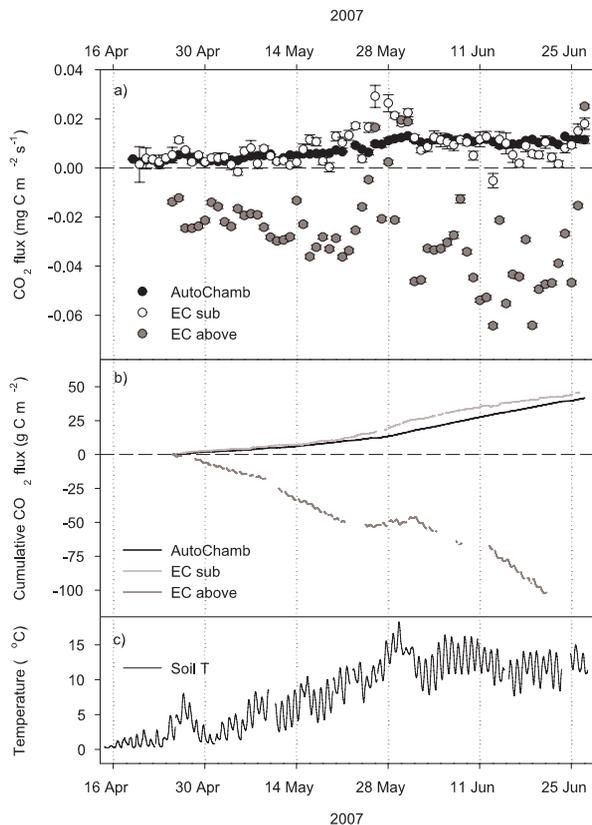


Fig. 3. (a) Daily mean CO₂ exchange measured with eddy covariance above the forest canopy (EC above) and inside the canopy (EC sub) and automatic chambers (AutoChamb), (b) cumulative CO₂ fluxes during the intensive measurement campaign (25 April–27 June 2007), and (c) soil temperature at 5 cm depth at the drained peatland pine forest.

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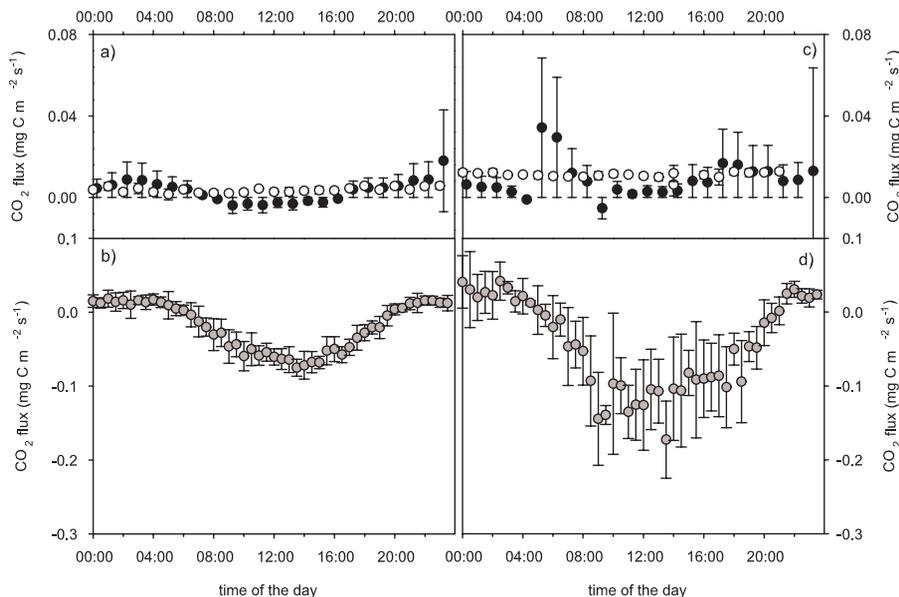


Fig. 4. Daily time course of CO₂ fluxes at the drained peatland pine forest measured with automatic chambers and sub-canopy eddy covariance (**a, c**) and above canopy eddy covariance (**b, d**) during a cold period in 30 April–10 May 2007 (**a, b**) and a warm period in 5–15 June 2007 (**c, d**). Dots represent median values for each hour over the 10-day period, error bars represent standard deviations.

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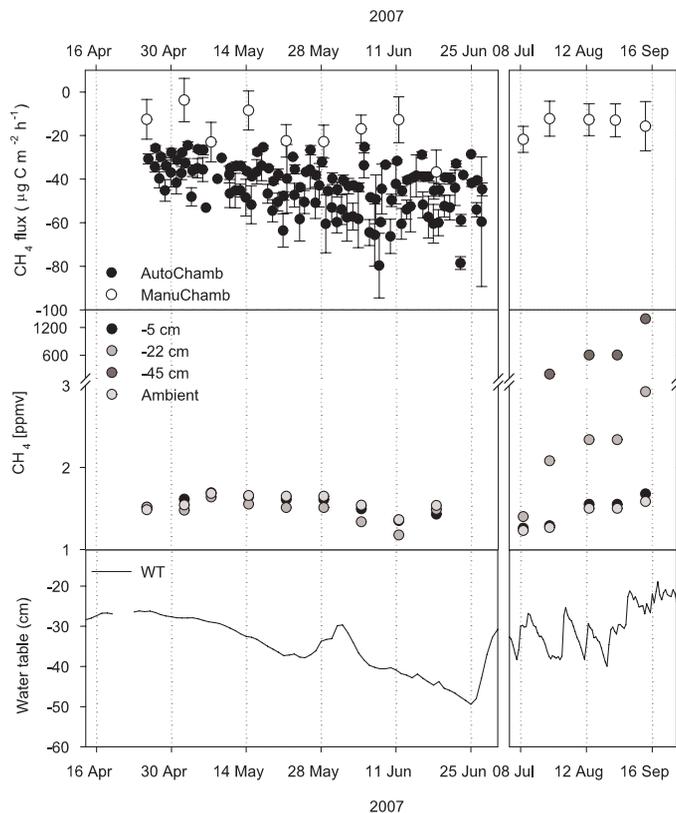


Fig. 5. (a) Daily mean fluxes of CH₄ measured with automatic ($n=9$) and manual ($n=16$) chambers, (b) soil concentrations of CH₄ at three depths and in the ambient air, and (c) ground water table depth measured at the drained peatland. First column of the figures represent the period of intensive measurements, the second shows the data outside the measurement campaign. Error bars stand for standard errors of the mean.

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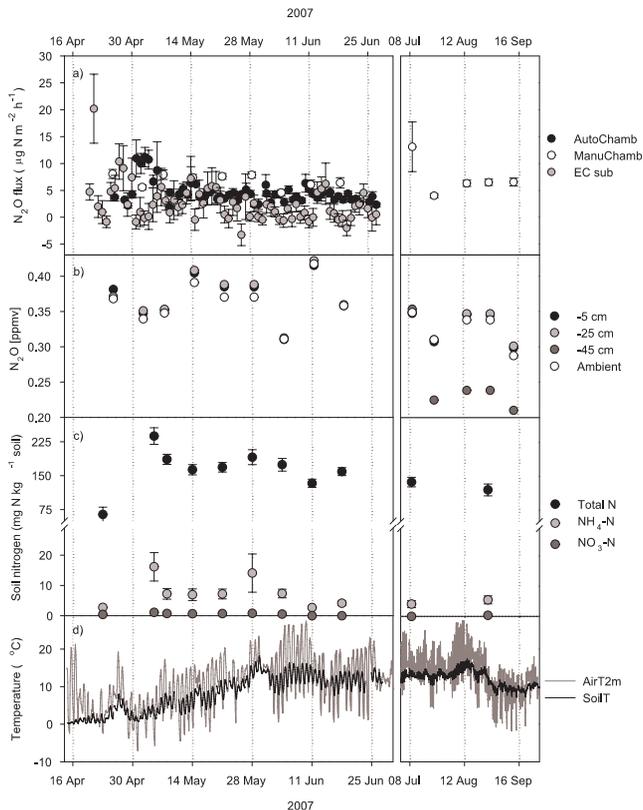


Fig. 6. (a) Mean soil N_2O fluxes measured with eddy covariance, automatic and manual chambers, (b) soil concentrations of N_2O at three depths and in the ambient air, (c) mineral nitrogen and total nitrogen concentrations in the litter layer of the soil, and (d) temperatures in the soil at 5 cm depth and in the air during April–September 2007 at the drained peatland pine forest. First column of the figures represent the period of intensive measurements, the second shows the data outside the measurement campaign. Error bars stand for standard errors of the mean.

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