



Annual emissions of CH₄ and N₂O, and ecosystem respiration, from eight organic soils in Western Denmark managed by agriculture

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Abstract. The use of organic soils by agriculture involves drainage and tillage, and the resulting increase in C and N turnover can significantly affect their greenhouse gas balance. This study estimated annual fluxes of CH₄ and N₂O, and ecosystem respiration (R_{eco}), from eight organic soils managed by agriculture. The sites were located in three regions representing different landscape types and climatic conditions, and three land use categories were covered (arable crops, AR, grass in rotation, RG, and permanent grass, PG). The normal management at each site was followed, except that no N inputs occurred during the monitoring period from August 2008 to October 2009. The stratified sampling strategy further included six sampling points in three blocks at each site. Environmental variables (precipitation, PAR, air and soil temperature, soil moisture, groundwater level) were monitored continuously and during sampling campaigns, where also groundwater samples were taken for analysis. Gaseous fluxes were monitored on a three-weekly basis, giving 51, 49 and 38 field campaigns for land use categories AR, PG and RG, respectively. Climatic conditions in each region during monitoring were representative as compared to 20-yr averages. Peat layers were shallow, typically 0.5 to 1 m, and with a pH of 4 to 5. At six sites annual emissions of N₂O were in the range 3 to 24 kg N₂O-N ha⁻¹, but at two arable sites (spring barley, potato) net emissions of 38 and 61 kg N₂O-N ha⁻¹ were recorded. The two high-emitting sites were characterized by fluctuating groundwater, low soil pH and elevated groundwater SO₄²⁻ concentrations. Annual fluxes of CH₄ were generally small, as expected, ranging from 2 to 4 kg CH₄ ha⁻¹. However, two permanent grasslands had tussocks of *Juncus effusus* L. (soft rush) in sampling points that were consistent sources of CH₄ throughout the year. Emission factors for organic soils in rotation and with permanent grass, respectively, were estimated

to be 0.011 and 0.47 g m⁻² for CH₄, and 2.5 and 0.5 g m⁻² for N₂O. This first documentation of CH₄ and N₂O emissions from managed organic soils in Denmark confirms the levels and wide ranges of emissions previously reported for the Nordic countries. However, the stratified experimental design also identified links between gaseous emissions and site-specific conditions with respect to soil, groundwater and vegetation which point to areas of future research that may account for part of the variability and hence lead to improved emission factors or models.

1 Introduction

On a global scale, organic soils (Histosols) represent a carbon stock that is equivalent to nearly 50 % of atmospheric CO₂ (Dröslér et al., 2008). In Europe organic soils cover approximately 5 % of the total land area (European Soil Bureau Network, 2005), and this proportion is similar in Denmark, where organic soils are widely used by agriculture as pastures or for crop production (Maljanen et al., 2010). With an organic matter content of 20 % or more in the top soil (FAO, 1998) the C and N turnover and gaseous exchanges of Histosols are significant for the greenhouse gas balance of Danish agriculture, even if their total area is relatively small (Gyldenkerne et al., 2005).

The greenhouse gas balance of organic soils may include contributions from CO₂, CH₄ and N₂O. The net flux of CO₂ is determined by the balance between total ecosystem respiration (R_{eco}) and photosynthesis, and R_{eco} can itself be separated into soil and plant respiration (Lambers et al., 1998). Jacobs et al. (2007), quantifying annual fluxes of CO₂ from several Dutch grasslands, found a net release of CO₂ from those on organic soil, but a net sequestration on mineral soils,

indicating that soil organic matter decomposition is critical for the carbon balance.

Methane production is expected to mainly occur below the groundwater table, but even here it can vary by several orders of magnitude (Segers, 1998). Controlling factors include anoxia, availability of substrates, the presence of microbial consortia capable of processing these substrates to CH₄, and competition from other processes such as sulfate reduction (Yavitt and Lang, 1990; Segers, 1998). Drainage will limit the production of CH₄, but also increase the potential for CH₄ oxidation during passage through the unsaturated zone to the atmosphere. As a result CH₄ fluxes from drained organic soils are consistently low or slightly negative (Langeveld et al., 1997; Drösler et al., 2008; Maljanen et al., 2010). Methane oxidation potentials appear to be highest near the oxic/anoxic interface. Hornibrook et al. (2009) found that CH₄ dissolved in the pore water of four Welsh peatland soils was nearly always zero at the groundwater table and concluded that emissions observed were predominantly mediated by vascular plants. The ability of plants with aerenchymous tissue to transport CH₄ to the atmosphere when CH₄ concentrations build up around the roots is well established (Laanbroek, 2010), and typically occurs when the soil is near saturation (Strack et al., 2006).

Degradation of soil organic matter as a result of drainage and cultivation will stimulate net N mineralization and N transformations via nitrification and denitrification which can then lead to N₂O production (Freibauer et al., 2004; Goldberg et al., 2010). Maljanen et al. (2010), reviewing GHG monitoring studies from the Nordic countries, reported that N₂O emissions from organic soils in agricultural use were on average four times higher than those from mineral soils, indicating that N₂O derived from soil organic matter decomposition dominate overall fluxes. According to Maljanen et al. (2010) annual N₂O emissions from managed organic soils range from 0.2 to 5.5 g m⁻², with an average of 1.6 g m⁻², but no studies from Denmark were available.

Denmark recently adopted Art. 3.4 of the Kyoto protocol concerning carbon stock changes within agriculture and forestry. For organic soils management such as drainage and cultivation will influence C turnover and losses, and consequently fluxes of CH₄ and N₂O derived from soil organic matter, and the total GHG balance of managed organic soils must therefore be accounted for. The field monitoring study reported here estimated annual fluxes of CH₄ and N₂O, as well as ecosystem respiration, from eight organic soils managed by agriculture. Protocols and instrumentation used at all monitoring sites were identical, as were procedures for sample analysis and data processing.

2 Materials and methods

2.1 Selection of monitoring sites

In the selection of locations for monitoring information about geology and geochemistry, as well as climate variables (insolation, precipitation, temperature) and land use were considered. Denmark has been sub-divided into landscape types, or geo-regions, based on age and genesis (Madsen et al., 1992). The three landscape types with the largest recorded areas of organic soil were: The outwash plains (including subglacial stream trenches) and hill islands of Western Jutland (total area 81 150 ha; region *W*), the raised sea bottom of Northern Jutland (total area 21 199 ha; region *N*), and the younger moraine landscape of Eastern Denmark, including kettle holes and lateral moraine (total area 34 335 ha; region *E*). The moraine deposits from the last (Weichselian) glaciation, which cover the eastern part of Denmark, have a high calcium content and thus differ geochemically from the deposits of northern and central Jutland. The latter regions, in contrast, have areas with high levels of pyrite (FeS₂).

Denmark is characterized by minor gradients in temperature and insolation, and a more significant gradient in precipitation, which ranges from around 500 to 900 mm yr⁻¹. Table 1 presents selected information about annual mean air temperatures and precipitation measured at the monitoring sites, together with the corresponding information for the period 88/89 to 08/09 based on data from a nation-wide 10 × 10 km² (precipitation) or 20 × 20 km² grid (temperature) of the Danish Meteorological Institute. Included as on-line supplementary information are graphical presentations of mean monthly temperatures and precipitation for the monitoring period and the preceding 20-yr period.

The predominant land uses for organic soils managed by agriculture were identified using the General Danish Agricultural Register (GLR). The land use categories arable crops in rotation (AR), permanent grassland (PG) and rotational grass (RG) together account for almost all of the area with organic soils managed by agriculture. Locations of monitoring sites were decided after a number of field trips to visit areas selected on the basis of existing maps of organic soil. Most sites inspected were discarded for reasons such as: the peat layer had disappeared; reluctance of the farmer to give access; or distance incompatible with logistical constraints which made it important to find different land uses near each other. Land use classes AR, PG and RG were identified in regions *N* and *E*, whereas only AR and PG were represented in region *W*. The monitoring sites had the following geographical coordinates (decimal degrees): region *W* – 55.94° N, 8.45° E; region *N* – 57.23° N, 9.84° E; region *E* – 56.38° N, 10.40° E. A map of Denmark indicating the location of sites is included as on-line supplementary information. The eight sites will be referred to by the unique combination of region and land use, e.g., W-AR.

Table 1. Average annual mean temperature, $T_{\text{ann}}(08/09)$, and precipitation, $P_{\text{ann}}(08/09)$, were calculated for each region for the period 21 September 2008 to 20 September 2009, the period that was used for estimating annual fluxes of CH₄ and N₂O. The table also shows 20-yr means and range of annual temperature and precipitation in each region.

Region	$T_{\text{ann}}(08/09)$	$T_{\text{ann}}(88/89 - 08/09)$ ^a			$P_{\text{ann}}(08/09)$	$P_{\text{ann}}(88/89 - 08/09)$ [§]		
		Mean	Min	Max		Mean	Min	Max
W – Skjern	9.5	8.6	6.5	10.6	913	806	391	1002
N – St. Vildmose	8.8	8.3	6.3	10.1	702	723	404	957
E – Mørke	9.1	8.4	6.4	10.0	579	662	381	947

^a Data from national grid of climate stations of the Danish Meteorological Institute.

The plant cover of the arable sites was dominated by the crop, i.e. spring barley (*Hordeum vulgare* L.) or potato (*Solanum tuberosum* L.); during fallow periods some weeds occurred. Grasslands in rotation were dominated by ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.). The latter two species also dominated the permanent grasslands in regions *N* and *E*. Region *N* featured the most diverse permanent grassland with approximately 15 commonly encountered grassland species. In region *E*, *L. perenne* was present in most of the area; however, dry parts of E-PG were dominated by *Agrostis capillaries* L., *Poa pratensis* L. and *Rumex acetosella* L.. The relatively small permanent grassland of region *W* contained a mixture of typical meadow grass species, as well as weeds from the surrounding cropland. *Juncus effusus* (soft rush) was present at sites N-PG and E-PG.

Information about N inputs in 2006–2008 was obtained from the farmers (Table 2). There were no additional inputs during the monitoring period, but as measurements started in August the management of 2008 had followed the normal practice at all sites, including fertilization and grazing. Management (cuts, harvest and soil cultivation) of the fenced-in monitoring sites followed the practice adopted by the farmers for each field. Cut plant material was collected to determine botanical composition and dry weight.

Nitrogen deposition (wet+dry) at the three sites was similar, 13–15 kg N ha⁻¹ in 2008 and 14–15.4 kg N ha⁻¹ in 2009 (National Environmental Research Institute, 2010).

2.2 Experimental design and supporting data

At each monitoring site six 55 cm × 55 cm sampling points for gas flux measurements were organized in three pairs at 5–10 m intervals. The pair-wise distribution was chosen to cover 1 to 10 m-scale variability, and each pair then served as a block in the statistical design. Boardwalks (1 m × 1.5 m) were placed in front of the sampling points during measurements only to minimize disturbances; in permanent grasslands the boardwalks rested on poles installed to > 1 m depth.

Piezometers, i.e. PEH tubes (Rotek A/S, Sdr. Felding, Denmark) were installed near each pair of sampling points, i.e., three per site. The depth of the 10-cm screen var-

ied between 60 and 130 cm depending on the groundwater level (GWL) in July–August 2008. A separate 10-cm diam. PVC tube with the screen at full length was also installed for continuous recording of GWL with a pressure transducer (H. F. Jensen, Copenhagen, Denmark); data were logged using a Micrologger ver. 3.0-3 (Campbell Scientific, UK). All piezometers were surveyed for inter-calibration of all GWL measurements to a common reference point.

Temperatures at 200 cm height and at 5, 10, 30 and 50 cm soil depth were monitored continuously using SKTS thermistors (Skye Instruments, Powys, UK). The average of 2-min readings were logged every hour with a Datalogger 2 data logger (Skye Instr.). Soil humidity at 5–10 cm and 15–20 cm depth were monitored in the same way using SKT600 tensiometers. Insolation was determined with a SKP215 PAR quantum sensor (Skye Instr.) using 1-min readings and logging of 30-min averages. Precipitation was monitored at 150 cm height with a rain gauge having an orifice of 200 cm² (Rain-o-matic pro; Pronamic, Silkeborg, Denmark). These data were logged with an event logger (Event 101, Madgetech, USA). In periods where climate data were lost due to technical problems, gaps were filled using data from the nearest monitoring site within the same region (distance ~100 m) or, in a few cases, with relevant grid data obtained from the Danish Meteorological Institute. Missing PAR data were taken from the nearest monitoring station and used directly, whereas soil temperatures were derived from air temperature using site-specific correlations between air and soil temperature.

A mast was installed at each site to support a mobile weather station (Kestrel 4500; Nielsen-Kellerman, Boothwyn, PA, USA), which was installed during measurement campaigns to record wind speed and direction, air temperature (backup), humidity and pressure.

Starting December 2008 concentrations of N₂O in the upper part of the saturated zone were monitored at each site using an equilibrium method. Gas was sampled from a piece of silicone tubing (length 14 cm, i.d. 2 cm) sealed at both ends with brass caps, which were held apart by three stainless steel rods. The diffusion cell was placed inside a piezometer tube with thick rubber washers to prevent entry of atmospheric air.

Table 2. Land use and N inputs via mineral fertilizers and manure during the period 2006–2009 at the eight monitoring sites. AR – arable crop; PG – permanent grassland; RG – rotational grass.

Region	Land use	Year	Crop/management	Fertilizer application	
W – Skjern	AR	2006	Barley with grass undersown	300 kg 21-2-1 NPK	
		2007	Barley with grass undersown	550 kg 21-3-10 NPK + 60 kg N in cattle slurry	
		2008	Barley with grass undersown	550 kg 21-3-10 NPK	
		2009	Barley with grass undersown	None ^a	
	PG	2006	Perm. grassland, grazed	None ^b	
		2007	Perm. grassland, grazed	None ^b	
		2008	Perm. grassland, no grazing	None	
		2009	Perm. grassland, no grazing	None	
	N – St. Vildmose	RG	2006	Grain crop with grass catch crop	183 kg N total, 63 kg N in slurry
			2007	Grass	159 kg N total, 66 kg N in slurry
2008			Grass	233 kg N total, 64 kg N in slurry	
2009			Grass	None ^a	
AR		2006	Grass	199 kg N total, 55 kg N in slurry	
		2007	Grain crop, catch crop undersown	188 kg N total, 106 kg in slurry	
		2008	Potato	125 kg N total, (no slurry)	
		2009	Potato	None ^a	
PG		2006	Perm. grassland, grazed	None ^b	
		2007	Perm. grassland, grazed	None ^b	
		2008	Perm. grassland, grazed	None ^b	
		2009	Perm. grassland, no grazing	None ^a	
E – Mørke		PG	2006	Perm. grassland, grazed	None ^b
			2007	Perm. grassland, grazed	None ^b
	2008		Perm. grassland, grazed	None ^b	
	2009		Perm. grassland, no grazing	None ^a	
	RG	2006	Spring barley, grass undersown	20 t cattle slurry	
		2007	Grass-clover	2 × 20 t cattle slurry (spring and summer)	
		2008	Grass-clover	60 kg N in cattle slurry April, June and August	
		2009	Spring barley, grass undersown	None ^a	
	AR	2006	Grass-clover	15 t cattle slurry	
		2007	Grass-clover	2 × 20 t cattle slurry (spring and summer)	
		2008	Spring barley, grass undersown	15 t cattle slurry primo April	
		2009	Grass-clover	None ^a	

^a None in experimental area.^b No assessment of N in excretal returns has been made.

The upper brass cap was connected via a 1/8" stainless steel tube to a three-way valve in an above-ground sampling unit. One port was connected to a 50-mL syringe for sampling of gas from the diffusion cell, and the other port was equipped with a hypodermic needle where an evacuated vial (12 mL Exetainer; Labco, High Wycombe, UK) could be mounted for sample collection. A 20-mL gas sample was collected, and then 20 mL helium was injected to re-expand the silicone cell (Jacinthe and Groffman, 2001). Concentrations of N₂O in the groundwater were calculated as described by Jacinthe and Groffman (2001).

Soil at 0–20 cm depth was sampled for analysis of mineral N on three occasions, in December 2008, April 2009 and September 2009. In each case six 20-mm diam. soil cores (0–20 cm depth) were pooled and 10 g fresh wt. soil extracted in 40 mL 1 M KCl. By the end of the monitoring program 50-mm diam. soil cores were taken to the lower boundary of the organic horizon, or a maximum of 132 cm. One core was taken near each pair of sampling points in 34-cm subsections; all sub-sections were analyzed for organic dry matter, SOC, total N and pH.

2.3 Flux chamber design

The two-part static chambers used in this study were constructed from 4-mm white PVC, largely following the design of Drösler (2005). The supports were 55 cm × 55 cm, 12 cm high and with a sharpened edge at the bottom. A 4-cm wide flange extended outwards 2 cm from the top, giving a maximum insertion depth of 10 cm. The support was fixed to the ground by four 40-cm pegs installed at an angle. The distance to the soil surface inside the supporting frame was determined in a 10 cm × 10 cm grid for correction of total enclosure volume during measurement.

Dimensions of the chamber unit were 60 cm × 60 cm × 41 cm including a closed-cell rubber profile (Emka Type 1011-34; Megatrade, Hvidovre, Denmark) at the bottom. Inter-sections of the same dimensions were used when required due to plant height. Inside the chamber was a 92 mm × 92 mm 12V fan (RS Components, Copenhagen, Denmark) for headspace mixing connected to an outside battery (Yuasa Battery Inc.; Laureldale, PA, USA). A vent tube, designed in accordance with the recommendations of Hutchinson and Mosier (1981), was included with outlet near the ground to minimize effects of wind (Conen and Smith, 1998). A temperature sensor (Conrad Electronic SE; Hirschau, Germany), extending 20 cm below the top, was connected to a digital display (Conrad Electronic SE). A butyl rubber septum was included for gas sampling. Finally, two handles were attached to the top which were also used for straps fixing the chamber firmly against the support.

2.4 Sampling protocol

Upon arrival at the field site weather conditions were recorded and the mobile weather station mounted. GWL was then determined at the continuous monitoring station, and in each piezometer at the pair-wise sampling points which were subsequently emptied with a 12V pump and left to refill while gas fluxes were measured.

Gas fluxes were determined using a 60-min enclosure period. Gas samples (20 mL) were taken with a syringe and hypodermic needle immediately after positioning of the chamber and attachment of straps, and then after 15, 30, 45 and 60 min. Gas samples were collected in 12-mL pre-evacuated Exetainer vials that were typically analyzed within 48 h, and always within a week from sampling. A preliminary test had shown that concentrations of CH₄, CO₂ and N₂O in these vials were stable during at least two months of storage (data not shown).

Soil temperatures at 5, 10 and 30 cm depth were recorded manually during chamber deployment. These measurements were made with a high precision thermometer (GMH3710, Omega Newport, Deckenpfronn, Germany) between the two chamber units of each block.

Following gas sampling, fresh groundwater was sampled from each piezometer except in a few cases where too little water had accumulated. Approximately 100 mL water was collected, part of which was used to immediately determine groundwater temperature, pH and electrical conductivity using a Cyberscan PC300 (Eutech Instruments; Singapore). The rest of the sample was filtered (0.45 μm nylon membrane SNY 4525, Frisnette, Denmark) directly into 10-mL test tubes that were transported back to the laboratory in a cooler for analysis of SO₄²⁻, Cl⁻, NH₄⁺ and NO₃⁻.

Measurement campaigns were conducted at 3-week intervals between August 2008 and October 2009; in the case of site W-PG frames had to be relocated in October 2008 due to flooding, and therefore the first sampling at this site was on 3 November 2008. Hence, 19 or 17 field campaigns were conducted per site, or in total 51, 49 and 38 campaigns for land use categories AR, PG and RG, respectively. One or two campaigns were included per field trip. Most gas flux measurements were initiated between 9:00 and 12:00, and in a few cases between 12:00 and 13:00.

2.5 Analytical techniques

2.5.1 Soil

Soil dry wt. was determined after drying to constant weight at 100 °C. Soil NH₄⁺ and NO₃⁻ in KCl extracts were analyzed by autoanalyzer using standard colorimetric methods (Keeney and Nelson, 1982). Total and organic C and total N were determined on representative subsamples of soil dried at 100 °C according to ISO 10694 and ISO 13878, respectively.

2.5.2 Groundwater

Ammonium was measured colorimetrically on a Shimadzu 1700 spectrophotometer (Shimadzu Corp., Kyoto, Japan) according to a Danish/European standard method (DS/EN ISO 11732). Chloride, SO₄²⁻ and NO₃⁻ were determined by ion chromatography on a Dionex ICS-1500 IC-system (Dionex Corp.; Sunnyvale, CA, USA) with an anion Micro Membrane Suppressor (AMMS III 4 mm). The system was equipped with two guard columns (IonPac AG22 and IonPac NG) and a separator column (IonPac AS22). The eluent was a mixture of 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃. Samples for ion chromatography were filtered <0.22 μm (nylon membrane SNY 2225; Frisnette, Knebel, Denmark).

2.5.3 Gas analyses

Nitrous oxide, CH₄ and CO₂ were determined on a dual-inlet Agilent 7890 GC system interfaced with a CTC CombiPal autosampler (Agilent, Nærum, Denmark). The configuration was developed to enable determination of CH₄, N₂O and CO₂ with a single 2000-μL injection which is split between

the two inlets. Two identical instruments were configured, as field sampling and gas analyses were shared between two laboratories.

Channel 1 of each system consisted of a 2-m backflushed pre-column with Hayesep P connected to a 2-m main column with Poropak Q via a 6-port valve. The other end of the main column was connected to a four-port valve diverting the gas stream either to an electron capture detector (ECD) for N₂O analysis, or to a flame ionization detector (FID) for CH₄ analysis. The carrier was N₂ at a flow rate of 45 mL min⁻¹. For the ECD, Ar-CH₄ (95%/5%) at 40 mL min⁻¹ was used as make-up gas. The FID was supplied with 45 mL min⁻¹ H₂, 450 mL min⁻¹ air and 20 mL min⁻¹ N₂. Temperatures of injection port, columns, ECD and FID were 80, 80, 325 and 200 °C, respectively. Channel 2 was equipped with a 3-m Poropak Q column and used helium at 42 mL min⁻¹ both as carrier and for the reference cell of the thermocouple detector (TCD). Temperature of inlet, column and TCD were 80, 80 and 250 °C, respectively, and with He at 7 mL min⁻¹ as make-up gas.

The chromatograms were processed using EZ Chrom Elite software. A calibration mixture with approximately 10 μL L⁻¹ CH₄, 2 μL L⁻¹ N₂O and 2000 μL L⁻¹ CO₂ (Linde Gas; Copenhagen, Denmark) was used to prepare a five-point dilution series for determination of unknown samples. Standards were included after every ten samples to ascertain the stability of detector responses.

Analyses of N₂O, CH₄ and CO₂ were carried out in two different laboratories using identical instruments and analytical methods as specified above. Method detection limits were determined to be 0.042, 0.20 and 61 μL L⁻¹ or better for N₂O, CH₄ and CO₂, respectively. An inter-calibration between the two instruments used for sample analysis was carried out using samples from two randomly selected sampling days, a batch being analyzed in lab 1 and then in lab 2 and vice versa. The regression slope of 2nd analysis against 1st analysis ($n = 42$) was 1.01, 1.04 and 1.03 for N₂O, CH₄ and CO₂, respectively, when analyzed first in lab 1, and 0.98, 1.01 and 0.96 for N₂O, CH₄ and CO₂ for the dataset analyzed first in lab 2. Small systematic errors could derive from concentration inaccuracies in the separate calibration mixtures used in the two laboratories.

2.6 Data analysis

2.6.1 Flux calculations

Non-linear concentration change over time was frequently observed, and the HMR procedure recently described by Pedersen et al. (2010) was therefore adopted. This procedure analyzes non-linear concentration-time series with a regression-based extension of the model described by Hutchinson and Mosier (1981), and linear data by linear regression; statistical information is provided for both categories of flux estimates. A flux model was selected for each

individual concentration-time series on the basis of a scatter plot. HMR is available in an add-on package in the free programming software R (<http://www.r-project.org>).

Annual fluxes of CH₄, N₂O and R_{eco} were calculated for the period 21 September 2008 to 20 September 2009 for each site and block; for site W-PG the daily flux prior to the relocation was fixed at the value of 3 November. Daily fluxes were calculated by linear interpolation between sampling days for each of the three blocks (with paired sampling points) of a given site. Annual fluxes were calculated for each block by summation over the period 21 September 2008 to 20 September 2009, the standard errors representing the variation between annual estimates for each block (i.e. within-block variation on individual sampling days was not included).

2.6.2 Effect of sampling time

Flux measurements should ideally be conducted under conditions representing the 24-h period of the sampling day. At 5 cm soil depth the temperature at 10:00 deviated between -2 and +1 °C from daily mean temperature during the period from 21 September 2008 to 20 September 2009 (data not shown), indicating that mid-morning is a suitable time of day for short-term measurements. In practice most measurement campaigns started between 9:00 and 12:00, a few even between 12:00 and 13:00. To evaluate the error associated with the variable time of measurement, annual estimates of N₂O fluxes and R_{eco} were corrected to daily mean temperature.

Q_{10} values for R_{eco} were estimated for individual sites by fitting the van't Hoff equation (Lloyd and Taylor, 1994) to scatter plots of R_{eco} vs. soil temperature at 5 cm depth using SigmaPlot 2000 (SPSS Inc.). This gave site specific apparent Q_{10} values ranging from 2 to 3.5. For N₂O a relationship with soil temperature could not be identified, and a fixed Q_{10} of 2 was used (Vicca et al., 2009). R_{eco} and N₂O flux data were corrected to daily mean temperature using the modified Van't Hoff equation (Davidson et al., 2006):

$$R = R_m \times Q_{10}^{((T-T_m)/10)} \quad (1)$$

where R is the flux at temperature T (here the daily mean temperature) and R_m is the measured flux at T_m , the soil temperature at the start of the measurement. Annual fluxes were calculated with corrected data as for measurement data.

No attempt was made to correct CH₄ fluxes, which depend on CH₄ production in saturated parts of the soil profile, and CH₄ oxidation that may also primarily occur near the groundwater table (Hornibrook et al., 2009). At this depth diurnal temperature variations are small, i.e., any error associated with sampling time would be small.

2.6.3 Effects of region and land use

Systematic effects of region (W, N, E), land use (AR, PG, RG), and the interaction between region and land use, on

annual fluxes of N₂O and CH₄ were determined by an approximate test by calculating F-values for each of these effects using the mean square of variations between blocks within each combination as the denominator. All mean squares were calculated using a linear model. To control variance heterogeneity CH₄ fluxes were square-root transformed and N₂O fluxes ln transformed prior to analysis. The F-tests were only approximate, because the distances between blocks were considered to be too small to represent the true variation within each of the region-land use combinations.

2.6.4 Effects of soil properties and climate

Empirical relationships between soil and environmental conditions and, respectively, fluxes of CH₄ and N₂O were explored by region using a linear mixed model. Flux rates were transformed as described above prior to testing. Based on a preliminary investigation of collinearity between independent variables the following main effects and interactions were included: Land use, soil temperature at 5 cm depth, GWL, soil moisture at 15–20 cm depth, precipitation during 48 h prior to sampling, peat depth, C:N ratio (0–30 cm), pH (0–30 cm), GW-EC (electrical conductivity), GW-pH, GW-NH₄⁺ and GW-NO₃⁻, as well as the interactions land use x soil temperature, land use x soil moisture, and soil moisture x precipitation. Groundwater SO₄²⁻ concentrations were strongly correlated with EC and therefore not included as independent variable.

2.6.5 Emission factors

Emission factors were calculated for rotational crops (AR and RG) and permanent grassland (PG), respectively. Mean fluxes and 95 % confidence limits of CH₄ and N₂O fluxes were calculated by back-transformation of square-root transformed and ln transformed data, respectively.

3 Results

3.1 Site characteristics

Most peat soils in Denmark are shallow following decades of drainage and cultivation. Peat depth at the eight monitoring sites included in this study was in most cases 50 to 100 cm except for site W-AR, where the peat at one end of the plot extended to 310 cm depth (Fig. 1a). Some characteristics of the peat materials are shown in Table 3. The C:N ratios ranged from 17 to 52 and were consistently lower in region W than in the other two regions. All soils were acidic, with pH values in the range 3.5 to 5.8. Minimum pH was generally observed at 34–64 cm depth in region W and N. At 0–30 cm depth there was a strong positive relationship between soil organic carbon concentration of the soil dry matter and C:N ratio ($P < 0.001$) (Fig. 1b).

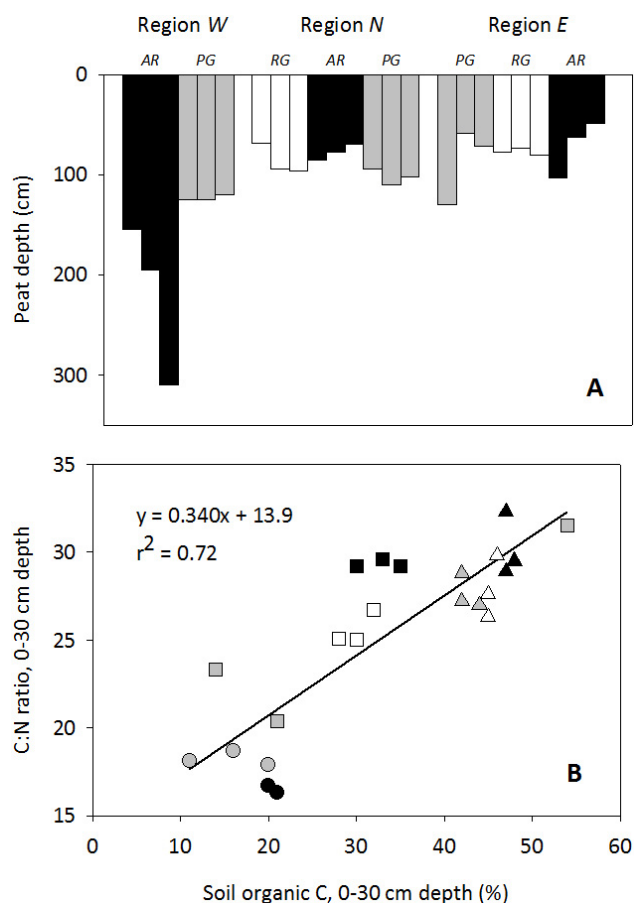


Fig. 1. (A). Peat depth by experimental block at the eight monitoring sites. Key: AR – arable crop; PG – permanent grassland; RG – rotational grass. (B) The scatter plot shows soil C:N ratio as a function of soil organic carbon (%). Key: W-AR, black circles; W-PG, grey circles; N-AR, black triangles; N-RG, white triangles; N-PG, grey triangles; E-AR, black squares; E-RG, white squares; E-PG, grey squares.

Soil mineral N data are shown in Table 4. Concentrations of NH₄⁺ and NO₃⁻ were generally higher in the soils of region N than in region W or E. The most notable observation was an accumulation of NO₃⁻ in the soil of site N-AR, i.e., the potato field, to 100 and 166 mg N kg⁻¹ dry wt. soil in April and September, respectively.

3.2 Climatic conditions

The annual mean temperatures recorded in region W, N and E were 9.5, 8.8 and 9.1 °C, respectively. Winter was colder and the early spring warmer than average, see on-line supplementary information. Annual precipitation in region W, N and E was 913, 702 and 579 mm, which was higher than average for region W, and slightly lower than average for region E. With respect to monthly means there were for the monitoring period only minor deviations from 20-yr average

Table 3. Soil organic carbon, C:N ratio and pH of the peat in the eight organic soils used in the monitoring study. Rotational grass (RG) was not represented in region W. AR – arable crop; PG – permanent grassland; RG – rotational grass.

Depth (cm)	Organic C (% of dry wt.)			C:N			pH		
	AR ^a	PG	RG	AR	PG	RG	AR	PG	RG
Region W – Skjern									
0–30	20.3	15.7	NA	17.0	18.2	NA	5.0	4.9	NA
34–64	38.7	41.0		18.3	22.1		3.9	3.8	
68–98	38.0	47.5		19.7	22.6		4.4	3.5	
102–132	31.0	22.3		19.1	26.3		4.7	4.5	
Region N – St. Vildmose									
0–30	47.3	42.7	45.3	30.2	27.7	27.9	4.5	5.1	4.9
34–64	31.0	52.7	40.0	25.4	52.5	26.9	4.2	4.6	4.5
68–98	11.6	40.3	4.0	25.6	31.1	23.3	4.7	5.3	5.2
Region E – Mørke									
0–30	32.7	29.7	30.0	29.3	25.1	25.6	4.9	4.7	5.8
34–64	40.7	46.3	37.7	29.0	27.7	27.5	4.3	4.8	5.5
68–98	– ^b	37.0	34.5	–	28.6	26.7	–	4.9	5.4
102–132	–	48.0	–	–	29.5	–	–	4.4	–

NA – not applicable.

^a AR was spring barley in Regions W and E, potato in Region N.^b No peat at this depth.**Table 4.** Soil mineral N (0–20 cm depth) was determined in the experimental areas on three occasions during the study. The data shown represent mean ± standard error (*n* = 6). AR – arable crop; PG – permanent grassland; RG – rotational grass.

Region	Land use	Dec 2008		Apr 2009		Sep 2009	
		NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻	NH ₄ ⁺	NO ₃ ⁻
W – Skjern	AR	ND	ND	1.3 (0.7)	6.1 (0.8)	3.9 (1.8)	15.2 (0.7)
	PG	ND	ND	10.9 (4.2)	7.5 (0.8)	3.7 (1.2)	15.6 (2.5)
N – St. Vildmose	AR	12.0 (1.7)	30.8 (2.2)	5.8 (2.2)	100 (11)	11.0 (7.2)	166 (4)
	PG	26.2 (2.0)	7.0 (3.5)	39.4 (12.2)	4.3 (2.6)	31.9 (2.4)	29.2 (6.7)
	RG	11.8 (1.0)	11.0 (0.5)	28.8 (20.4)	10.5 (1.3)	9.4 (2.7)	30.7 (1.7)
E – Mørke	AR	9.4 (0.4)	1.3 (0.4)	4.7 (1.4)	4.2 (0.5)	8.5 (1.5)	13.2 (1.1)
	PG	11.4 (2.4)	0.6 (0.6)	10.2 (1.8)	1.0 (0.6)	6.2 (0.5)	2.3 (1.1)
	RG	9.8 (3.9)	1.1 (0.5)	18.0 (4.8)	23.2 (1.9)	4.4 (0.5)	6.6 (0.4)

ND – not determined.

values except for a general tendency for higher precipitation in May, June and July 2009; the 107-mm excess precipitation in region W was fully accounted for by extremely high rainfall in October 2008; see supplementary information which also shows unusually high rainfall in August 2008, prior to the beginning of the monitoring period, in all regions.

Figure 2 shows air temperature and soil temperatures at 5 cm depth at the time of measurement campaigns, the data shown were extracted from the database with continuous data. No sub-zero soil temperatures were observed below 5 cm depth.

3.3 Groundwater

Figure 3 presents mean GWL of the piezometers. Regions W and N were characterized by significant seasonal fluctuations in GWL, where the unsaturated zone varied from –10 to –50 cm during winter and spring and dropped to between –80 and –100 cm during summer and early autumn. In contrast region E showed a high degree of stability in GWL, but GWL at the arable site, E-AR, was much lower than at sites E-PG and E-RG. At sites N-PG and E-PG the gradients in GWL were due to the topography at these sites.

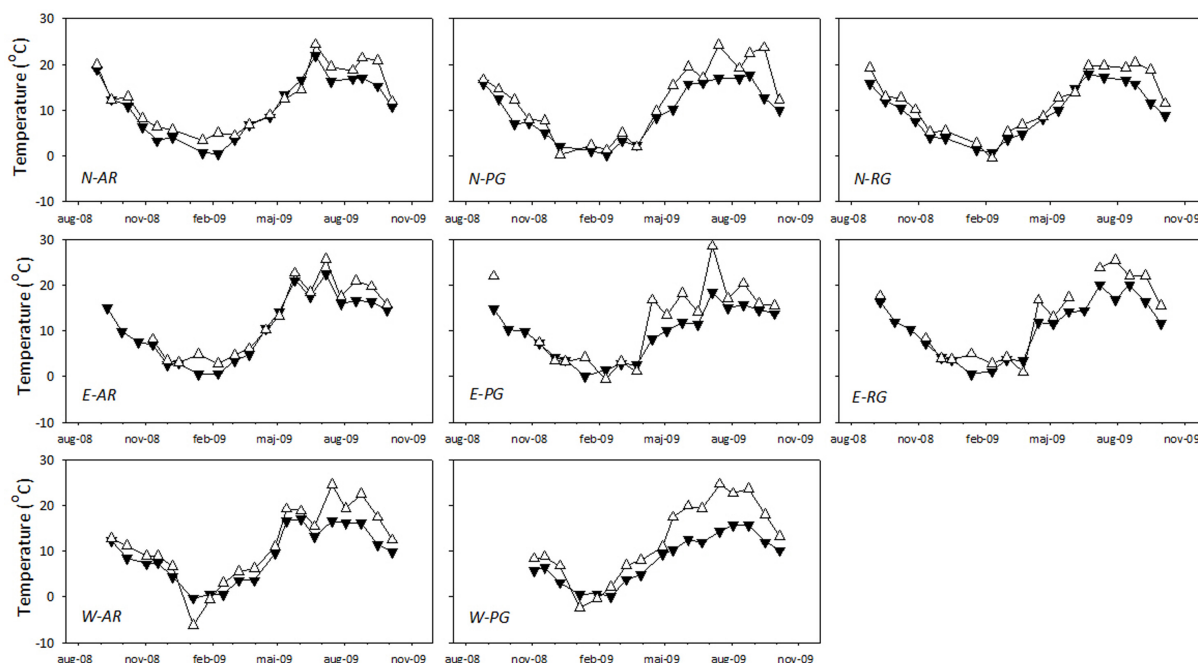


Fig. 2. Seasonal variations in soil temperature at 5 cm depth (▼) and air temperature at 200 cm height (Δ) at the eight monitoring sites representing three regions (*W*, *N* and *E*) and three land use categories (AR – arable crop; RG – rotational grass; and PG – permanent grass). The data shown were extracted from a database with continuous data to indicate conditions on sampling days. In region *E* some data were lost due to technical problems.

Concentrations of SO_4^{2-} are presented in Fig. 4 (not all samples were analyzed due to resource limitations). The SO_4^{2-} level varied little across the year, but significantly between sites. In region *N* the land uses AR and RG, located side-by-side but with different crops, had very similar levels of SO_4^{2-} at the first sampling, 120 and 130 mg L^{-1} in N-RG and N-AR, respectively, but diverged steadily with concentrations decreasing to 92 mg L^{-1} at site N-RG, but increasing to 155 mg L^{-1} at site N-AR (potato). Highest overall groundwater SO_4^{2-} concentrations were observed at site W-AR, in particular where the deepest peat was recorded (Fig. 1a). During autumn the concentrations were nearly twice as high, up to 600 $\text{mg SO}_4^{2-} \text{ L}^{-1}$, at block 3 as at the other two blocks.

Groundwater NO_3^- concentrations were low, <3 mg L^{-1} (Fig. 5). At site E-PG NO_3^- occurred only in block 1 where N_2O emission was consistently recorded (cf. Sect. 3.4.1). In autumn 2009 NO_3^- was only recorded at two sites used for arable crops (W-AR and N-AR). Here the accumulation of NO_3^- coincided with a drop in GWL to 100 cm depth. The dynamics of groundwater NH_4^+ were modest, but characterized by large differences between sites. The concentration of groundwater NH_4^+ was always low with land uses AR and RG except in region *W* where 10 to 20 $\text{mg NH}_4^+ \text{ N L}^{-1}$ was found during autumn 2008, with the highest concentrations at block 3 with the deep peat.

Groundwater pH in regions *N* and *E* were largely constant, but varied among land use categories, i.e., between pH 5 and 6 in region *N* and between 5.8 and 7 in region *E* (data not shown). At site W-AR groundwater pH remained at pH 5 to 6 during autumn 2008 and the following winter, but then dropped around 1 pH unit following spring during a period with an 80-cm lowering of the groundwater table. At the last site, W-PG, groundwater pH were low, between 3 and 6, but highly variable between samplings and blocks (data not shown). Groundwater EC levels varied between 400 and 700 $\mu\text{S cm}^{-1}$ except at site W-AR, where EC averaged 1000 $\mu\text{S cm}^{-1}$ during autumn 2008 and then declined to a constant level of 800 $\mu\text{S cm}^{-1}$. Chloride concentrations varied little within site, with concentrations in the range 20 to 40 mg L^{-1} except at site N-AR, where it was 50 to 60 mg L^{-1} (data not shown).

Figure 6 shows dissolved N_2O in the saturated zone as calculated from N_2O concentrations in a silicone diffusion cell. Jacinthe and Groffman (2001) reported that at 11 °C the concentration at equilibrium with atmospheric air is 0.44 $\mu\text{g N}_2\text{O L}^{-1}$, and hence dissolved N_2O was mostly below or slightly above atmospheric concentrations, but with a notable exception. At site N-AR, the potato field, extremely high levels of N_2O were consistently recorded, the actual values reported being highly uncertain because they were outside the range of the calibration curve. In contrast, the groundwater N_2O concentration at site N-RG, located at <20 m distance from site N-AR, never exceeded 2 $\mu\text{g N}_2\text{O L}^{-1}$ (Fig. 6).

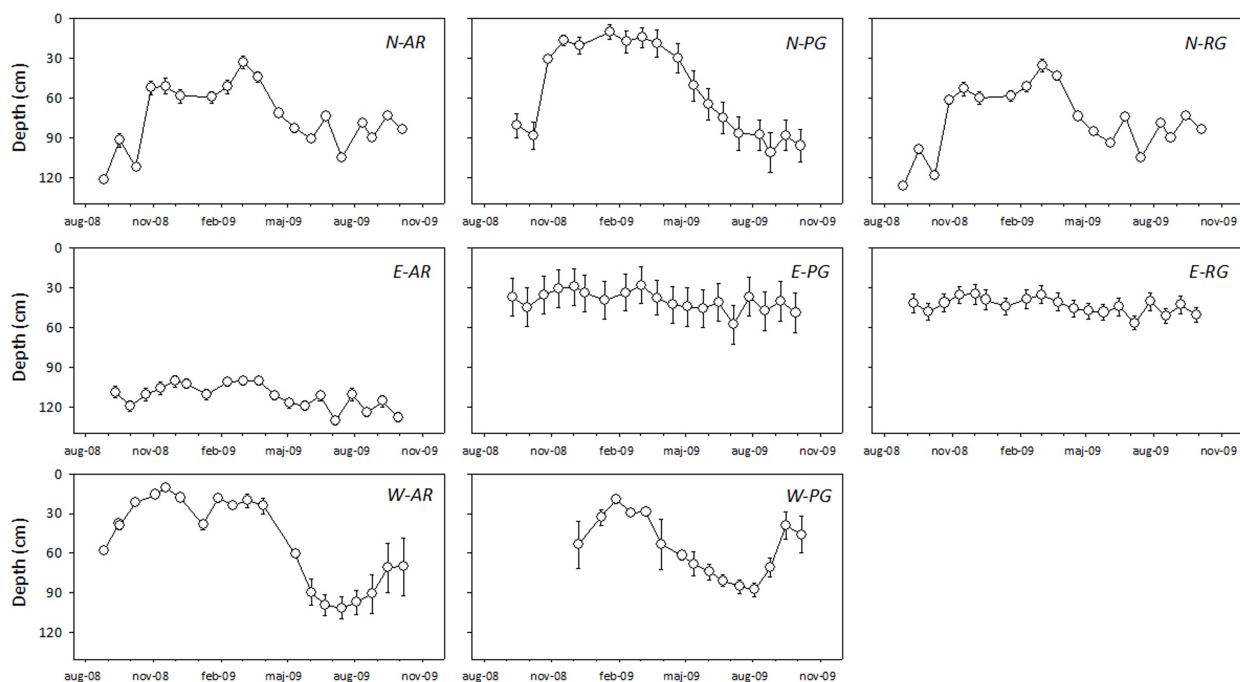


Fig. 3. Seasonal variations in groundwater level (GWL) at the eight monitoring sites; for information about site ID, see legend to Fig. 2. The data (mean \pm standard error) represent GWL in piezometers at the paired sampling points during gas flux measurement campaigns ($n = 3$).

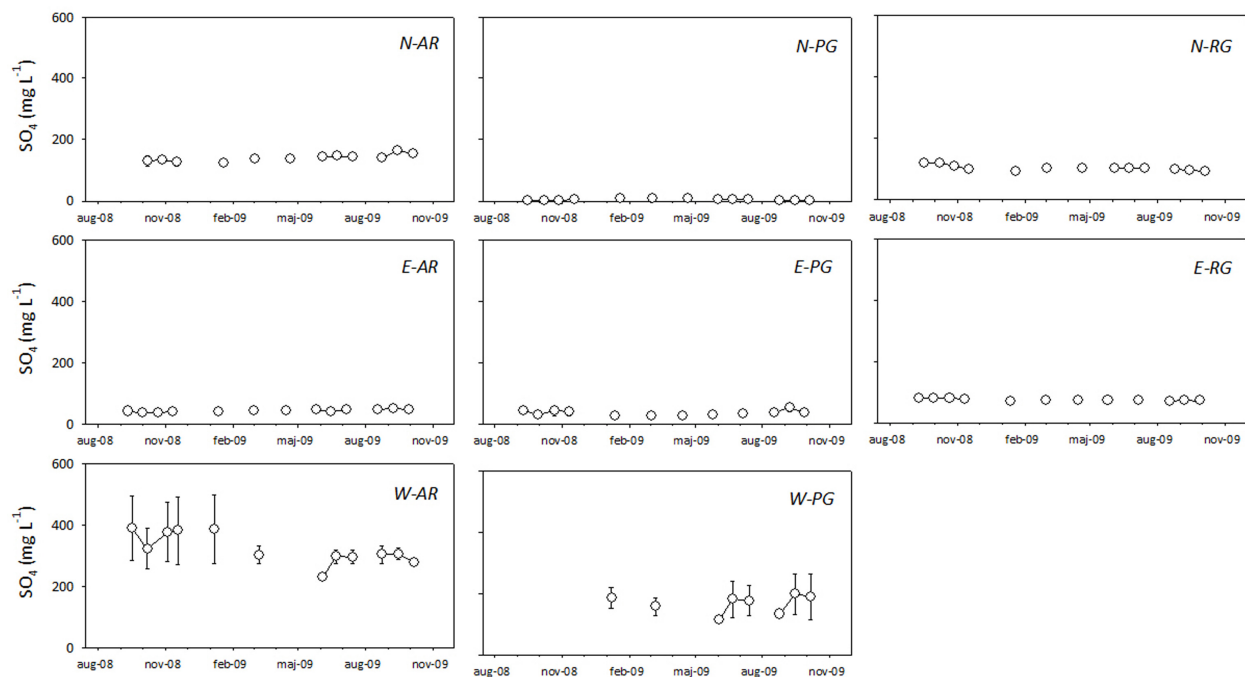


Fig. 4. Seasonal variations in groundwater sulfate (GW-SO₄²⁻) at the eight monitoring sites; for information about site ID, see legend to Fig. 2. Fresh groundwater was sampled from piezometers at the paired sampling points during gas flux measurement campaigns (the data shown represent mean \pm standard error, $n = 3$). The data set was incomplete due to resource limitations.

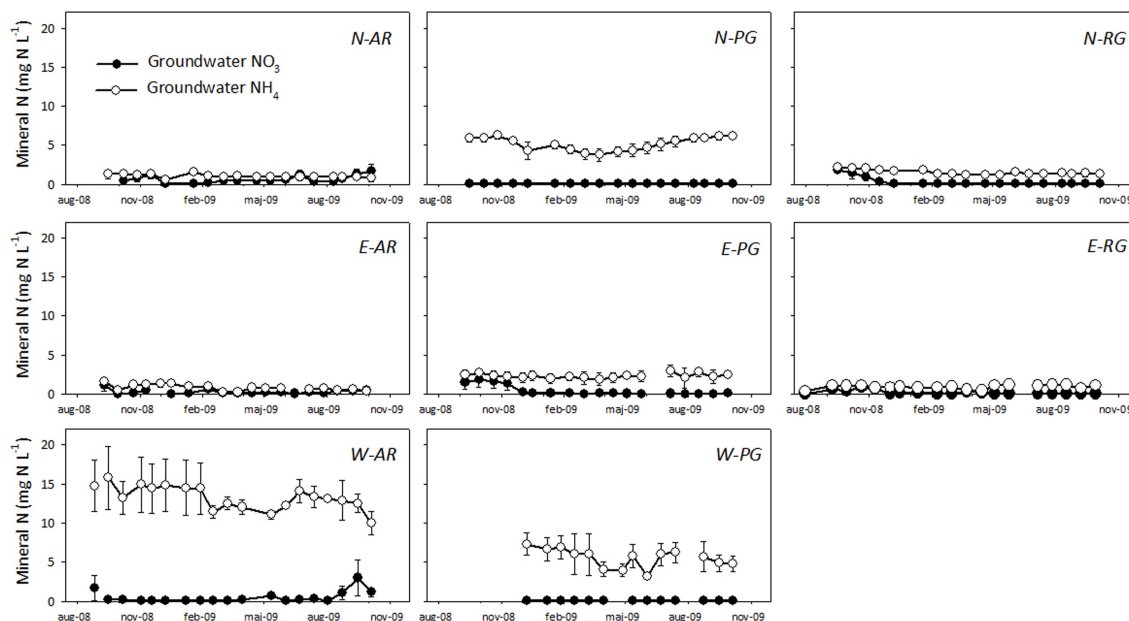


Fig. 5. Seasonal variations in groundwater ammonium (GW-NH₄⁺) and nitrate (GW-NO₃⁻) at the eight monitoring sites; for information about site ID, see legend to Fig. 2. Fresh groundwater was sampled from piezometers at the paired sampling points during gas flux measurement campaigns (the data shown represent mean \pm standard error, $n = 3$).

3.4 Seasonal dynamics and annual fluxes of N₂O, R_{eco} and CH₄

The following sections will present seasonal dynamics of N₂O, R_{eco} and CH₄, as well as annual fluxes representing the period 21 September 2008 to 20 September 2009. Fluxes are by definition positive when referring to emissions, and negative when referring to net uptake by the soil.

3.4.1 Nitrous oxide

Fluxes of N₂O from permanent grasslands (PG) were always low, 0 to 500 $\mu\text{g N}_2\text{O m}^{-2} \text{h}^{-1}$ (Fig. 7). At site E-PG N₂O emissions only occurred from block 1 located on a ridge where GWL was at -60 to -80 cm, as opposed to -20 to -40 cm at blocks 2 and 3. Also, peat depth was greater at block 1 (Fig. 1a). In region E low N₂O fluxes were also observed with land use AR and RG. At site W-AR some cases with headspace concentrations of N₂O in excess of 10 $\mu\text{L L}^{-1}$ were observed at the two first samplings in autumn 2008 which were outside the range that could be quantified. Attempts to reanalyze after dilution failed, and a total of six individual observations were excluded from further analysis for this reason. A similar pattern was not seen in early autumn 2009. Subsequent peaks in N₂O flux at site W-AR were observed in late winter, after spring cultivation, and following harvest in late July 2009. Elevated rates of N₂O emission, though less dramatic, were also recorded in late summer 2008 at site N-AR, followed by emission maxima during winter, spring and early autumn 2009 that coincided

with accumulation of NO₃⁻ in the soil (Table 4). Site N-RG showed a consistent increase in N₂O emissions during early spring despite the absence of any fertilization or cultivation. The GWL declined from -30 to -100 cm during this period, and presumably this N₂O was derived from a pool of mineralizable organic N released upon drainage of the top soil.

Annual fluxes of N₂O are shown in Table 5. The highest rates, recorded at the arable sites W-AR and N-AR, corresponded to 38 and 61 $\text{g N}_2\text{O-N kg ha}^{-1}$; some extreme rates at site W-AR during autumn were probably missed as explained above. The remaining sites ranged from 0.5 to 3.7 $\text{g N}_2\text{O m}^{-2}$, corresponding to annual losses of 3 to 24 $\text{g N}_2\text{O-N ha}^{-1}$.

3.4.2 Ecosystem respiration

Ecosystem respiration (R_{eco}) showed a similar pattern at all monitoring sites, following seasonal trends in temperature (Fig. 8). There was, however, also a reciprocal relationship ($P < 0.05$) with GWL (Fig. 3) at all but one site (E-PG), and thus CO₂ fluxes could also be partly controlled by drainage.

Annual values of R_{eco} ranged from 5.3 $\text{kg CO}_2 \text{m}^{-2}$ (1.5 kg C m^{-2}) at site N-AR (potato) to a maximum of 12.2 $\text{kg CO}_2 \text{m}^{-2}$ (3.3 kg C m^{-2}) at site N-RG, where R_{eco} was significant also during winter (Table 5). Hence, the lowest and the highest R_{eco} values occurred from neighbouring fields, the main difference being that the soil of land use AR had no vegetation during an extended period from October 2008 until May 2009, whereas RG was covered by a grass sward throughout the monitoring period.

Table 5. Annual fluxes (g m⁻²) of CH₄, N₂O and ecosystem respiration (R_{eco}) for the period 21 September 2008 to 20 September 2009. Fluxes of CH₄ and N₂O are also expressed as CO₂ equivalents (t ha⁻¹). The data represent mean \pm standard error ($n = 6$). AR – arable crop; PG – permanent grassland; RG – rotational grass.

Region	Land use	CH ₄	CO ₂ eq	N ₂ O	CO ₂ eq	R_{eco}	CO ₂ eq
W – Skjern	AR	-0.02 (0.07)	-0.01	6.0 (2.4)	18	9350 (510)	94
	PG	-0.16 (0.06)	-0.04	1.2 (0.2)	4	6710 (250)	67
N – St. Vildmose	AR	0.03 (0.08)	0.01	9.6 (1.6)	29	5350 (210)	53
	PG	2.8 (2.87)	0.7	0.5 (0.2)	1	10 240 (1360)	102
	RG	-0.03 (0.03)	-0.01	3.7 (0.6)	11	12 200 (900)	122
E – Mørke	AR	0.38 (0.23)	0.09	1.0 (0.1)	3	5850 (350)	59
	PG	4.7 (4.53)	1.2	1.4 (0.9)	4	10 200 (1370)	102
	RG	0.03 (0.03)	0.01	0.6 (0.1)	2	7540 (260)	75

3.4.3 Methane

Except for sampling points which included *J. effusus*, fluxes of CH₄ were small, mostly fluctuating within the range -100 to 200 $\mu\text{g CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ (Fig. 9). Fluxes of CH₄ from site N-PG and E-PG are presented with a separate curve for two (site N-PG) or one sampling point (site E-PG) with tussocks of *J. effusus*, which all showed consistent net emissions of CH₄ throughout the year. The dry matter of *J. effusus* in cuts taken during the monitoring period in the two blocks with *J. effusus* was positively related to the annual mean flux of CH₄ from these sampling points (Fig. 10).

3.5 Flux controls and emission factors

3.5.1 Effect of sampling time

The representativeness of fluxes recorded between mid-morning and noon was evaluated for R_{eco} and N₂O fluxes by temperature adjustment using site-specific Q_{10} (R_{eco}) or a fixed Q_{10} (N₂O). For R_{eco} the deviations from daily mean temperature in the actual sampling program would give relative errors in estimated annual fluxes ranging from 1 to 25 % (Fig. 11). The range and magnitude of relative errors estimated for N₂O fluxes were smaller, i.e., 2 to 7 %.

3.5.2 Effects of geo-region and land use

In the test of system effects (region, land use) on CH₄ fluxes the two blocks with *J. effusus* were omitted, as it was not possible to avoid extreme variance heterogeneity despite data transformation. The variation between regions was much higher than within-site variability, whereas there was no effect of land use, and no interaction between region and land use (Table 6). Hence, CH₄ fluxes differed between landscape types (geo-regions) but not land use, but as mentioned above

fluxes were generally low. Hence, in permanent grasslands emission hotspots such as those associated with *J. effusus* in the present study may dominate the CH₄ budget.

The variation in N₂O flux between regions was not significantly higher than the variation between blocks within a site, but there was a significant effect of land use, and a strong tendency ($P = 0.0653$) that the effect of land use differed between regions (Table 6). These differences were caused mainly by emissions from arable sites (see Discussion).

3.5.3 Effects of soil and climatic conditions

Empirical relationships between, respectively, N₂O and CH₄ fluxes and several independent variables were examined by region using a linear mixed model. Significant effects were identified in all cases (Table 7), but no consistent patterns that would indicate general controls of N₂O or CH₄ fluxes were found. Nitrous oxide fluxes were related to mineral N in the groundwater in region *E* only. In Region *E* there were significant effects of top soil C:N ratio and pH on CH₄ fluxes. Gradients in soil and groundwater properties at the block level probably contributed to these effects (data not shown). Temperature and water (GWL, soil moisture or precipitation) was involved in most significant effects, either as main effect or interaction. In view of the importance of temperature and O₂ availability for biological processes, the effects of seasonal changes in climate and GWL are not surprising.

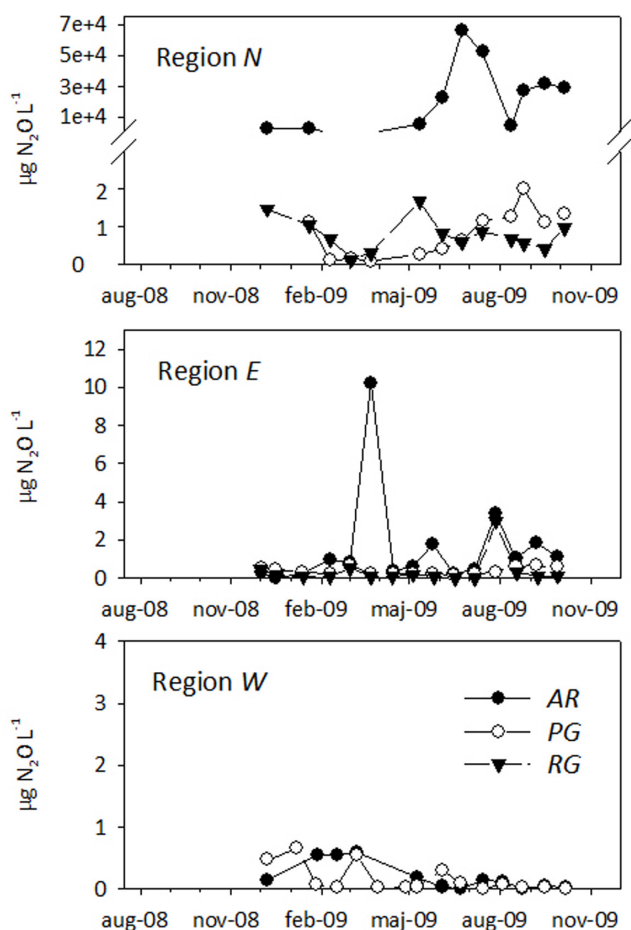
3.5.4 Emission factors

Emission factors with 95 % confidence intervals are presented in Table 8. Emission factors were calculated for soils in rotation (land use categories AR and RG) and permanent grasslands (land use category PG), respectively. Land use categories AR and RG were combined for derivation of

Table 6. Effects of region and land use were evaluated with an approximative linear mixed model (see text). Methane fluxes were square-root transformed, and N₂O fluxes ln transformed, prior to testing.

	Effect	df, num	df, denom	F value	P
Methane ^a	Region	2	14	5.58	0.017
	Land use	2	14	1.83	0.197
	Region x Land use	3	14	0.55	0.658
Nitrous oxide	Region	2	16	2.95	0.081
	Land use	2	16	6.12	0.011
	Region x Land use	3	16	2.93	0.065

^a Blocks with *Juncus* were not included.

**Fig. 6.** Concentrations of N₂O dissolved in the groundwater were determined in a central location at each of the eight monitoring sites using a silicone diffusion cell (see text) starting December 2008. Gas samples at equilibrium with the surrounding water were collected during gas flux measurement campaigns.

emission factors because rotational grass will alternate with other crops of the rotation at regular intervals. Although the system analysis showed an effect of region, rather than

Table 7. Relationships between soil and environmental conditions and, respectively, CH₄ and N₂O fluxes during the monitoring period were investigated with a linear mixed model. Methane fluxes were square-root transformed, and N₂O fluxes ln transformed, prior to testing. See text for an explanation of the independent variables and interactions included in the model.

	N ₂ O			CH ₄		
	W	N	E	W	N	E
Region						
Effects ^a						
Land use						
<i>T</i> _{-5 cm}					**	**
<i>T</i> _{-5 cm} × Land use	**	***		***		
GWL	*			*		
GW _{NO₃}			*			
GW _{NH₄}			*			
GW _{EC}	*					
GW _{pH}		*				
Soil _{H₂O}						
Soil _{H₂O} × Land use			**	*		
Prec _{48 h}	**			*		
Soil _{H₂O} × Prec _{48 h}	*					
Peat depth						
Soil _{C:N}						**
Soil _{pH}						**

^a *T*_{-5 cm} – Soil temperature at 5 cm depth; GWL – groundwater level; GW_X – groundwater concentration of nitrate or ammonium, or groundwater electrical conductivity, or pH; Soil_{H₂O} – soil water tension at 5–10 cm depth; Prec_{48 h} – precipitation during 48 h prior to Sampling; Soil_{C:N} – soil C:N ratio at 0–30 cm depth; Soil_{pH} – soil pH at 0–30 cm depth. *, *P* < 0.05; **, *P* < 0.01; ***, *P* < 0.001.

land use, on CH₄ fluxes when excluding experimental blocks with *J. effusus* (Table 6), the overall flux was dominated by these emission hotspots in permanent grasslands. The CH₄ emission factor for permanent grasslands (0.47 g m⁻²) was significantly (*P* < 0.001) higher than from crops in rotation (0.011 g m⁻²), although the confidence limits of both land use categories included net uptake. The N₂O emission factors for permanent grasslands and crops in rotation were 0.5 and 2.5 g m⁻², respectively, but the difference was not statistically significant (0.05 < *P* < 0.10).

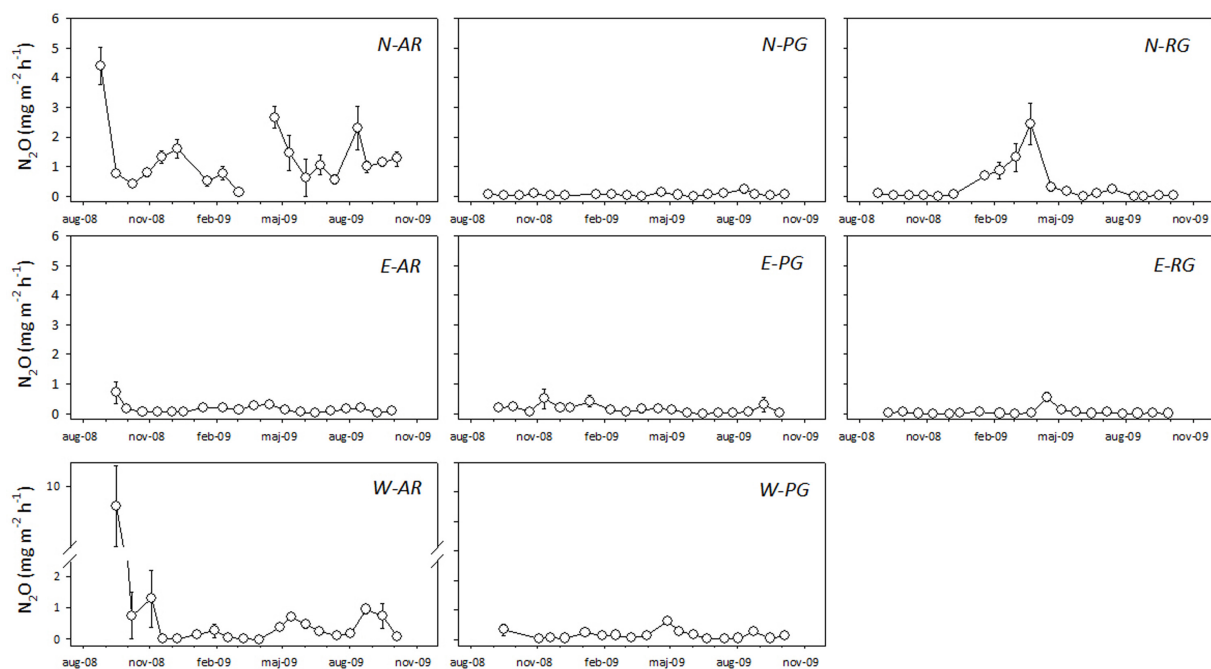


Fig. 7. Seasonal variations in N₂O fluxes at the eight monitoring sites; for information about site ID, see legend to Fig. 2. One data set from April 2009 at site N-AR was omitted due to unresolved analytical problems. The data represent mean \pm standard error ($n = 6$).

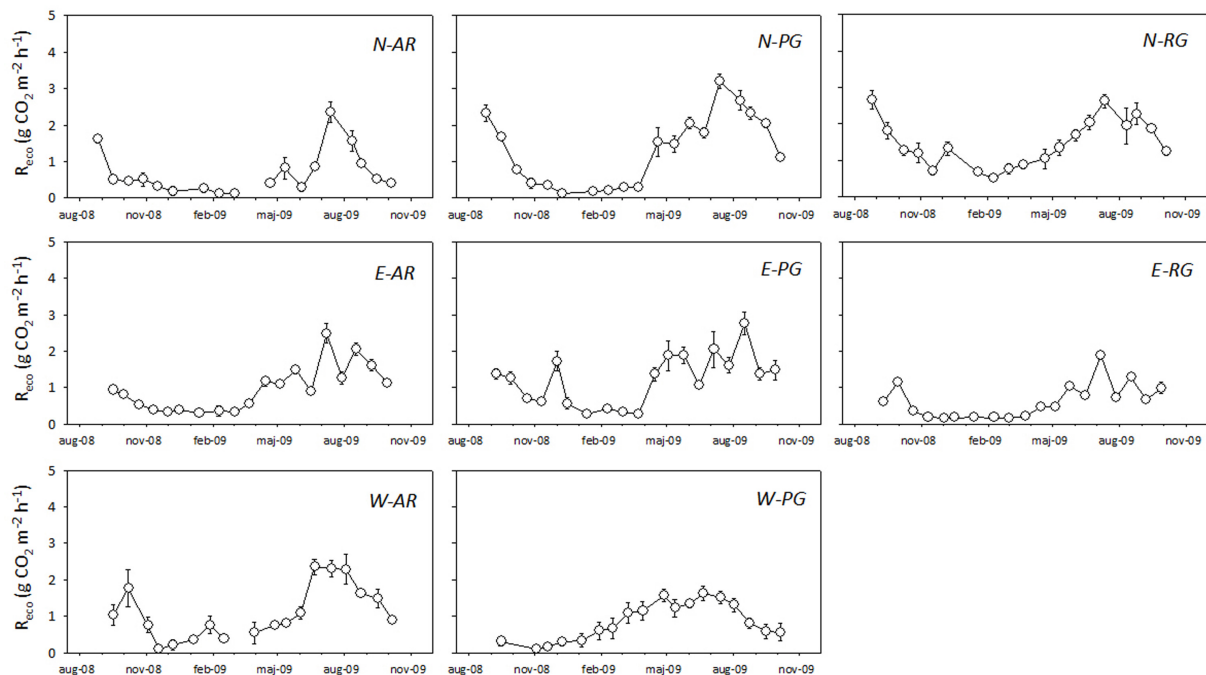


Fig. 8. Seasonal variations in ecosystem respiration (R_{eco}) at the eight monitoring sites; for information about site ID, see legend to Fig. 2. One data set from April 2009 at site N-AR was omitted due to unresolved analytical problems. The data represent mean \pm standard error ($n = 6$).

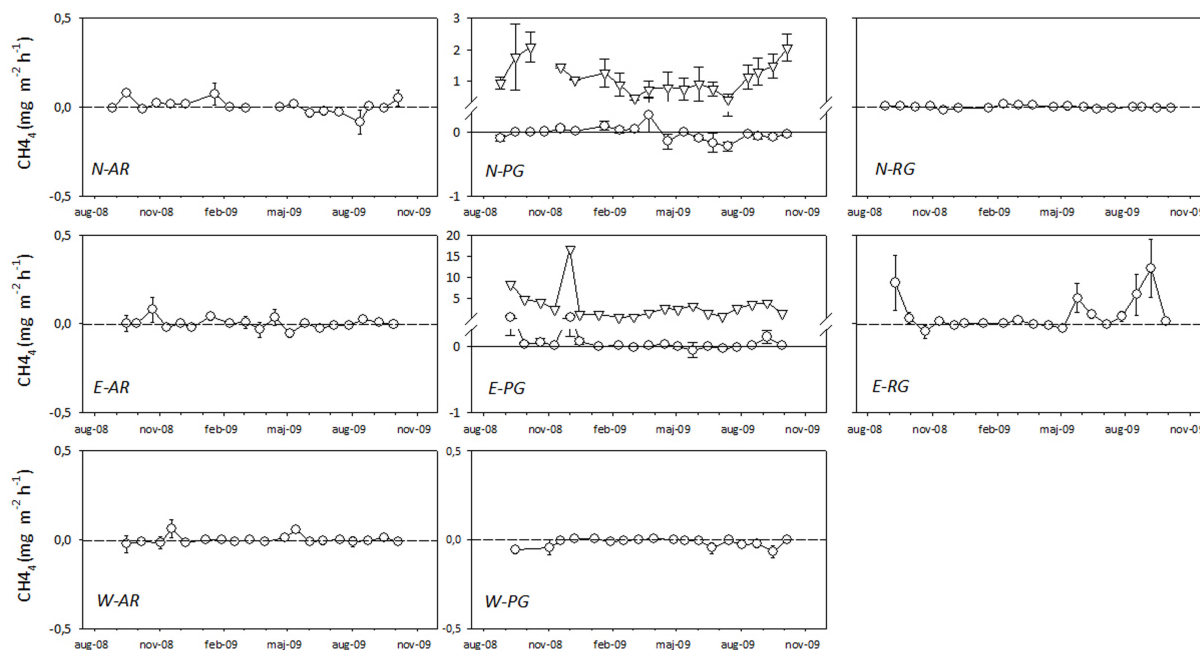


Fig. 9. Seasonal variations in CH₄ fluxes at the eight monitoring sites; for information about site ID, see legend to Fig. 2. One data set from April 2009 at site N-AR was omitted due to unresolved analytical problems. At sites N-PG and E-PG there were a few sampling points, with tussocks of *J. effusus* (soft rush) that showed consistent emissions of CH₄. Circles represent mean \pm standard error ($n = 6$ at sites without soft rush). Sampling points with soft rush at site N-PG ($n = 2$) and E-PG ($n = 1$) are shown separately (triangles).

Table 8. Annual emission factors (g m^{-2}) for CH₄ and N₂O were calculated for soils in rotation (land use categories AR and RG in this study) and permanent grassland (PG), respectively, using experimental block (paired sampling points) as the basic unit.

Land use	CH ₄		N ₂ O	
	Rotation (AR+RG)	Grassland (PG)	Rotation (AR+RG)	Grassland (PG)
N	15	9	15	9
Mean	0.011	0.47	2.5	0.5
Median	0.016	0.05	3.3	0.8
95 % confidence limits	-0.005 to 0.08	-0.1 to 2.9	1.4 to 4.5	0.2 to 1.6

4 Discussion

4.1 Gas sampling and analysis

The monitoring study was planned to cover major landscape and land use categories. Spatial variability was addressed by the use of a stratified sampling scheme with selection of representative landscape types and land use categories, in accordance with the recommendations of the Intergovernmental Panel on Climate Change (IPCC, 2006). The distribution of sampling points at each site was also stratified to account for 1- to 10-m scale variability, and the experimental blocks were the basic unit used for calculation of annual fluxes.

A sampling strategy based on manually operated chambers was selected. While enclosure-based methods rely on proper replication to cover spatial variability, they also allow

fluxes to be linked to soil conditions at the individual sampling points. Between 38 and 51 measurement campaigns were conducted for a given land use category (across all regions), and with a 3-week sampling frequency on average at the individual site. Hence, sampling intensity at the individual site was low, but the ability of a given sampling strategy to precisely estimate cumulative fluxes also depends on the temporal variability (Parkin, 2008). In the present study fluxes were driven by soil organic matter turnover and therefore mainly depended on climatic conditions and soil properties, i.e., there were no short-term dynamics due to fertilizer inputs or excretal returns.

Chamber measurements were initiated between 9:00 and 13:00 in this study. In an attempt to evaluate the representativeness of sampling time we estimated the effect of deviations from daily mean temperature for N₂O emissions and

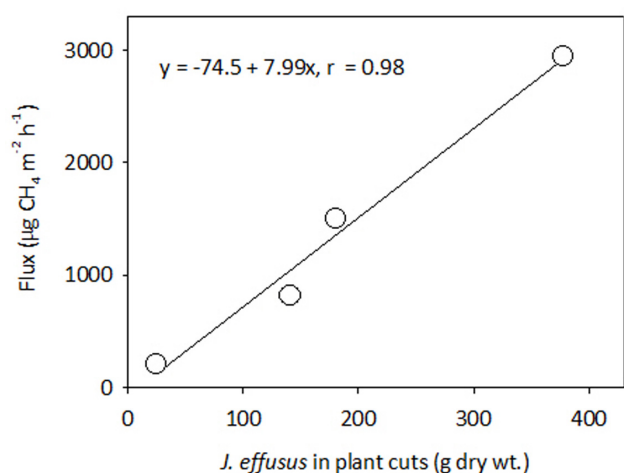


Fig. 10. Relationship between dry wt. of *J. effusus* stems in the biomass of plant cuts and the mean flux of CH₄. *J. effusus* occurred in four individual sampling points, although in one of them only with a few scattered stems.

R_{eco} . Fluxes of N₂O were less sensitive to variations in sampling time than R_{eco} (Fig. 11), and deviations could not be explained by the use of a variable Q_{10} for R_{eco} (data not shown). Diurnal variation in soil temperature is dampened with depth (Fang and Moncrieff, 1998; Bahn et al., 2008), and the difference between R_{eco} and N₂O could be due to a different vertical distribution of CO₂ producing and N₂O producing processes. Soil temperature at 5 cm depth was used here, but a representative temperature does not exist for either process (Vicca et al., 2009). Also, the apparent Q_{10} values of up to 3.5 observed probably included indirect effects of temperature, for example on substrate availability (Davidson et al., 2006).

Ecosystem respiration and fluxes of CH₄ and N₂O were determined using a chamber deployment time of 60 min. Trace gas accumulation was often not linear, which would lead to under-estimation of fluxes if linear regression is used (Davidson et al., 2002). Shortening the deployment time can improve the accuracy of flux estimates, but precision may be lost (Venterea et al., 2009). In the present study a non-linear method, HMR (Pedersen et al., 2010), was used for flux estimation in 17, 41 and 73 % of all cases with CH₄, N₂O and R_{eco} , respectively. HMR is an exponential model with certain restrictions on parameter estimates. The theoretical analysis of Pedersen et al. (2010), as well as subsequent experimental evidence comparing 1- and 2-h deployment (unpublished results), has indicated that the pre-deployment fluxes estimated by HMR are robust against declining headspace accumulation during chamber deployment.

4.2 Nitrous oxide fluxes

This study was planned to quantify fluxes associated with decomposition of soil organic matter in representative His-

tosols used by agriculture. According to the IPCC methodology, estimates of N₂O emissions from managed organic soils should distinguish between emissions derived from external N inputs and this background emission (de Klein et al., 2006). The partitioning of N₂O emissions is hampered by a complex microbial response to N amendments, and by a significant effect of groundwater table on background emissions (Clough et al., 1996; Augustin et al., 1998; van Beek et al., 2010, 2011). In the present study monitoring started in autumn 2008, following a growth season in accordance with current practices for each respective land use, including fertilization and grazing, and continued throughout the following year. Hence, long-term, but not short-term (<3 months) effects, of N amendments were accounted for in the emissions recorded. The system analysis (Table 6) suggested a significant effect of land use on N₂O fluxes, and a nearly significant region x land use interaction ($P < 0.065$). This was mainly due to high annual N₂O emissions at the two arable sites W-AR and N-AR, and low emissions from the arable soil in region E (Fig. 7).

The potential for N₂O emission is influenced by a number of factors such as electron donor availability, mineral N concentrations, oxygen status and soil pH (Groffman et al., 2000; Flessa et al., 1998; Baggs and Philippot, 2011). Nitrate accumulated during 2009 in the top soil at site N-AR (Table 4), where the highest N₂O emissions were generally observed (Fig. 7). Extremely high N₂O concentrations were also dissolved in the groundwater at site N-AR (Fig. 6), but the importance of subsoil N₂O production for atmospheric emissions remains to be shown. At site W-AR the highest emissions of N₂O were observed during autumn 2008, where unfortunately no information is available about top soil N status. Groundwater NO₃⁻ concentrations were <5 mg N L⁻¹, whereas GW NH₄⁺ concentrations were consistently at 10–20 mg N L⁻¹ (Fig. 5). At site W-AR the soil pH at 34–64 and 68–98 cm depth was very low at <4 (Table 3) and potentially inhibitory to nitrifiers. Regina et al. (1996) found potential nitrification (accumulation of NO₂⁻ + NO₃⁻) in drained minerotrophic peat soils at pH 4 despite low counts of ammonia oxidizing bacteria and speculated that heterotrophic organisms could be involved. In our study a supply of NH₄⁺ in early autumn, derived from mineralization activity or the rising groundwater, may have triggered N₂O production via nitrification and/or denitrification (Regina et al., 1996; Martikainen and de Boer, 1993). Goldberg et al. (2010) reported that high N₂O emissions during 15 d following an increase in the water table of a minerotrophic fen accounted for 20–40 % of total emissions during a >500 d monitoring period. Such a pattern would be in accordance with the high N₂O fluxes observed at sites W-AR and N-AR where GWL increased during August and September 2008 (Fig. 7). A similar response was not seen at sites W-PG, N-RG or N-PG despite similar increases in GWL, nor at site E-AR despite a high potential for net N mineralization in the

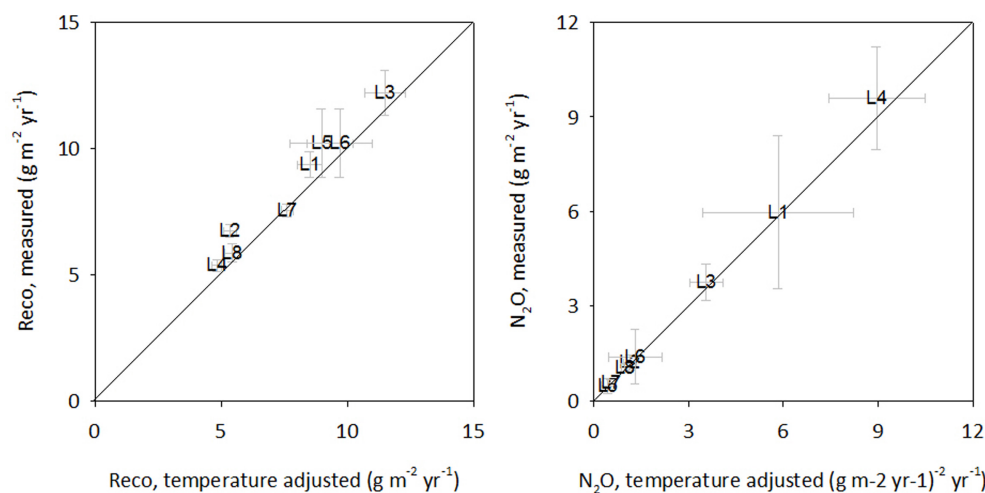


Fig. 11. The scatter plots show the effect of correcting ecosystem respiration (R_{eco}) and N_2O fluxes at the actual measurement time to a temperature corresponding to the daily mean of each sampling day. The correction was made with a modified Van't Hoff equation and Q_{10} values that were site-specific (R_{eco}) or fixed (N_2O) (see text). The data represent mean \pm standard error ($n = 3$).

cultivated soil. The high N_2O emissions observed in arable soil may thus have been caused by the interaction between rising groundwater level and a high potential for N mineralization following tillage and fertilization the previous spring (Table 2). In accordance with this, van Beek et al. (2004) concluded that a substantial part of an estimated N_2O production of $126 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ from an intensively managed grassland on peat was produced at depth in the soil, and that N_2O emissions were regulated by NO_3^- availability and groundwater level.

A second difference between sites W-AR and N-AR relative to E-AR was the relatively high concentrations of groundwater SO_4^{2-} . Microbial sulfate reduction may lead to formation of pyrite (FeS_2), although this will depend on pH as FeS_2 is unstable at $\text{pH} < 4$ (Shotyk, 1988). In regions W and N the groundwater table dropped by up to 100 cm during spring and summer (cf. Fig. 3), allowing for acidifying processes such as nitrification and possibly Fe(II) oxidation in the drained peat (Lüdecke et al., 2010; McLaughlin and Webster, 2010). Following a rise in water table dissolution of FeS_2 in the acid soil could stimulate N_2O emissions as Fe(II) may serve as electron donor in denitrification if NO_3^- is present (Madsen and Jensen, 1988; Jørgensen et al., 2009). Also, the relative importance of N_2O as product of denitrification is higher at low pH (Cuhel et al., 2010). Groundwater SO_4^{2-} was high at the sites W-AR, N-AR and N-RG with significant N_2O emissions, but also at site W-PG with no significant N_2O emission (Fig. 4). However, in contrast to site W-PG the sites in rotation had a prehistory of N fertilization (cf. Table 2) and, consequently, a high potential for net N mineralization and nitrification activity.

4.3 Methane fluxes

Currently CH_4 fluxes are considered to be insignificant for the GHG balance of cultivated organic soils in Denmark (Gyldenkerne et al., 2005), which is supported by the present study. Four of the eight monitoring sites were neutral with respect to CH_4 fluxes, one site (W-PG) was a small sink at $-0.16 \text{ k CH}_4 \text{ m}^{-2} \text{ yr}^{-1}$, and the two other permanent grasslands were consistent sources at 2.8 and $4.7 \text{ k CH}_4 \text{ m}^{-2} \text{ yr}^{-1}$, though only as a result of high emissions from a few samplings points; within these the mean flux of CH_4 was positively related to the biomass of soft rush (*J. effusus*) in plant cuts (Fig. 10). Drösler (2005), using a non-destructive approach, also found a linear relationship between aerenchymous leaf tissue and CH_4 emissions. Soft rush often invades pastures on poorly drained soil (Agnew, 1961), and its capacity to mediate transport of CH_4 from saturated soil to the atmosphere is well known (Garnet et al., 2005). Surprisingly, however, CH_4 fluxes at these emission hotspots were largely constant around the year despite fluctuating soil temperature (Fig. 2) and GWL (Fig. 3, region N only). Apparently CH_4 transport to the atmosphere was severely delayed except around soft rush tussocks at these two grazed pastures; soil porosity could be higher around tussocks due to reduced trampling, but CH_4 emissions at site N-PG proceeded during a period with standing water at these sampling points, which points to *J. effusus* as the main route of CH_4 transport. Kechavarzia et al. (2010) characterized physical and hydraulic properties of drained fen peat soils used by agriculture, and they found that both horizontal and vertical hydraulic conductivity was strongly reduced in the amorphous peat at 0–15 cm depth, which also had a lower porosity and drained more slowly than less decomposed peat. The loss of peat structure is a possible cause of preferential gas exchange

via aerenchymous plants, and it suggests that the role of soft rush in mediating CH₄ emissions from low-lying pastures on peat should be further investigated.

At the permanent grassland W-PG there were no indications of net CH₄ emission at any time around the year. Watson and Nedwell (1998) found that CH₄ production was inversely related to SO₄²⁻ availability, probably as a result of competitive inhibition by sulfate reducing bacteria. Groundwater SO₄²⁻ (Fig. 4) was high at this site in accordance with this explanation. On the other hand, occasional emissions of CH₄ were observed at sites W-AR where groundwater SO₄²⁻ was even higher.

4.4 GHG balance of the eight monitoring sites

The two permanent grasslands with soft rush were minor sources of CH₄, with average net emissions equivalent to 0.7 and 1.2 t CO₂ eq ha⁻¹ yr⁻¹, respectively. Nitrous oxide fluxes were equivalent to 1–11 t CO₂ eq ha⁻¹ yr⁻¹ at six of the sites, while at the arable sites in region *W* and *N* they were 18 and 29 t CO₂ eq ha⁻¹ yr⁻¹; the particular soil conditions at these two sites were discussed above. *R*_{eco} constituted 53–122 t CO₂ eq ha⁻¹ yr⁻¹ in this study, of which plant respiration may account for 35–45 % during periods of active growth (Silvola et al., 1996). A parallel study on net ecosystem exchange of CO₂ determined net fluxes of CO₂ at the eight monitoring sites to range from 13 to 50 t CO₂ eq ha⁻¹ yr⁻¹ (L. Elsgaard, personal communication, 2011). Hence, CO₂ emissions dominated the GHG balance of these Danish organic soils except at the two arable sites with high N₂O fluxes, i.e. site W-AR and N-AR. Kasimir-Klemedtsson et al. (1997) presented GHG balances for selected managed organic soils in Northern Europe. They reported total emissions from drained organic soils under different management to be 11–70 t CO₂ eq ha⁻¹ yr⁻¹, the C loss always dominating the GHG balance. A similar conclusion was reached by Jungkunst and Fielder (2007) in a compilation of data from peatlands across three climate zones.

Only one full year was represented in the monitoring program, and clearly more robust emission factors would be achieved with a longer monitoring period to better represent the full range of climatic conditions encountered at the sites (Table 1). High rainfall in August 2008, shortly before the monitoring was initiated, and in region *W* again in October 2008, as well as higher than average (2 °C) temperatures in April and slightly higher precipitation in early summer may have influenced fluxes, but overall the deviations between actual climatic conditions and 20-yr average values for temperature and precipitation were not dramatic.

In the absence of an extended national database it may be useful to consider emission factors for organic soils in other Nordic countries. Maljanen et al. (2010), in a review of GHG balances for organic soils in the Nordic countries, reported emissions from perennial grasslands to be 0.32 ± 0.64 g CH₄ m⁻² (*n* = 11), which is compara-

ble to the 0.47 g CH₄ m⁻² of this study. Similarly, for N₂O the average emission observed at grassland sites on peat in previous studies in Nordic countries was 1.50 ± 1.60 g N₂O m⁻² (*n* = 12), a range that includes the average emission of 0.5 g N₂O m⁻² of the present study (Table 8). For barley an average flux of CH₄ of -0.03 ± 0.18 g m⁻² (*n* = 5) was reported (Maljanen et al., 2010), the range and lower level relative to permanent grasslands was confirmed by the present study. Finally, N₂O emission factors for barley grown on peat soil were reported to average 1.7 ± 0.5 g m⁻² (*n* = 5), with one study of a potato field in the same range; these values are also comparable to the 2.5 g N₂O m⁻² determined in the present study. In summary, the new emission factors for the Danish organic soils investigated are consistent with existing data from a much wider range of organic soils in the Nordic countries.

The Danish GHG inventory for organic soils until recently used estimates of soil organic C degradation as a proxy for net N mineralization and N₂O emission by assuming a fixed relationship between soil organic C and C:N ratio (Gyldenkerne et al., 2005). The previously derived relationship between SOC and C:N ratio agreed closely with the relationship in Fig. 1b, but there was no simple relationship between N₂O emissions and C:N ratio (Table 7), which questions the approach. For N₂O the Intergovernmental Panel on Climate Change has proposed a default emission factor of 8 (range 2–24) kg N₂O-N ha⁻¹ for managed organic soils under temperate climate conditions (IPCC, 2006). Annual fluxes of N₂O in the present study varied greatly between sites. Six sites were within the 2–24 kg N₂O-N ha⁻¹ range (Table 5). The two remaining sites, W-AR and N-AR, showed annual fluxes corresponding to 38 and 61 kg N₂O-N ha⁻¹, values matching or exceeding most previously reported fluxes from arable peat soils in Europe (Flessa et al., 1998; Drösler et al., 2008; Maljanen et al., 2010). These two sites received >100 kg fertilizer N during 2008 (Table 2), which was probably excessive considering the N mineralization potential of organic soils. However, manure N had also been applied prior to the monitoring study at sites E-AR and E-RG where fluxes were only 5–10 kg N₂O-N ha⁻¹. Hence, site-specific conditions with respect to soil properties, groundwater and management can influence the level of N₂O emissions, and there is a need to consider a differentiation of N₂O emission factors for managed organic soils.

5 Conclusions

This study is part of the first assessment of GHG balances for Danish organic soils drained for agriculture. Annual fluxes of CH₄ and N₂O were consistent with previous studies of cultivated organic soils in the Nordic countries, but more importantly the stratified experimental design with identical procedures and supporting data acquired at all eight sites helped isolate effects of soil conditions and land use. Contrasting

seasonal dynamics of N₂O emissions at the three arable sites suggested that extremely high emissions were a result of interactions between fluctuating water table, net N mineralization and low pH, possibly involving sulfur transformations; this has implications for acid sulfate soils in agricultural use and should be further investigated. As expected CH₄ fluxes from the drained organic soils were low, but in two pastures on degraded peat aerenchymous plants were a consistent source of CH₄. There appears to be scope for a future disaggregation of the N₂O emission factor for organic soils, and possibly also for taking CH₄ emissions into account in the GHG balance of grazed pastures on peat with a shallow groundwater table.

Supplementary material related to this article is available online at:
<http://www.biogeosciences.net/9/403/2012/bg-9-403-2012-supplement.pdf>.

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References

- Agnew, A. D. Q.: The ecology of *Juncus effusus* L. in North Wales, *J. Ecol.*, 49, 83–102, 1961.
- Augustin, J., Merbach, W. and Rogasik, J.: Factors influencing nitrous oxide and methane emissions from minerotrophic fens in northeast Germany, *Biol. Fertil. Soils*, 28, 1–4, 1998.
- Baggs, E. M. and Philippot, L.: Nitrous oxide production in the terrestrial environment, in: Nitrogen Cycling in Bacteria – Molecular Analysis, edited by: Moir, J. W. B., Chapter 11, Caister Academic Press, 2011.
- Bahn, M., Rodeghiero, M., Anderson-Dunn, M., Dore, S., Gimeno, C., Drösler, M., Williams, M., Ammann, C., Berninger, F., Flechard, C., Jones, S., Balzarolo, M., Kumar, S., Newsely, C., Priwitzer, T., Raschi, A., Siegwolf, R., Susiluoto, S., Tenhunen, J., Wohlfahrt, G., and Cernusca, A.: Soil respiration in European grasslands in relation to climate and assimilate supply, *Ecosyst.*, 11, 1352–1367, 2008.
- Clough, T. J., Sherlock, R. R., Cameron, K. C., and Ledgard, S. F.: Fate of urine nitrogen on mineral and peat soils in New Zealand, *Plant Soil*, 178, 141–152, 1996.
- Conen, F. and Smith, K. A.: A re-examination of closed flux chamber methods for the measurement of trace gas emissions from soils to the atmosphere, *Eur. J. Soil Sci.*, 49, 701–707, 1998.
- Cuhel, J., Simek, M., Laughlin, R. J., Bru, D., Chèneby, D., Watson, C. J. and Philippot, L.: Insights into the effect of soil pH on N₂O and N₂ emissions and denitrifier community size and activity, *Appl. Environ. Microbiol.*, 76, 1870–1878, 2010.
- Davidson, E. A., Janssens, I. A., and Luo, Y. Q.: On the variability of respiration in terrestrial ecosystems: moving beyond Q₁₀, *Global Change Biol.*, 12, 154–164, 2006.
- Davidson, E. A., Savage, K., Verchot, L. V. and Navarro, R.: Minimizing artefacts and biases in chamber-based measurements of soil respiration, *Agric. Forest Meteorol.*, 113, 21–37, 2002.
- de Klein, C., Novoa, R. S. A., Ogle, S., Smith, K. A., Rochette, P., Wirth, T. C., McConkey, B. G., Mosier, A., and Rypdal, K.: N₂O emissions from managed soils, and CO₂ emissions from lime and urea application. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Chapter 11, 2006.
- Drösler, M.: Trace gas exchange and climatic relevance of bog ecosystems, Southern Germany. Dissertation an der Technischen Universität München, 179 pp., 2005.
- Drösler, M., Freibauer, A., Christensen, T., and Friborg, T.: Observation and status of peatland greenhouse gas emission in Europe, in: The Continental-Scale Greenhouse Gas Balance of Europe, edited by: Dolman, H., Valentini, R., and Freibauer, A., Ecological Studies, 203, Springer, 243–261, 2008.
- Fang, C. and Moncrieff, J. B.: The dependence of soil CO₂ efflux on temperature, *Soil Biol. Biochem.*, 33, 155–165, 1998.
- FAO: World reference base for soil resources, Food and Agriculture Organization of the United Nations, Rome, 1998.
- Flessa, H., Wild, U., Klemisch, M., and Pfenhauer, J.: Nitrous oxide and methane fluxes from organic soils under agriculture, *Eur. J. Soil Sci.*, 49, 327–335, 1998.
- Freibauer, A., Rounsevell, M. D. A., Smith, P., and Verhagen, J.: Carbon sequestration in the agricultural soils of Europe, *Geoderma*, 122, 1–23, 2004.
- Garnet, K. N., Megonigal, J. P., Litchfield, C., and Taylor, G. E.: Physiological control of leaf methane emission from wetland plants, *Aquat. Bot.*, 81, 141–155, 2005.
- Goldberg, S. D., Knorr, K.-H., Blodau, C., Lischeid, G., and Gebauer, G.: Impact of altering the water table height of an acidic fen on N₂O and NO fluxes and soil concentrations, *Global Change Biol.*, 16, 220–233, 2010.
- Groffman, P., Gold, A. J., and Addy, K.: Nitrous oxide production in riparian zones and its importance to national emission inventories, *Chemosphere – Global Change Sci.*, 2, 291–299, 2000.
- Gyldenkerne, S., Münier, B., Olesen, J. E., Olesen, S. E., Petersen, B. M., and Christensen, B. T.: Accounting for CO₂ emissions associated with land use and land use change. Working report from the National Environmental Research Institute No. 213, 80 pp., 2005.
- Hornibrook, E. R. C., Bowes, H. L., Culbert, A., and Gallego-Sala, A. V.: Methanotrophy potential versus methane supply by pore water diffusion in peatlands, *Biogeosciences*, 6, 1491–1504, doi:10.5194/bg-6-1491-2009, 2009.
- Hutchinson, G. L. and Mosier, A. R.: Improved soil cover method for field measurement of nitrous oxide fluxes, *Soil Sci. Soc. Am. J.*, 45, 311–316, 1981.

- IPCC: IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Intergovernmental Panel on Climate Change, Annex 1, Conceptual basis for uncertainty analysis, in: Prepared by the National Greenhouse Gas Inventories Programme, edited by: Eggleston, H. S., Buendia, L., Miwa, K., Ngara, T. and Tanabe, K., IGES, Japan, 2006.
- Jacinte, P.-A. and Groffman, P.: Silicone rubber sampler to measure dissolved gases in saturated soils and waters, *Soil Biol. Biochem.*, 33, 907–912, 2001.
- Jacobs, C. M. J., Jacobs, A. F. G., Bosveld, F. C., Hendriks, D. M. D., Hensen, A., Kroon, P. S., Moors, E. J., Nol, L., Schrier-Uijl, A., and Veenendaal, E. M.: Variability of annual CO₂ exchange from Dutch grasslands, *Biogeosciences*, 4, 803–816, doi:10.5194/bg-4-803-2007, 2007.
- Jungkunst, H. F. and Fielder, S.: Latitudinal differentiated water table control of carbon dioxide, methane and nitrous oxide fluxes from hydromorphic soil: feedbacks to climate change, *Global Change Biol.*, 13, 2668–2683, 2007.
- Jørgensen, C. J., Jacobsen, O. S., Elberling, B., and Aamand, J.: Microbial oxidation of pyrite coupled to nitrate reduction in anoxic groundwater sediment, *Environ. Sci. Technol.*, 43, 4851–4857, 2009.
- Kasimir-Klemmedtsson, Å., Klemmedtsson, L., Berglund, K., Martikainen, P., Silvola, J., and Oenema, O.: Greenhouse gas emissions from farmed organic soils: A review, *Soil Use Manage.*, 13, 245–250, 1997.
- Kechavarzia, C., Dawson, Q., and Leeds-Harrison, P. B.: Physical properties of low-lying agricultural peat soils in England, *Geoderma*, 154, 196–202, 2010.
- Keeney, D. R. and Nelson, D. W.: Nitrogen–inorganic forms, in: *Methods of Soil Analysis. Part 2.*, edited by: Page, A. L., Miller, T. H., and Keeney, D. R., *Agronomy Monographs*, 9, second ed., American Society of Agronomy and Soil Science Society of America, Madison, WI, 643–693, 1982.
- Laanbroek, H. J.: Methane emission from natural wetlands: interplay between emergent macrophytes and soil microbial processes, A mini-review, *Ann. Bot.-London*, 105, 141–153, 2010.
- Lambers, H., Chapin, F. S., and Pons, T. L.: *Plant physiological ecology*. Springer Science and Business Media Inc., New York, 540 pp., 1998.
- Langeveld, C. A., Segers, R., Dirks, B. O. M., van den Pol-van Dasselaar, A., Velthof, G., and Hensen, A.: Emissions of CO₂, CH₄ and N₂O from pasture on drained peat soils in the Netherlands, *Eur. J. Agron.*, 7, 35–42, 1997.
- Lloyd, J. and Taylor, J. A.: Temperature dependence of soil respiration. *Functional Ecol.* 8, 315–323, 1994.
- Lüdecke, C., Reiche, M., Eusterhues, K., Nietsche, S., and Küsel, K.: Acid-tolerant microaerophilic Fe(II)-oxidizing bacteria promote Fe(III)-accumulation in a fen, *Environ. Microbiol.*, 12, 2814–2825, 2010.
- Madsen, H. B. and Jensen, N. H.: Potentially acid sulfate soils in relation to landforms and geology, *Catena*, 15, 137–145, 1988.
- Madsen, H. B., Holst, K. A., and Nørr, A. H.: *The Danish Soil Classification*, Reitzel, 56 pp., Copenhagen, 1992.
- Maljanen, M., Sigurdsson, B. D., Guðmundsson, J., Óskarsson, H., Huttunen, J. T., and Martikainen, P. J.: Greenhouse gas balances of managed peatlands in the Nordic countries – present knowledge and gaps, *Biogeosciences*, 7, 2711–2738, doi:10.5194/bg-7-2711-2010, 2010.
- Martikainen, P. J. and de Boer, W.: Nitrous oxide production and nitrification in acidic soil from a dutch coniferous forest, *Soil Biol. Biochem.* 25, 343–347, 1993.
- McLaughlin, J. W. and Webster, K. L.: Alkalinity and acidity cycling and fluxes in an intermediate fen peatland in northern Ontario, *Biogeochem.*, 99, 143–155, 2010.
- National Environmental Research Institute: On-line database of N deposition, http://www2.dmu.dk/1_viden/2_Miljoe-tilstand/3_luft/4_spredningsmodeller/5_Depositionsberegninger/deposition.asp, 2010.
- Parkin, T. B.: Effect of sampling frequency on estimates of cumulative nitrous oxide emissions, *J. Environ. Qual.*, 37, 1390–1395, 2008.
- Pedersen, A. R., Petersen, S. O., and Schelde, K.: A comprehensive approach to soil-atmosphere trace-gas flux estimation with static chambers, *Eur. J. Soil Sci.*, 61, 888–902, 2010.
- Regina, K., Nykänen, H., Silvola, J., and Martikainen, P. J.: Fluxes of nitrous oxide from boreal peatlands as affected by peatland type, water table level and nitrification capacity, *Biogeochem.*, 35, 401–418, 1996.
- Segers, R.: Methane production and methane consumption: a review of processes underlying wetland methane fluxes, *Biogeochem.*, 41, 23–51, 1998.
- Shoty, W.: Review of the Inorganic geochemistry of peats and peatland waters, *Earth-Sci. Rev.*, 25, 95–176, 1988.
- Silvola, J., Alm, J., Ahlholm, U., Nykänen, H., and Martikainen, P.: The contribution of plant roots to CO₂ fluxes from organic soils, *Biol. Fertil. Soils*, 23, 126–131, 1996.
- Strack, M., Waller, M. F., and Waddington, J. M.: Sedge succession and peatland methane dynamics: a potential feedback to climate change, *Ecosys.*, 9, 278–287, 2006.
- van Beek, C. L., Hummelink, E. W. J., Velthof, G. L., and Oenema, O.: Denitrification rates in relation to groundwater level in a peat soil under grassland, *Biol. Fertil. Soils*, 39, 329–336, 2004.
- van Beek, C. L., Pleijter, M., Jacobs, C. M. J., Velthof, G. L., van Groenigen, J. W., and Kuikman, P. J.: Emissions of N₂O from fertilized and grazed grassland on organic soil in relation to groundwater level, *Nutr. Cycl. Agroecosys.* 86, 331–340, 2010.
- van Beek, C. L., Pleijter, M., and Kuikman, P. J.: Nitrous oxide emissions from fertilized and unfertilized grasslands on peat soil, *Nutr. Cycl. Agroecosys.* 89, 453–461, 2011.
- Venterea, R., Spokas, K. A., and Baker, J. M.: Accuracy and precision analysis of chamber-based nitrous oxide gas flux estimates, *Soil Sci. Soc. Am. J.*, 73, 1087–1093, 2009.
- Vicca, S., Janssens, I. A., Flessa, H., Fiedler, S., and Jungkunst, H. F.: Temperature dependence of greenhouse gas emissions from three hydromorphic soils at different groundwater levels, *Geobiol.*, 7, 465–476, 2009.
- Watson, A. and Nedwell, D. B.: Methane production and emission from peat: The influence of anions (sulphate, nitrate) from acid rain, *Atmos. Environ.*, 32, 3239–3245, 1998.
- Yavitt, J. B. and Lang, G. E.: Methane production in contrasting wetland sites: Response to organic-chemical components of peat and to sulfate reduction, *Geomicrobiol. J.*, 8, 27–46, 1990.