Biogeochemistry (2012) 108:233–243
DOI 10.1007/s10533-011-9593-z

Minor long-term effects of ultraviolet-B radiation on methane dynamics of a subarctic fen in Northern Finland

Sami K. Mörsky · Jaana K. Haapala · Riikka Rinnan · Sanna Saarnio · Hanne Suokanerva · Kirsi Latola · Esko Kyrö · Jouko Silvola · Toini Holopainen · Pertti J. Martikainen

Received: 6 June 2010 / Accepted: 27 February 2011 / Published online: 12 March 2011

Abstract The effects of elevated ultraviolet-B (UV-B) radiation on methane dynamics was studied in a natural fen in Northern Finland for three growing seasons (2003–2005). This is the first in situ study on the effects of elevated UV-B radiation on methane dynamics in a natural fen. The experimental setup consisted of 30 study plots (120 × 120 cm) that were randomly divided into three treatments: ambient control, UV-A control and elevated UV-B. The UV-B enhancements were 63, 37 and 21% above ambient during the growing seasons 2003, 2004 and 2005, respectively. Elevated UV-B did not affect net methane emission. Stable isotope composition of methane indicated that methane was produced by the acetate fermentation. Under elevated UV-B there was a slight increase in the concentrations of acetate and propionate but decrease in the oxalate concentration suggesting UV-B-induced changes in the belowground processes. The results emphasize the need for long-term field studies under moderately enhanced exposures to estimate whether the function and feedbacks of mire ecosystems change under increased UV-B radiation.

Keywords *Eriophorum russeolum* · Fen · Methane · Organic acid · Sedge · Ultraviolet-B radiation

S. K. Mörsky (✉) · T. Holopainen · P. J. Martikainen
Department of Environmental Science,
University of Eastern Finland, Kuopio Campus,
PO Box 1627, 70211 Kuopio, Finland
e-mail: Sami.Morsky@uef.fi

J. K. Haapala · J. Silvola
Department of Biology, University of Eastern Finland,
Joensuu Campus, PO Box 111, 80101 Joensuu, Finland

R. Rinnan
Terrestrial Ecology Section, Department of Biology,
University of Copenhagen, Øster Farimagsgade 2D,
1353 Copenhagen, Denmark

S. Saarnio
Finnish Environment Institute & Ecological Research Institute, University of Eastern Finland, Joensuu Campus,
PO Box 111, 80101 Joensuu, Finland

H. Suokanerva · E. Kyrö
Finnish Meteorological Institute, Sodankylä, Tähteläntie 62, 99600 Sodankylä, Finland

K. Latola
Thule Institute, University of Oulu, PO Box 7300,
90014 Oulu, Finland

Introduction

At high latitudes, as in Finland, boreal and subarctic mires form a remarkable part of the landscape. Generally, these wet ecosystems are a major sink of atmospheric carbon (Turunen et al. 2002) but a source of methane (Lai 2009). Methane dynamics of Northern peatlands have been studied in relation to environmental and ecosystem related factors, such as water table (Nykänen et al. 1998; Strack 2004), vegetation (Bubier 1995; Saarnio et al. 2004; Ström et al. 2005) and elevated ozone concentration

(Mörsky et al. 2008; Rinnan et al. 2003). However, to our knowledge, there is no field data to show how elevated UV-B radiation affects methane dynamics on natural peatlands. Moreover, there is limited information available on the effects of UV-B radiation on peatland ecosystems in general.

The stratospheric ozone layer, which protects living organisms from hazardous ultraviolet radiation (UV-B 280–315 nm), has become thinner especially above the Antarctic but also above the Arctic (Taalas et al. 2000). Ozone depletion was more severe in earlier times and the ozone layer has now been gradually recovered in the upper stratosphere (Austin and Wilson 2006). However, recent studies have highlighted the possibility of intensive periods of enhanced UV-B radiation at high latitudes still in the future (Rösevall et al. 2007).

Natural mires often lack higher shading vegetation. Therefore, peat-forming vegetation is directly affected by enhanced UV-B exposure and harmful UV-B effects would be expected. However, in natural field conditions plants seem to tolerate moderately enhanced UV-B radiation. Enhanced UV-B radiation has been reported to increase concentrations of UV-B-absorbing compounds in plants, but plant height, shoot biomass and photosynthetic processes have not congruently responded towards enhanced UV-B radiation (Searles et al. 2001). A recent meta-analysis by Newsham and Robinson (2009) summarized the UV-B effects on bryophytes and angiosperms in the Arctic and Antarctic. Vegetation in Polar Regions often responds to UV-B radiation by increasing the synthesis of UV-B absorbing compounds and negative effects on aboveground biomass production, plant height growth and DNA could occur.

In a microcosm study, representing a minerogenic, oligotrophic low-sedge pine fen, for one growing season in outdoor conditions, Niemi et al. (2002b) reported significant reduction in gross photosynthesis, net ecosystem carbon dioxide (CO_2) exchange (NEE) and methane emissions under elevated UV-B radiation (30% above ambient). However, in another microcosm study with a similar peatland type, conducted in a cloudy summer, methane emissions were not affected by elevated UV-B (Rinnan et al. 2003). Additionally, when carbon dioxide balance of a natural subarctic fen (the present study site) was studied for three years, the results showed that NEE at light saturation was slightly higher in elevated UV-B radiation (21–63% above ambient) but the gross photosynthesis was not affected (Haapala et al. 2009).

There is some evidence that elevated UV-B radiation could affect aboveground processes, such as photosynthesis, of peatland vegetation. Additionally, belowground processes can be affected by UV-B radiation. After three growing seasons under elevated UV-B exposure in the natural subarctic fen, described earlier in the text, enhanced UV-B radiation reduced the sugar concentration of sedge *Eriophorum russeolum* leaves and simultaneously increased the total phenolics concentration in roots (Rinnan et al. 2008). In another study, where peatland mesocosms were exposed to elevated UV-B radiation (simulated 15% ozone depletion) for 8 weeks, enhanced UV-B radiation decreased monocarboxylic acid concentration in *Narthecium ossifragum* mesocosms but not in the mesocosms with *E. angustifolium* (Rinnan et al. 2006). It is still unclear how these changes in carbon allocation under long-term elevated UV-B radiation in natural conditions could affect methanogenesis, which is fuelled by carbon derived from peatland vegetation (Ström et al. 2003). Furthermore, there is no information available whether elevated UV-B radiation affects methane stable isotope composition in peatland ecosystems.

The aim of this study was to assess whether enhanced UV-B radiation in situ affects methane dynamics of a subarctic fen ecosystem. Since weather related factors can significantly affect methane dynamics (e.g. Danevčič et al. 2010; Daulat and Clymo 1998), we followed the processes during three consecutive growing seasons. In addition to traditional methane emission measurements, we applied isotopic ratio mass spectrometry and advanced ion chromatography to study the belowground processes and water chemistry related to methane dynamics. Based on the earlier microcosm study by Niemi et al. (2002b), we hypothesized that long-term elevated UV-B radiation would decrease net methane emissions from the peat to the atmosphere and this could be associated with decrease in the availability of usable organic acids in peat.

Materials and methods

Experimental design

A natural subarctic flark fen ecosystem (Halssiaapa, 67°22′N, 26°39′E, 179 m a.s.l) was exposed to

elevated ultraviolet-B radiation for three growing seasons (2003–2005). Halssiaapa fen consists of hummock strings with wet flarks in between. A sedge *E. russeolum* and a moss *Warnstorfia exannulata* dominate the vegetation in the study area. Additionally, shoots of *Carex limosa*, *Scheuchzeria palustris*, *Carex magellanica*, *Menyanthes trifoliata*, *Andromeda polifolia* and *Vaccinium oxycoccos* were present. The study area was surrounded by a reindeer fence and boardwalks were constructed to minimize the disturbance of walking in the area. In the springtime (May–June) the study site was thoroughly flooded and generally the water table remained a few centimetres below the peat surface (Fig. 1). To estimate the maximum lateral water flow velocity in peat (0–30 cm), a tracer experiment was conducted in four randomly selected locations, outside the study plots, in early June 2005, with NaCl-solution (67 g l^{-1}). The results showed that lateral water flow velocity below ground was slow (20 ± 7 cm d^{-1}) meaning that the waters between the study plots were not remarkably mixed (Ronkanen A-K, personal communication). The more detailed method is described in Ronkanen and Klove (2007).

The experimental setup consisted of 30 study plots (120 × 120 cm) of which 10 represented ambient controls, 10 were UV-A controls and 10 were treated with elevated UV-B. The UV-A control was included in the experiment because the UV-B treatment enhanced, as an unwanted side-effect, also UV-A radiation (see Newsham et al. 1996). The ambient controls had wooden frames with equal shading as under the irradiation lamp arrays. Irradiation treatments were conducted by using four fluorescent tubes Philips TL 40 W/12 RS (Philips Lighting, Eindhoven, The Netherlands) that were placed 120 cm above the peat surface in each study plot. In the UV-B treatment, the fluorescent tubes were covered with a thin (0.1 mm) cellulose-acetate filter (Expopak Oy, Jäminkipohja, Finland) to cut off wavelengths below 290 nm. In UV-A control a thin (0.125 mm) polyester filter (Melinex/Polyfoil, KTA-yhtiöt Oy, Helsinki, Finland) was used to cut off wavelengths below 315 nm. During the experiment the lamps were checked daily and the filters were changed monthly.

The computer controlled irradiation system was constructed to maintain UV-B irradiation enhancement at a constant 46% above the current ambient level, simulating 20% ozone depletion. Irradiation levels at the plot centre were continuously monitored by erythemally (CIE) weighted PMA1102 (UV-B) and PMA1111 (UV-A) sensors (Solar Light Co. Inc., Glenside, PA, USA). Every UV-B plot was equipped with a PMA1102 sensor. Ambient control and UV-A control plots had only one PMA1102 sensor in each treatment since there was no high, shading vegetation present. One PMA1111 sensor per treatment was used to monitor UV-A levels. All of the sensors were installed at the vegetation level. The data of the PMA sensors was collected by a QLI50 data logger (Vaisala Oyj, Helsinki, Finland) and processed with a LabView application (National Instruments, Austin, TX, USA). One minute averages of PMA output data were used to adjust Quictronic HF 2 × 36/230-240 V DIM lamp faders (Osram Oy, Vantaa, Finland) through an analogous output PCI-6216 V card (AD-Link Technology Inc., Chungho City, Taiwan).

Peat temperatures at depths of 5, 10, 20 and 30 cm below the mire surface were measured using a Fluke 52 II thermometer (Fluke Corporation, Everett, WA, USA) with a soil probe (SAB Bröckskes, Viersen, Germany). Measurements were made from each study plot along with the gas exchange measurements. Water table was measured four times a week during growing seasons from perforated pipes located within each study plot (Fig. 1).

Methane emission

One aluminium collar (60 × 60 × 30 cm) per study plot was installed into the peat in June 2002. Methane emission was principally measured every other week during the growing seasons (June–September) from 2003 to 2005. The measurements were conducted using an opaque aluminium chamber that was set on a water-filled groove of the collar. The chamber was ventilated with a capillary tube to minimize internal air pressure changes during gas sampling. Gas samples (50 ml) were drawn through a thin tube from the chamber's headspace into 50 ml polypropylene syringes (Terumo Europe N.V., Leuven, Belgium) equipped with three-way stopcocks (Variostop, Fresenius Kabi, Bad Hersfeld, Germany) at 2-min intervals (four samples per measurement). Air temperature in the chamber was recorded during the measurement. Gas samples were immediately injected into pre-evacuated 12 ml glass tubes (Labco

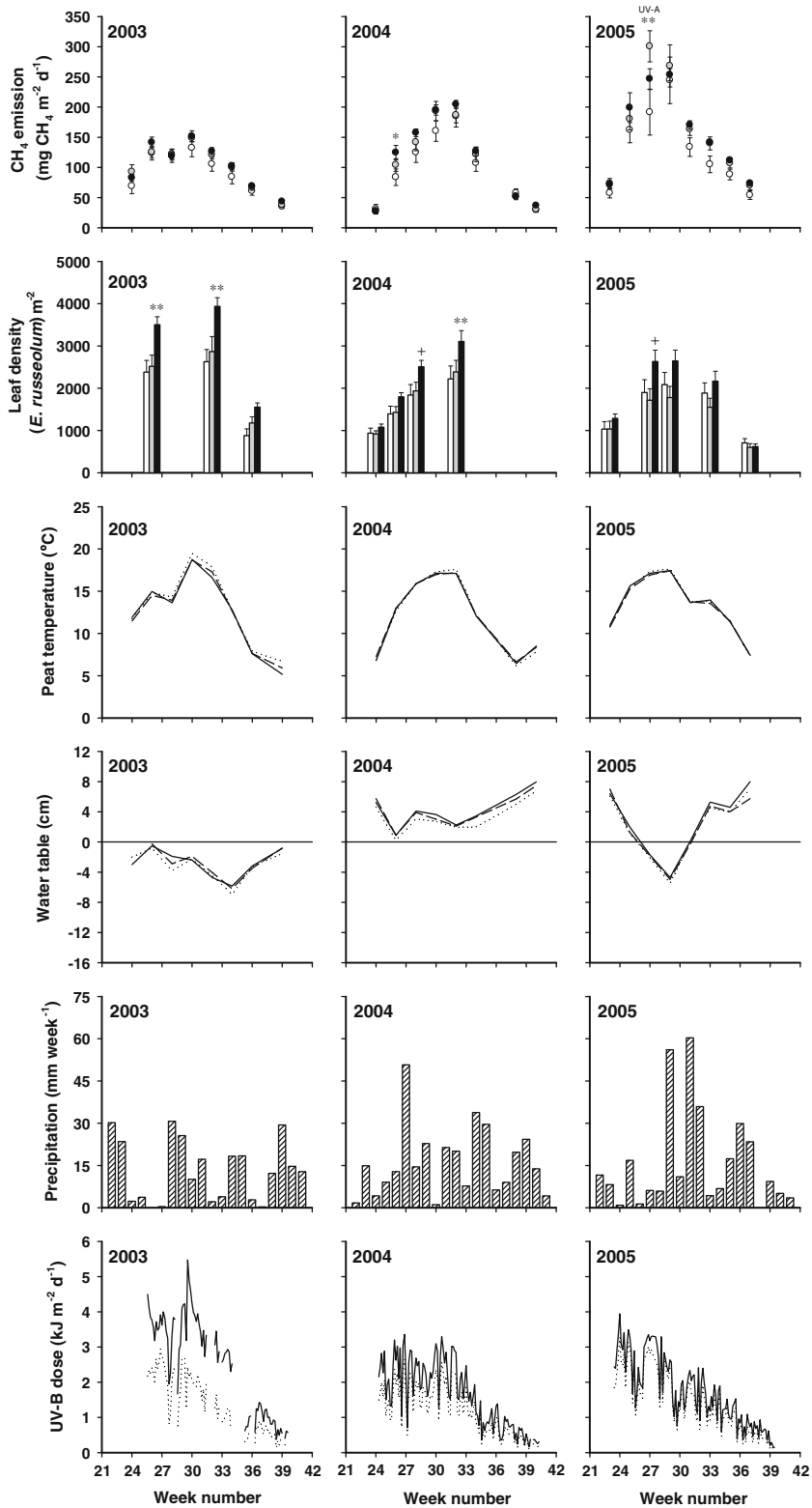

Fig. 1 Methane emission, leaf density of *Eriophorum russeolum*, peat temperature (depth 10 cm), water table, weekly sum of precipitation and UV-B dose during three growing seasons, 2003–2005. *Open circle*, *open bar* and *dotted line* represent ambient control; *grey circle*, *grey bar* and *dashed line* UV-A control; and *closed circle*, *closed bar* and *solid line* UV-B treatment, respectively. *Error bars* show the standard error (SE) of the mean ($n = 10$). The data for weekly precipitation was obtained from the Finnish Meteorological Institute that is located in the vicinity of the experimental field. *Asterisks* show significant differences between ambient control and UV-B treatment or UV-A control within separate measurements. $+P < 0.1$; $*P < 0.05$; $**P < 0.01$ (linear mixed models, Bonferroni's test)

Exetainer; Labco Limited, Buckinghamshire, UK). The gas samples were later analysed at University of Eastern Finland, Department of Environmental Science, using an Agilent 6890 N gas chromatograph (Agilent Technologies, PA, USA) with a Gilson 222XL auto sampler (Gilson Inc., Middleton, WI, USA). The gas chromatograph was equipped with a flame ionization detector (FID) and two Haysep Q 80/100 packed columns (pre-column: length 0.91 m, ∅ 3.2 mm; analytical column: length 2.74 m, ∅ 3.2 mm). Pure 99.96% nitrogen (Oy AGA Ab, Espoo, Finland) was used as a carrier gas at flow rate of 20 ml min^{-1}. A standard gas (2.02 ppm ± 10% CH_4 in synthetic air, AGA Gas AB, Pullach, Germany) was used to quantify the gas concentrations. Methane emission was calculated from the linear change in the chamber gas concentration during the 8 min measurement. A few data points (8%) were rejected because the methane concentration of the first sample was more than 50% higher than the ambient level, or the change in the chamber gas concentration was non-linear ($r^2 < 0.90$).

The leaf density of *E. russeolum* in the collars was counted every three weeks during the growing seasons. The counting was performed from five sub-areas (10 × 10 cm) to achieve a representative mean. In data analyses, the leaf density was used as a covariate to methane emissions.

During the winters, 2003–2004 and 2004–2005, the wintertime methane emissions were measured from the study plots four times using the snow gradient method (Maljanen et al. 2003; Sommerfeld et al. 1993). Two gas samples (40 ml) were taken through a thin metal tube into 60 ml polypropylene syringes. The first sample was taken from the snowpack, 2 cm above the peat surface, and the second from the air above the snow surface. The snow depth at the site was measured and the porosity of snow was determined. The gas samples were analyzed with an HP 5890 Series II gas chromatograph equipped with an FID detector (Nykänen et al. 1995). The density of pure ice (0.9168 g cm^{-3}) and the diffusion constant (0.22 cm^2 s^{-1}) for CH_4, adopted from Sommerfeld et al. (1993), were used to calculate the methane emission. The samplings were started when the snow depth exceeded 20 cm and ended in the early spring when the surface of the snow temporarily melted and refroze forming an ice cover on the snow.

Organic acids in peat

In June 2004, a perforated water collection cell (∅ 16 mm, length 300 mm, PVC) equipped with a sampling tube (∅ 4.0 mm) and three-way stopcock was horizontally embedded into the peat (depth 15 cm) close to the gas exchange measurement collar on every study plot. Once a month (June–August 2004 and 2005) a water sample (40 ml) was drawn through the sampling tube using a 60 ml polypropylene syringe and stored at −20°C until analysis at the National Public Health Institute in Kuopio, Finland. The concentrations of lactate, acetate, propionate and oxalate were analyzed with a DX-600 ion chromatograph system (Dionex, Sunnyvale, CA, USA) as described by Rantakokko et al. (2004).

Methane stable isotopes

To determine the peat depth where methane concentration started to stabilize (reflecting anaerobic conditions), two peat monoliths (depth 40 cm, ∅ 10.5 cm) were cored with a special corer device (Mörsky et al. 2008) from the randomly selected locations of the study site in the middle of the third growing season (2005). Methane concentrations at different depths in the peat profile were measured using a membrane inlet mass spectrometer (MIMS) system (Sheppard and Lloyd 2002).

The stable isotopic composition of methane ($\delta^{13}C$–CH_4) in peat and methane released to the atmosphere were analyzed four times. The first three trials were conducted in the third growing season (2005) and the last full scale campaign in the fifth growing season (2007). Perforated water collection cells were set at a depth of 15 cm, based on the MIMS data, to collect water samples to determine the stable isotopic composition of methane in peat pore water. A water sample (30 ml) was drawn through the sampling tube using a 60 ml polypropylene syringe and 30 ml of 99.96% nitrogen was added prior to shaking for three minutes in the laboratory. The water–gas-phase was left to stabilize (20°C) for two hours and a gas sample (20 ml) was injected into a pre-evacuated 12 ml glass tube.

The closed chamber method, described earlier in the text, was used to collect gas samples to determine the stable isotopic composition of methane released from the peat into the atmosphere. Four gas samples

(0.5, 5, 13, 20 min) were drawn from the headspace of the chamber and injected into 30 ml pre-evacuated glass bottles (Wheaton Industries Inc., Millville, NJ, USA). The samples were analysed with a Delta plus XP isotope ratio mass spectrometer (Thermo, Bremen, Germany; for technical details of the system, see Kankaala et al. 2007). The $\delta^{13}C$–CH_4 ratios were calculated using the method described in Werner and Brand (2001) with appropriate corrections. In addition, a Keeling plot approach (Keeling 1958) was used to calculate the $\delta^{13}C$–CH_4 values of the methane released from the peat to the atmosphere.

To determine the most evident methane producing biogeochemical pathway, stable isotopic composition of methane and carbon dioxide was determined from one fresh peat profile (layer 0–10 cm) that was cored from the centre of the experimental field at the end of the third growing season (2005). The peat profile was stored at 4°C prior to the laboratory incubation experiment. Stable isotopic composition of methane and carbon dioxide was determined from three replicate incubation flasks during a 6-day incubation at 20°C. An isotope ratio mass spectrometer (Delta plus XP IRMS, Thermo, Bremen, Germany) was used in the analysis and the fractionation factors (α_C) were calculated. The detailed method is described in Mörsky et al. (2008).

Statistical analyses

Before the statistical analyses, the data were tested with the Kolmogorov–Smirnov test for normality and square root or log-transformed when appropriate. Normality tests were verified by inspecting the data distribution diagrams of each variable. Treatment effects, temporal changes and interactive effects between treatment and time were tested using the linear mixed models (LMM) followed by Bonferroni's test for pairwise comparisons. The model was applied for methane emissions, organic acid concentrations, *E. russeolum* leaf densities and $\delta^{13}C$–CH_4-values. In this model, treatment, time and their interaction were regarded as fixed factors. Additionally, treatment plot was set as a random factor. The leaf density of *E. russeolum* was used as a covariate for summertime methane emissions. The analyses described above were performed with the SPSS 14.0 statistical package (SPSS Inc., Chicago, IL, USA). The correlation between methane emission, *E. russeolum* leaf densities, water table, peat temperature, organic acid concentrations and $\delta^{13}C$–CH_4-values were studied with principal component analysis (PCA) using SIMCA-P 11.5 application (Umetrics Inc., Umeå, Sweden). Unit variance scaling was performed for the variables and a model with two principal components was applied.

Results

Environmental particulars

The target level of UV-B enhancement was 46% above the ambient. For technical reasons (a regulation error in the system in 2003, moisture related connection flaws in UV lamps in 2004–2005), there was some variation in the enhancement between growing seasons (Fig. 1). In the first growing season (2003), the cumulative UV-B dose was 147 kJ m^{-2} in the ambient and 239 kJ m^{-2} (+63%) in the UV-B treatment. In the second growing season (2004), the UV-B doses were 135 kJ m^{-2} and 185 kJ m^{-2} (+37%) in ambient and UV-B treatments, respectively. In the third growing season (2005), the UV-B doses were 165 kJ m^{-2} in ambient and 199 kJ m^{-2} (+21%) in UV-B treatments.

The first growing season (2003) was the driest. The precipitation (weeks 22–41) was 259 mm, close to the long-term average (Finnish Meteorological Institute, 2003). In the following growing seasons, 2004 and 2005, precipitation within the same time period was 322 and 314 mm, respectively (Finnish Meteorological Institute, 2004, 2005). Water table in the study plots followed precipitation with a slight delay (Fig. 1).

The leaf density of *E. russeolum* was already greater in the UV-B-treated plots than in the ambient control plots at the beginning of the UV-B treatment (Fig. 1). The difference was significant throughout the experiment (LMM, Time: $F = 55.301$, $P < 0.0005$; Treatment: $F = 6.872$, $P = 0.004$; Time x Treatment: $F = 1.675$, $P = 0.031$). The leaf density of *E. russeolum* was used as a covariate in the statistical analyses of methane emission to suppress the effect of *Eriophorum* leaves.

Methane emission

Methane emissions followed typical seasonal pattern i.e. the efflux was highest in the middle of the growing season and correlated positively with peat temperature (Fig. 1). In general, the methane emissions from the UV-B-treated plots were higher than from the ambient control plots throughout the experiment. However, only the temporal effect was statistically significant (LMM, Time: $F = 150.063$, $P < 0.0005$; Treatment: $F = 2.479$, $P = 0.103$; Time x Treatment: $F = 1.191$, $P = 0.256$). The variation within the treatments slightly increased towards the end of the study (Fig. 1).

Wintertime methane emission rates were less than 10% of those during the growing seasons 2004 and 2005 (Fig. 2). The emissions were higher at the beginning of the winter and decreased until the snow cover started to melt. There were no significant treatment effects of aggregated data on methane emissions, but the temporal effect was significant (LMM, Time: $F = 54.128$, $P < 0.0005$; Treatment: $F = 0.337$, $P = 0.717$; Time × Treatment: $F = 0.987$, $P = 0.475$).

Methane stable isotopes

Two peat monoliths were cored from the study site at the end of the third growing season (2005) and the methane concentration in the peat core was analyzed with MIMS (data not shown). The variation in methane concentrations between the studied peat profiles was insignificant. Methane concentration was rather constant to a depth of 9 cm but then rapidly increased down to a depth of 12 cm, indicating anoxic conditions.

Methane stable isotopes ($\delta^{13}C$–CH_4) were analyzed three times in 2005 and once in 2007 (Table 1). Linear mixed models with repeated measurements revealed no significant differences between the treatments. However, the $\delta^{13}C$–CH_4 values in peat pore water (LMM, Time: $F = 24.389$, $P = 0.001$) and in emitted methane (LMM, Time: $F = 169.519$, $P < 0.0005$) varied significantly with time. In 2005, methane extracted from peat pore water became more enriched with $\delta^{13}C$ towards the end of the growing season. In contrast to the $\delta^{13}C$–CH_4 values determined in 2005 (week 31) methane released from the peat to the atmosphere was more depleted in 2007 (week 31). However, the $\delta^{13}C$–CH_4 signal in peat was similar in 2005 (week 35) and in 2007 (week 31).

The principal component analysis revealed that the $\delta^{13}C$–CH_4 signal of the peat pore water was positively correlated with net methane emission and leaf density of *E. russeolum* (Fig. 3). Fractionation factors (α_C), determined from the laboratory incubation experiment of a fresh peat profile, were rather stable during the laboratory incubation. The fractionation factors varied from 1.049 to 1.056. The correlation between *E. russeolum* leaf density and organic acid concentrations was insignificant.

Organic acids in peat

Concentrations of organic acids, precursors for methane, were analyzed twice in 2004 and three times

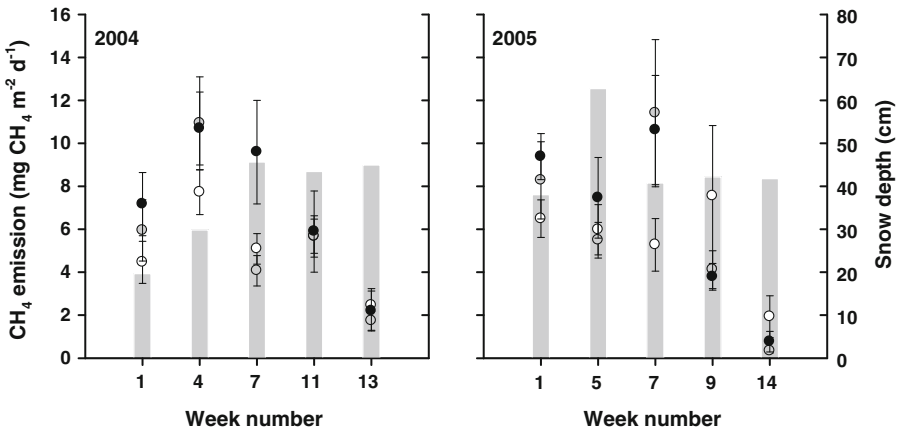

Fig. 2 Wintertime methane emissions (mean ± SE, $n = 10$) in 2004 and 2005. *Open circles* represent ambient control, *grey circles* UV-A control and *closed circles* UV-B treatment, respectively. *Bars* behind represent mean snow depth at the experimental field. Statistically significant treatment or interaction effects with time were not apparent (linear mixed models)

Table 1 Stable isotope ratios ($\delta^{13}C$–CH_4, mean ± SE ‰, n = 1–10) of methane extracted from peat pore water and from chamber measurements in situ using the Keeling plot approach

	2005			2007
	Week 23	Week 31	Week 35	Week 31
Peat water				
Ambient	−79.52 ± 0.49	nd	−74.41 ± 0.28	−77.41 ± 1.10
UV-A	−82.44 ± 1.49	nd	−75.70 ± 1.00	−75.41 ± 1.79
UV-B	−78.27 ± 2.29	nd	−75.22 ± 2.31	−75.19 ± 0.95
Chamber				
Ambient	−64.32 ± 1.71	−63.53*	nd	−82.02 ± 0.82
UV-A	−65.89 ± 1.56	−62.97*	nd	−81.53 ± 1.10
UV-B	−63.52 ± 0.43	−63.48 ± 0.50	nd	−80.10 ± 0.50

Measurements were conducted three times in 2005 and once in 2007

No statistically significant treatment effects were found (linear mixed models). *nd* Not determined, * Only one measurement

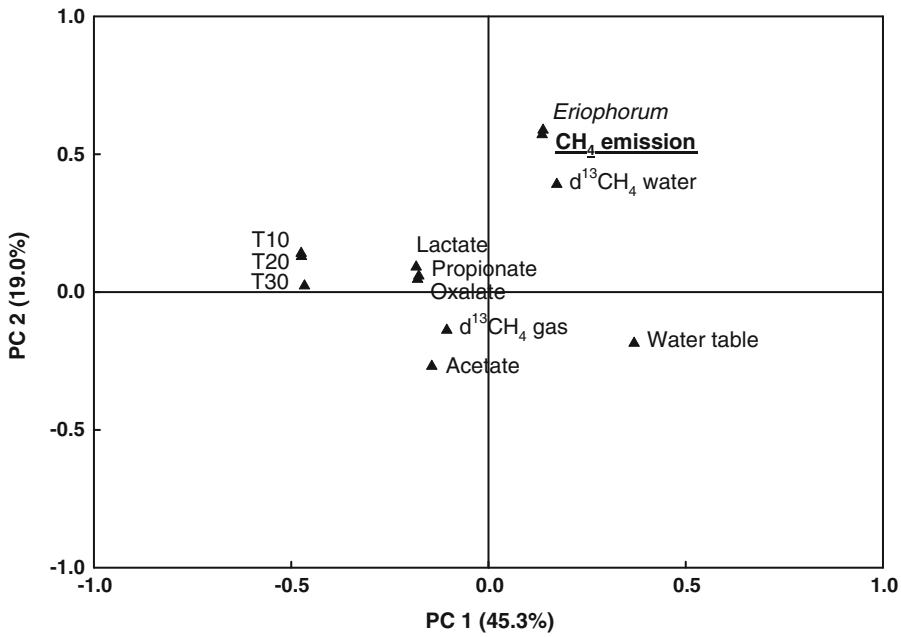

Fig. 3 Loading plot of the principal component analysis on methane emission, *Eriophorum russeolum* leaf density, water table, peat temperature (depths 10–30 cm), organic acid concentrations and $\delta^{13}C$–CH_4-values (peat pore water and chamber measurements) in 2005 and 2007. The data for organic acid concentrations were only available for 2005. The explained variance of the model is shown in parentheses (PC 1 and PC 2)

in 2005 (Table 2). Concentrations of lactate, acetate, propionate and oxalate varied between the measurements. The concentrations of all organic acids analyzed were higher in the growing season of 2004 than in 2005 decreasing towards the end of the growing seasons. The most abundant organic acids were acetate and propionate. The concentrations of acetate and propionate were slightly but not significantly higher in the UV-B treatment. Highest concentrations were measured in the middle of the second growing season (week 30, 2004). Meanwhile, only small amounts of lactate and oxalate were present. Linear mixed models with repeated measurements showed that the oxalate concentration in the UV-B treatment was significantly lower than that in the ambient control (LMM, Time: $F = 60.873$, $P < 0.0005$; Treatment: $F = 4.545$, $P = 0.020$; Time x Treatment: $F = 0.942$, $P = 0.486$).

Discussion

Methane emissions and dynamics of the subarctic fen

Peat temperature and the leaf density of *E. russeolum* appeared to have a major impact on the net methane

Table 2 Organic acid concentrations (μg l^{-1}) in peat pore water (depth 15 cm) during two growing seasons 2004–2005 (mean ± SE, $n = 10$)

	2004		2005		
	Week 30	Week 34	Week 23	Week 29	Week 35
Lactate					
Control	31 ± 10	11 ± 2	37 ± 8	7 ± 1	16 ± 4
UV-A control	18 ± 4	15 ± 4	22 ± 4	13 ± 2	14 ± 5
UV-B	34 ± 12	10 ± 1	33 ± 13	11 ± 1	8 ± 1
Acetate					
Control	2492 ± 546	378 ± 45	1477 ± 517	75 ± 4	44 ± 4
UV-A control	2914 ± 846	572 ± 128	1015 ± 422	84 ± 8	35 ± 3
UV-B	3190 ± 807	642 ± 234	1734 ± 797	94 ± 8	41 ± 5
Propionate					
Control	781 ± 197	159 ± 42	326 ± 127	13 ± 3	12 ± 5
UV-A control	865 ± 297	357 ± 111	260 ± 91	12 ± 2	6 ± 2
UV-B	1017 ± 224	404 ± 164	633 ± 233	13 ± 3	6 ± 1
Oxalate					
Control	73 ± 6	32 ± 2	48 ± 4	31 ± 3	30 ± 3
UV-A control	65 ± 5	32 ± 2	38 ± 8+	26 ± 4	22 ± 2
UV-B	75 ± 6	28 ± 2	37 ± 10+	28 ± 3	21 ± 2+

Plus signs show marginally significant differences between ambient control and UV-B treatment or UV-A control within separate measurements. $+P < 0.1$ (linear mixed models, Bonferroni's test)

emission to the atmosphere. Hence, the highest methane emissions were measured in the middle of the growing seasons when the peat temperature and the *E. russeolum* leaf density reached the summer maximums. These findings are congruent with earlier studies of fen ecosystems (Rinne et al. 2007; Suyker et al. 1996; Treat et al. 2007). The results showed that our experimental setup did not alter or disturb the natural methane dynamics of the studied fen.

The snow gradient method was used to estimate the wintertime methane emissions from the study plots. The wintertime methane emissions were rather stable from year to year. Snow cover in the experimental field was homogenous and there were only a few measurements where ice layers caused problems by altering methane diffusion through the snow pack. Even though the natural variation of methane emissions between the plots was remarkable, our results are in accordance with another study of a natural boreal fen where the rate of methane emission in winter was less than 20 mg CH_4 m^{-2} d^{-1} (Alm et al. 1999). In that site, wintertime methane emissions produced 10% of the annual emission.

A laboratory incubation method was used to determine methane producing mechanisms in Halssiaapa fen. The α_C results showed that the methane, at least in shallow peat layers, is mainly produced via the acetoclastic pathway (Conrad 2005). However, sample handling and incubation procedures might obscure methanogenic conditions in peat (Yavitt and Seidman-Zager 2006).

The stable isotope ratio showed seasonal variation in emitted methane and methane in the peat water. At the beginning of the growing season methane was depleted but became more enriched with $\delta^{13}C$ towards autumn. Similar results were reported from a fen in northern Minnesota, USA (Chasar 2000). The increased enrichment in $\delta^{13}C$ towards autumn might be a result of enhanced methane oxidation with a greater number of *E. russeolum* leaves. However, in a single measurement campaign in 2007 the emitted methane was surprisingly depleted compared to earlier measurements. There are at least two possible explanations. Firstly, the emitted methane could have originated in deep peat layers and been transported through vascular plants. Secondly, the methane oxidizers could have temporarily been ineffective. However, the study site was not flooded at the time of sampling (data not shown). Moreover, it is possible that lower organic acid concentration in the latter part of the growing season (Table 2) could benefit

hydrogenotrophic methanogenesis over the acetoclastic type. This phenomenon should be studied further.

Elevated UV-B has only minor effects on the methane dynamics of the natural fen

During this study of three growing seasons (2003–2005), elevated UV-B radiation did not significantly affect the net methane emissions to the atmosphere. In general, the highest emissions were measured from the UV-B-treated plots, but after normalization by leaf density of *E. russeolum* the difference appeared to be insignificant. Simultaneously, the gross photosynthesis was determined along the present methane emissions and no treatment effect was observed (Haapala et al. 2009). These results are in line with each other but do not support the research hypothesis that enhanced UV-B will decrease methane emission based on the microcosm study by Niemi et al. (2002b). When summarizing the results of two earlier microcosm studies (Niemi et al. 2002a; Niemi et al. 2002b) and the present field study, there is some evidence that UV-B radiation could alter methane emission, but only when radiation intensity is high enough. Although, the UV-B radiation was transiently exceptionally high in the first growing season, there was no reduction in methane emissions in this natural fen ecosystem.

The concentrations of organic acids, precursors for methanogenesis, were slightly higher in the UV-B treatment. The highest concentrations were measured at the beginning of the growing seasons when the plants were developing rapidly. We have earlier reported similar stress related results when peatland microcosms with intact vegetation were exposed to elevated ozone concentration (Mörsky et al. 2008). Additionally, Rinnan et al. (2008) showed that elevated UV-B reduced sugar content in *E. russeolum* leaves and directed the carbon allocation towards rhizomes and roots. Moreover, the results of the mesocosm study with *E. angustifolium* under elevated UV-B radiation indicated enhanced root exudation (Rinnan et al. 2006). All these results are in accordance with each other and emphasize the result that UV-B radiation stimulates various belowground processes. It is likely that increased carbon allocation below ground could also increase root exudation and eventually affect methane emissions in long range.

Three years is rather a long time for an open-field UV-B experiment of a natural peatland ecosystem, but it is obviously not long enough to bring forth the effects of belowground processes on net methane emissions. The present study shows that when the major methane producing process is acetoclastic methanogenesis, excess organic acids in peat do not necessarily enhance net methane emissions. Moderately elevated UV-B radiation has impacts below ground but it is difficult to predict whether there will be changes in net methane emissions and carbon balance in the future.

Acknowledgments This study was financially supported by the Academy of Finland (projects 200884 and 200888), the Environmental Risk Assessment Centre–ERAC and the Graduate School in Forest Sciences. We are grateful to the staff of the Arctic Research Centre of the Finnish Meteorological Institute for maintaining the exposure field throughout the study and for the environmental data. We would like to thank Merja Mustonen, Saara Patronen and Tuulia Venäläinen for their assistance with fieldwork, Nina Kontinaho for conducting the stable isotope incubation experiment in the laboratory and Hannu Koponen for technical assistance with the stable isotope analysis. The English language was revised by James Blande.

References

Alm J, Saarnio S, Nykanen H, Silvola J, Martikainen PJ (1999) Winter CO_2, CH_4 and N_2O fluxes on some natural and drained boreal peatlands. Biogeochemistry 44:163–186

Austin J, Wilson RJ (2006) Ensemble simulations of the decline and recovery of stratospheric ozone. J Geophys Res 111:D16314

Bubier JL (1995) The relationship of vegetation to methane emission and hydrochemical gradients in Northern Peatlands. J Ecol 83:403–420

Chasar L (2000) Methane concentration and stable isotope distribution as evidence of rhizospheric processes: comparison of a fen and bog in the glacial lake agassiz peatland complex. Ann Bot 86:655–663

Conrad R (2005) Quantification of methanogenic pathways using stable carbon isotopic signatures: a review and a proposal. Org Geochem 36:739–752

Danevčič T, Mandic-Mulec I, Stres B, Stopar D, Hacin J (2010) Emissions of CO_2, CH_4 and N_2O from Southern European peatlands. Soil Biol Biochem 42:1437–1446

Daulat WE, Clymo RS (1998) Effects of temperature and water table on the efflux of methane from peatland surface cores. Atmos Environ 32:3207–3218

Haapala JK, Morsky SK, Saarnio S, Rinnan R, Suokanerva H, Kyro E, Latola K, Martikanen PJ, Holopainen T, Silvola J (2009) Carbon dioxide balance of a fen ecosystem in northern Finland under elevated UV-B radiation. Glob Change Biol 15:943–954

Kankaala P, Taipale S, Nykänen H, Jones RI (2007) Oxidation, efflux, and isotopic fractionation of methane during autumnal turnover in a polyhumic, boreal lake. J Geophys Res-Biogeosci 112:G02003

Keeling CD (1958) The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas. Geochim Cosmochim Acta 13:322–334

Lai DYF (2009) Methane Dynamics in Northern Peatlands: A Review. Pedosphere 19:409–421

Maljanen M, Liikanen A, Silvola J, Martikainen PJ (2003) Measuring N_2O emissions from organic soils by closed chamber or soil/snow N_2O gradient methods. Eur J Soil Sci 54:625–631

Mörsky SK, Haapala JK, Rinnan R, Tiiva P, Saarnio S, Silvola J, Holopainen T, Martikainen PJ (2008) Long-term ozone effects on vegetation, microbial community and methane dynamics of boreal peatland microcosms in open-field conditions. Global Change Biol 14:1891–1903

Newsham KK, Robinson SA (2009) Responses of plants in polar regions to UVB exposure: a meta-analysis. Glob Change Biol 15:2574–2589

Newsham KK, McLeod AR, Greenslade PD, Emmett AA (1996) Appropriate controls in outdoor UV-B supplementation experiments. Glob Change Biol 2:319–324

Niemi R, Martikainen PJ, Silvola J, Sonninen E, Wulff A, Holopainen T (2002a) Responses of two *Sphagnum* moss species and *Eriophorum vaginatum* to enhanced UV-B in a summer of low UV intensity. New Phytol 156:509–515

Niemi R, Martikainen PJ, Silvola J, Wulff A, Turtola S, Holopainen T (2002b) Elevated UV-B radiation alters fluxes of methane and carbon dioxide in peatland microcosms. Glob Change Biol 8:361–371

Nykänen H, Alm J, Lång K, Silvola J, Martikainen PJ (1995) Emissions of CH_4, N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland. J Biogeogr 22:351–357

Nykänen H, Alm J, Silvola J, Tolonen K, Martikainen PJ (1998) Methane fluxes on boreal peatlands of different fertility and the effect of long-term experimental lowering of the water table on flux rates. Glob Biogeochem Cyc 12:53–69

Rantakokko P, Mustonen S, Yritys M, Vartiainen T (2004) Ion chromatographic method for the determination of selected inorganic anions and organic acids from raw and drinking waters using suppressor current switching to reduce the background noise. J Liq Chromatogr Rel Technol 27: 829–842

Rinnan R, Impio M, Silvola J, Holopainen T, Martikainen PJ (2003) Carbon dioxide and methane fluxes in boreal peatland microcosms with different vegetation cover - effects of ozone or ultraviolet-B exposure. Oecologia 137: 475–483

Rinnan R, Gehrke C, Michelsen A (2006) Two mire species respond differently to enhanced ultraviolet-B radiation: effects on biomass allocation and root exudation. New Phytol 169:809–818

Rinnan R, Nerg A, Ahtoniemi P, Suokanerva H, Holopainen T, Kyro E, Baath E (2008) Plant-mediated effects of elevated ultraviolet-B radiation on peat microbial communities of a subarctic mire. Glob Change Biol 14:925–937

Rinne J, Riutta T, Pihlatie M, Aurela M, Haapanala S, Tuovinen J, Tuittila E, Vesala T (2007) Annual cycle of methane emission from a boreal fen measured by the eddy covariance technique. Tellus B 59:449–457

Ronkanen A, Klove B (2007) Use of stabile isotopes and tracers to detect preferential flow patterns in a peatland treating municipal wastewater. J Hydrol 347:418–429

Rösevall JD, Murtagh DP, Urban J (2007) Ozone depletion in the 2006/2007 Arctic winter. Geophys Res Lett 34: L21809

Saarnio S, Wittenmayer L, Merbach W (2004) Rhizospheric exudation of *Eriophorum vaginatum* L. - Potential link to methanogenesis. Plant Soil 267:343–355

Searles PS, Flint SD, Caldwell MM (2001) A meta analysis of plant field studies simulating stratospheric ozone depletion. Oecologia 127:1–10

Sheppard SK, Lloyd D (2002) Direct mass spectrometric measurement of gases in soil monoliths. J Microbiol Meth 50:175–188

Sommerfeld RA, Mosier AR, Musselman RC (1993) CO_2, CH_4 and N_2O flux through a Wyoming snowpack and implications for global budgets. Nature 361:140–142

Strack M (2004) Effect of water table drawdown on northern peatland methane dynamics: Implications for climate change. Glob Biogeochem Cyc 18:GB4003

Ström L, Ekberg A, Mastepanov M, Rojle Christensen T (2003) The effect of vascular plants on carbon turnover and methane emissions from a tundra wetland. Glob Change Biol 9:1185–1192

Ström L, Mastepanov M, Christensen TR (2005) Species-specific effects of vascular plants on carbon turnover and methane emissions from Wetlands. Biogeochemistry 75:65–82

Suyker AE, Verma SB, Clement RJ, Billesbach DP (1996) Methane flux in a boreal fen: Season-long measurement by eddy correlation. J Geophys Res Atmos 101:28637–28647

Taalas P, Kaurola J, Kylling A, Shindell D, Sausen R, Dameris M, Grewe V, Herman J (2000) The impact of greenhouse gases and halogenated species on future solar UV radiation doses. Geophys Res Lett 27:1127–1130

Treat CC, Bubier JL, Varner RK, Crill PM (2007) Timescale dependence of environmental and plant-mediated controls on CH_4 flux in a temperate fen. J Geophys Res 112: G01014

Turunen J, Tomppo E, Tolonen K, Reinikainen A (2002) Estimating carbon accumulation rates of undrained mires in Finland - application to boreal and subarctic regions. Holocene 12:69–80

Werner RA, Brand WA (2001) Referencing strategies and techniques in stable isotope ratio analysis. Rapid Commun Mass Spectrom 15:501–519

Yavitt J, Seidman-Zager M (2006) Methanogenic conditions in Northern peat soils. Geomicrobiol J 23:119–127