CO_2 and CH_4 budgets and global warming potential modifications in *Sphagnum*-dominated peat mesocosms invaded by *Molinia caerulea*

Fabien Leroy[1,2,3], Sébastien Gogo[1,2,3], Christophe Guimbaud[4,5], Léonard Bernard-Jannin[1,2,3], Xiaole Yin[6], Guillaume Belot[4,5], Wang Shuguang[6], Fatima Laggoun-Défarge[1,2,3]

[1]Université d'Orléans, ISTO, UMR 7327, 45071, Orléans, France
[2]CNRS, ISTO, UMR 7327, 45071 Orléans, France
[3] BRGM, ISTO, UMR 7327, BP 36009, 45060 Orléans, France
[4]Université d'Orléans, LPC2E, UMR 7328, 45071, Orléans, France
[5]CNRS, LPC2E, UMR 7328, 45071, Orléans, France
[6]School of Environmental Science and Engineering, Shandong University, Jinan, China

Correspondence to: Fabien Leroy (fabien.leroy@univ-orleans.fr)

Abstract. Plant communities play a key role in regulating greenhouse gas (GHG) emissions in peatland ecosystems and therefore in their ability to act as carbon (C) sinks. However, in response to global change, a shift from *Sphagnum* to vascular plant-dominated peatlands may occur, with a potential alteration in their C-sink function. To investigate how the main GHG fluxes (CO_2 and CH_4) are affected by a plant community change (shift from dominance of *Sphagnum* mosses to vascular plants, i.e. *Molinia caerulea*), a mesocosm experiment was set up. Gross primary production (GPP), ecosystem respiration (ER) and CH_4 emission models were used to estimate the annual C balance and global warming potential under both vegetation covers. While the ER and CH_4 emission models estimated an output of, respectively, 376 ± 108 and 7 ± 4 g C m^{-2} y^{-1} in *Sphagnum* mesocosms, this reached 1018 ± 362 and 33 ± 8 g C m^{-2} y^{-1} in mesocosms with *Sphagnum rubellum* and *Molinia caerulea*. Annual modelled GPP was estimated at -414 ± 122 and -1273 ± 482 g C m^{-2} y^{-1} in *Sphagnum* and *Sphagnum* + *Molinia* plots, respectively, leading to an annual CO_2 and CH_4 budget of – 30 g C m^{-2} y^{-1} in *Sphagnum* plots and of -223 g C m^{-2} y^{-1} in *Sphagnum* + *Molinia* ones (i.e., a C-sink). Even if, CH_4 emissions accounted for a small part of the gaseous C efflux (ca. 3%), their global warming potential value makes both plant communities have a climate warming effect. The shift of vegetation from *Sphagnum* mosses to *Molinia caerulea* seems beneficial for C sequestration at a gaseous level. However, roots and litters of *Molinia caerulea* could provide substrates for C emissions that were not taken into account in the short measurement period studied here.

1 Introduction

Peatlands are wetlands that act as a carbon (C) sink at a global scale. They cover only 3% of the land area but have accumulated between 473 to 621 Gt C (Yu et al., 2010) representing 30% of the global soil C. The C-storage capacity of northern peatlands is closely linked to environmental conditions and plant cover characteristics which limit the activity of soil decomposers. As a result, in spite of the relatively small net ecosystem production in peatlands, the imbalance between primary production and decomposition is enough to allow high organic matter (OM) accumulation as peat (Bragazza et al., 2009). Accumulating Sphagnum litter forms a major component of peat (Turetsky, 2003) and creates acidic, nutrient poor, wet and anoxic condition that favours the peat accumulation. Thus, *Sphagnum* species are able to outcompete vascular plants and reduce microbial decomposition (van Breemen, 1995). However, due to global change, environmental modifications (nutrient input, water table drop, warmer climate, etc.) are expected to cause a plant community shift in peatlands with an increase in vascular plants (especially graminoids) to the detriment of *Sphagnum* species (Berendse et al., 2001; Buttler et al., 2015; Dieleman et al., 2015). Vascular plant invasion could lead to a faster decomposition of peat OM due to a change in litter quality as a substrate for decomposers, thereby decreasing C-sequestration (Strakova et al., 2011). Furthermore, OM already stored in deep peat may be subject to increased decomposition through the stimulating effect of rhizospheric C input (Girkin et al., 2018). If these losses are not compensated by an increased gross primary productivity, peatlands could shift from a sink to a source of C and could increase greenhouse gas emissions, mainly carbon dioxide (CO_2) and methane (CH_4). Vascular plant invasion in peatlands has mostly been studied through a change in decomposition rates (Moore et al., 2007; Gogo et al., 2016) and modification in decomposer activities (Krab et al., 2013; Strakova et al., 2011). Some studies have paid attention to CH_4 emissions with and without the presence of *Carex* or *Eriophorum* (Noyce et al., 2014; Green and Baird, 2012; Greenup et al., 2000) and to CO_2 fluxes with different plant community compositions (Neff and Hooper, 2002; Ward et al., 2013). In spite of observed changes in C fluxes, the role of vascular plant invasion on the C balance in peatlands remains to be elucidated. The aim of this study was to investigate how an invading graminoid species, *Molinia caerulea*, can affect the Greenhouse Gases C Budget (GGCB) of a *Sphagnum*-dominated peatland. *Molinia caerulea* encroachment is well acknowledged problem in Europe linked to anthropogenic pressures such as nutrient deposition and management practices but studies of the effects on peatland ecosystem are still limited (Ritson et al., 2017, Berendse et al., 2001, Chambers et al., 1999). Here, CO_2 fluxes and CH_4 emissions were regularly measured in mesocosms entirely covers by *Sphagnum rubellum* with or without *Molinia caerulea* during fourteen months and were related to biotic and abiotic factors to estimate the annual C budget. The experimental design and a part of the data have been used in Leroy et al. 2017 and Leroy et al. 2019 to explore different questions than those explored in the present manuscript: the temperature sensitivity and N deposition effect on C and N cycle with two different plants communities in peatlands, respectively. In this paper, the novelty were: 1) treatment of the GPP data (which was not done in any of the other 2 published papers) and 2) the modelisation of the C fluxes (GPP, ER and CH_4 emissions) to *in fine* estimate the C balance under these two plants communities. Such C budget calculation allowed the estimation of the global warming potential, a key feature of the paper, which was not studied in the previous papers and deserve a communication on its own.

2 Materials and methods

2.1 Experimental design, sampling and methods

Twelve cylindrical peat mesocosms (30 cm in thickness and diameter) and water were collected in La Guette peatland (France) in March 2015. The site is a *Sphagnum*-dominated transitional fen that has been invaded by *Molinia caerulea* and *Betula spp* (*Betula verrucosa* and *Betula pubescens*) promoted by hydrological disturbances and nutrient inputs (Gogo et al., 2011). The mesocosms were buried near the laboratory in mineral soil with a waterproof tarpaulin containing peat water surrounding them. Environmental conditions were monitored with a weather station including solar radiation, relative humidity, air and soil temperature at 5 and 20 cm depth every 15 minutes. The mesocosms were separated into 2 treatment groups: 6 mesocosms containing only *Sphagnum rubellum* (called '*Sphagnum'* plots), and 6 containing both *Sphagnum rubellum* and *Molinia caerulea* (called '*Sphagnum* + *Molinia'* plots). All mesocosms were entirely and exclusively covers by *Sphagnum rubellum*. *Molinia caerulea* appeared in May and increased up to 60% of mesocosms on average until its senescence in November (Leroy et al., 2017) and did not affect *Sphagnum* cover (unpublished data). *Molinia caerulea* seedlings (roots and stems) were manually removed from *Sphagnum* plots. The water table level (WTL) was measured by a piezometer installed within each mesocosm and was maintained between 5 and 10 cm depth with addition of peat water when necessary. The number and height of *Molinia caerulea* leaves were measured.

2.2 Greenhouse gas measurements

Measurements were performed with the static chamber method from May 2015 to June 2016. The global principle of this method is to pose a hermetic chamber on the mesocosms in order to monitor the gases concentrations inside this chamber from which gas fluxes between soil-atmosphere can be calculated. Here, CO_2 and CH_4 fluxes were measured once or twice per week during the growing season (April-October 2015 and April-June 2016) and every two weeks during the winter (November 2015-March 2016). The measurement was usually performed between 9:00 and 17:00. Here, the effect of diurnal cycle on fluxes are supposed to be taking account be the modelization processes because of this diurnal variation seems related to the environmental parameters (Wright et al., 2013). The CO_2 and CH_4 emissions reported here are also used in Leroy et al., 2017 to discuss their temperature sensitivity but used only one year of measurement (from May 2015 to April 2016). Here, these emissions are used to establish a C balance in complement of the GPP. CO_2 concentrations were estimated using a GMP343 Vaisala probe inserted into a transparent PVC chamber (D'Angelo et al., 2016; Leroy et al., 2017). This clear chamber was used to measure the net ecosystem exchange (NEE), the balance between gross primary production (GPP; absorption of CO_2 by photosynthesis) and ecosystem respiration (ER, release of CO_2 into the atmosphere). ER was measured by placing an opaque cover on the chamber to block photosynthesis. The difference between NEE and ER corresponded to the GPP. The measurements lasted a maximum of 5 min and CO_2 concentration was recorded every 5 seconds. The slope of the relationship between CO_2 concentration and time allowed fluxes (in µmol CO_2 m^{-2} s^{-1}) to be calculated. CH_4 emissions were measured using SPIRIT, a portable infrared laser spectrometer (Guimbaud et al., 2016), measuring CH_4 concentration in a transparent chamber. Measurements take several to twenty minutes with time resolution of 1.5 s (Guimbaud et al., 2011).

2.3 Carbon flux modelling

2.3.1 Ecosystem Respiration

The ER increased with increasing air temperature and decreasing WTL in both vegetation covers (Supplementary material), as found by Bortoluzzi et al. (2006). Here, in order to improve the data analysis from Leroy et al. (2017) and established a C balance, the ER was derive for the entire year by using the equation from Bortoluzzi et al. (2006) for *Sphagnum* plots (Eq. 1):

$$ER_{sph} = \left[a * \frac{WTL}{WTL_{ref}} + b\right] * \left(\frac{(T_a - T_{min})}{(T_{ref} - T_{min})}\right)^c \qquad (1)$$

ER is the ecosystem respiration flux (µmol CO_2 m^{-2} s^{-1}). T_{ref} is the reference air temperature and T_{min} the minimum air temperature. These two parameters were set as in Bortoluzzi et al. (2006) at 15°C and -5°C, respectively. T_a refers to the measured air temperature (°C). The reference for the WTL (WTL_{ref}) was set at -15cm corresponding to the deepest WTL recorded in the mesocosms. The coefficients a, b and c (temperature sensitivity parameters) are empirical parameters.

In *Sphagnum* + *Molinia* plots, ER was significantly correlated to the number of *Molinia caerulea* leaves (r^2=0.44; Supplementary material). Following Bortoluzzi et al. (2006) and Kandel et al. (2013), we included, in addition to WTL and temperature, a vegetation index based on the number of *Molinia caerulea* leaves in the ER model for *Sphagnum* + *Molinia* plots (Eq. 2):

$$ER_{mol} = \left[(a * \frac{WTL}{WTL_{ref}}) + (b * Mc_{leaves})\right] * \left(\frac{(T_a - T_{min})}{(T_{ref} - T_{min})}\right)^c \qquad (2)$$

Mc_{leaves} is the number of *Molinia caerulea* leaves.

2.3.2 Gross primary production

The relationship between GPP and photosynthetic photon flux density (PPFD) is often described by a rectangular hyperbola saturation curve with:

$$GPP = \frac{i * PPFD * GPP_{max}}{i * PPFD + GPP_{max}} \qquad (3)$$

where i (µmol CO_2 µmol $^{-1}$ photon) is the initial slope of the hyperbola, GPP_{max}, the maximum GPP (µmol m^{-2} s^{-1}) and PPFD, the photosynthetic photon flux density (µmol m^{-2} s^{-1}). This approach was modified by Mahadevan et al. (2008) and Kandel et al. (2013) to include the effect of temperature and vegetation on the GPP model. The vegetation index was implemented (Mc_{leaves}) in the models after studying relationship between GPP and photosynthetic photon flux density at different vegetation stages (described in the result section; Fig. 2 and Fig. S1). The same equation was used in this study with (Eq. 4):

$$GPP = \frac{GPP_{max} * PPFD}{k + PPFD} * Mc_{leaves} * Tscale \qquad (4)$$

where GPP_{max} (μmol m^{-2} s^{-1}) represents the GPP at light saturation, the parameter k (μmol m^{-2} s^{-1}, Eq. 4) is the half saturation value and Mc_{leaves} is the number of *Molinia caerulea* leaves. T_{scale} is the temperature sensitivity of photosynthesis based on Kandel et al. (2013) and calculated as:

$$T_{scale} = \frac{(T-T_{min})(T-T_{max})}{(T-T_{min})(T-T_{max})-(T-T_{opt})^2} \quad (5)$$

where T is the air temperature measured with the weather station and T_{min}, T_{opt} and T_{max} represent the minimum, optimum and maximum air temperature for photosynthesis, and were set at 0, 20 and 40°C, respectively.

2.3.3 CH_4 emissions

The CH_4 emissions were significantly correlated to the soil temperature and the water table level (Leroy et al., 2017; Supplementary material). An equation similar to Eq. 1 was used to model the emissions (Eq. 6):

$$CH_4 = \left[d * \frac{WTL}{WTL_{ref}} + e\right] * \left(\frac{(T_s-T_{min})}{(T_{ref}-T_{min})}\right)^f \quad (6)$$

where WTL_{ref}, T_{min}, T_{ref} and T_{min} were set as for the ER equation. T_s refers to the measured soil temperature (°C).

2.3.4 Models calibration and validation

Two, randomly selected, thirds of the ER and CH_4 emission measurements were used to calibrate the equations and the other third was used for validation in order to verify the calibrated model. Calibration of the GPP models were done using additional measurements with nets decreasing the PPFD (allowing to have 6 GPP measurements under different luminosity per mesocosms) in order to calibrate the GPP_{max} and k parameters based on the Michaelis-Menten equation. In this ways, all measurement points were used to validate the model. Model quality was evaluated using the determination coefficient (r^2) and the Normalized Root Mean Square Error (NRMSE) calculated as:

$$NRMSE = 100 * \frac{\sqrt{(\frac{\sum(y-\hat{y})^2}{n})}}{\bar{y}} \quad (7)$$

where y is the measured value, ŷ the computed value, n the number of values and $\bar{y}$ the average of the measured value. The NRMSE indicates the percentage of variance between the measured and the predicted values.
The parameters of ER (a, b and c) and CH_4 emissions (d, e and f) models were calibrated by minimizing the NRMSE using the "SANN" method of the optim function in R (R Core Team, 2016).

2.3.5 Greenhouse Gases C Budget and global warming potential

The net ecosystem C balance (NECB) represents the net rate of C accumulation or release in or from the ecosystem (Chapin et al., 2006) and is calculated as:

$$NECB= -GPP+ER+F_{CH4}+F_{CO}+F_{VOC}+F_{DIC}+F_{DOC}+F_{PC} \quad (8)$$

where GPP is the gross primary production (µmol m^{-2} s^{-1}), ER, the Ecosystem Respiration (µmol m^{-2} s^{-1}) and F_{CH4}, F_{CO}, F_{VOC}, F_{DIC}, F_{DOC}, F_{PC}, the fluxes in µmol m^{-2} s^{-1} of methane (CH_4), C monoxide (CO), volatile organic C (VOC), dissolved inorganic C (DIC), dissolved organic C (DOC) and particulate C (PC), respectively. In this study, we used a simplified approach based on the GPP, ER and CH_4 emissions that we referred as the Greenhouse Gases C Budget (GGCB, g C m^{-2} y^{-1}). To calculate annual emissions, we run our models with 15 minutes time step using continuous weather and vegetation data.

The global warming potential over 100 years (GWP_{100}; g CO_2 eq m^{-2} y^{-1}) was calculated for both plant communities based on the annual GHG fluxes (GPP and ER and the CH_4 emissions) with the Eq. (9):

$$GWP_{100} = (x + y) * \frac{Molecular\ weight\ of\ CO_2}{Molecular\ weight\ of\ C} + z * \frac{Molecular\ weight\ of\ CH_4}{Molecular\ weight\ of\ C} * GWP_{100}\ of\ CH_4 \tag{9}$$

With x and y representing the annual GPP and ER fluxes (in g C m^{-2} y^{-1}), z the annual CH_4 emissions (in g C m^{-2} y^{-1}). The radiative force (GWP_{100}) of CH_4 is 34 times that of CO_2 (Myhre et al., 2013).

2.4 Statistics

The effects of *Molinia caerulea* were assessed by comparing *Sphagnum* + *Molinia* plots to *Sphagnum* plots with two-ways repeated-measure ANOVAs (with plant cover and date as factors).

3 Results

3.1 Environmental conditions

The environmental conditions of our measurements did not significantly differ between *Sphagnum* + *Molinia* and *Sphagnum* plots (Table 1). The only significant differences concerns the GHG fluxes with higher fluxes in *Sphagnum* + *Molinia* plots compared to the *Sphagnum* plots.

Table 1: Mean values of measurements of net ecosystem exchange (NEE), gross primary production (GPP), ecosystem respiration (ER), CH_4 emissions (CH_4), photosynthetic photon flux density (PPFD), water table level (WTL) and air temperature (Ta) in *Sphagnum* + *Molinia* and *Sphagnum* plots. Significant differences of two-way repeated-measure ANOVAs are expressed as ***p < 0.001 (n = 6). Data are presented as mean ± SE, n =12.

	Mean		Significance
	Sphagnum	*Sphagnum* + *Molinia*	
GHG fluxes			
NEE (µmol m^{-2} s^{-1})	-1.15 ± 0. 25	-4.63 ± 1.72	***
GPP (µmol m^{-2} s^{-1})	-2.25 ± 0. 40	-7.19 ± 2.28	***
ER (µmol m^{-2} s^{-1})	1.10 ± 0. 37	2.56 ± 0. 74	***
CH_4 (µmol m^{-2} s^{-1})	0.028 ± 0. 013	0.093 ± 0. 005	***
Environmental parameters			

WTL (cm)	-5.00 ± 0. 70	-6.81 ± 0.63
PPFD (μmol m^{-2} s^{-1})	707 ± 159	669 ± 160
Ta (°C)	12.27± 2.44	12.37 ± 2.49

3.2 Measured GHG fluxes

ER was significantly higher in *Sphagnum* + *Molinia* plots compared to *Sphagnum* ones. In both vegetation covers, the ER was maximum in July and minimum in January-February (Fig. 1a). GPP increased during the vegetation period (linked to the number of *Molinia* leaves), whereas in *Sphagnum* plots the GPP was relatively constant (Fig. 1b). After the senescence of *Molinia caerulea*, the GPP did not differ between the two treatments, unlike ER that remained higher in *Molinia* plots compared to *Sphagnum* ones. As a result, the NEE was higher in *Sphagnum* + *Molinia* plots than in *Sphagnum* ones during the growing season, but was lower the rest of the time (Fig. 1c). CH_4 emissions significantly increased in *Sphagnum* + *Molinia* plots with a peak of emissions in summer (June to August) and the lowest emissions in winter (Fig. 1d).

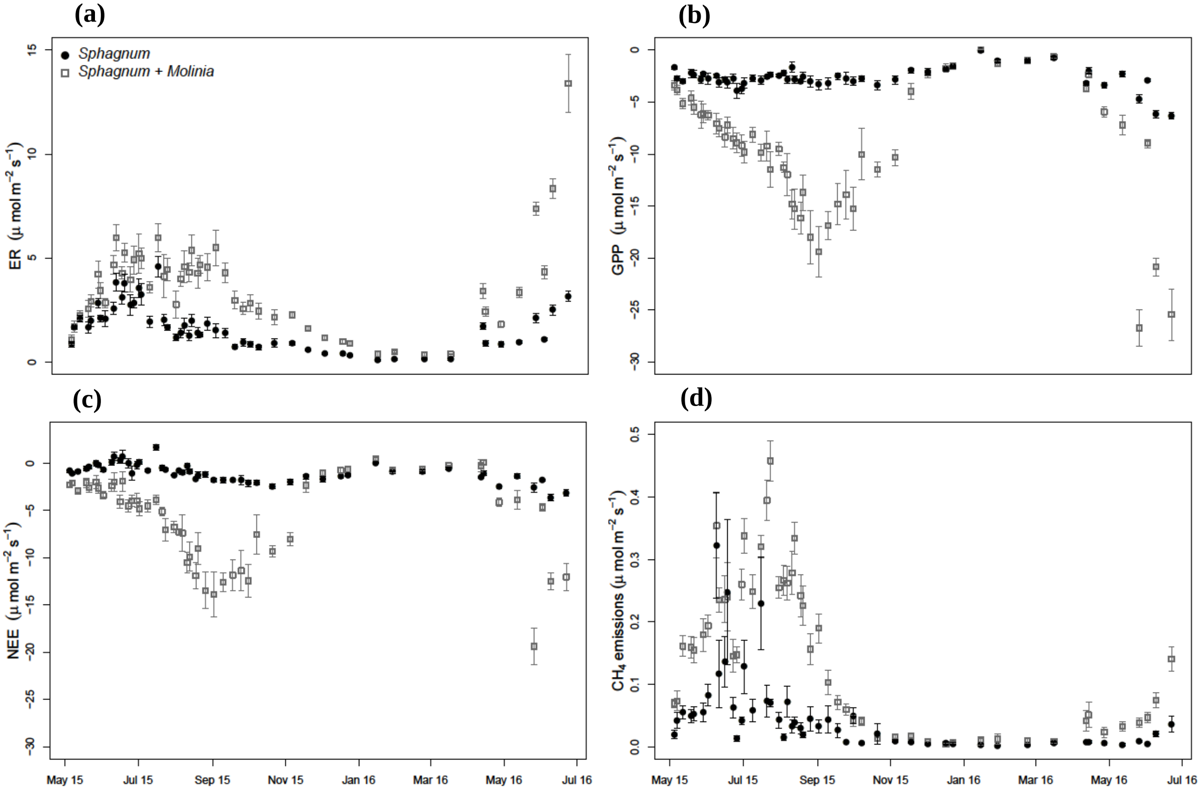

Figure 1: Measurements of ecosystem respiration (ER; a), gross primary production (GPP, b), net ecosystem exchange (NEE, c) and CH_4 emissions (d) in *Sphagnum* and *Sphagnum* + *Molinia* plots (± SE, n=6) from May 2015 to June 2016.

3.3 Calibration and validation of the GPP models

GPP parameters were calibrated using the photosynthesis – PPFD curves based on the Michaelis-Menten equation using four additional measurements (Fig. 2). The GPP_{max} decreased from -4.6 to -7.4 µmol m^{-2} s^{-1} in *Sphagnum* plots and from -7.2 in April to -25.7 µmol m^{-2} s^{-1} at the end of June in *Sphagnum* + *Molinia* plots.

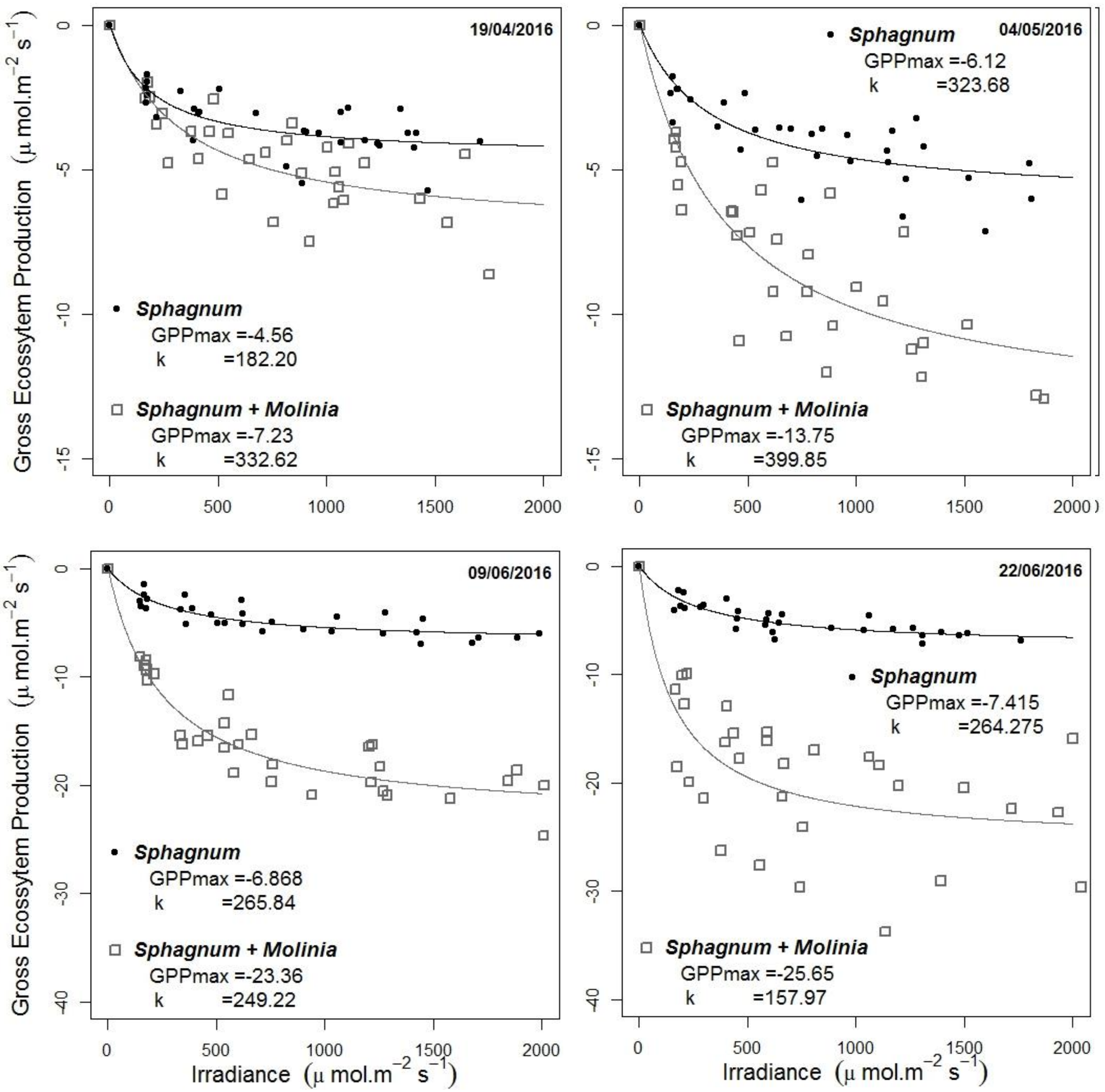

Figure 2: Dependence of gross primary production (GPP) on PPFD at four dates. The photosynthesis - PPFD curve shows the maximum rate of photosynthesis (GPP_{max}) and the half saturation value (k).

These increases are linked to *Sphagnum growth* and the number of *Molinia caerulea* leaves, respectively (Supplementary materials). The parameter k (µmol m^{-2} s^{-1}, Eq. 4) is the half saturation value and was set at the mean k value of the four dates with a k equal to 259 µmol m^{-2} s^{-1} for *Sphagnum* plots and 285 µmol m^{-2} s^{-1} for *Sphagnum* + *Molinia* ones.

Models validations were done using all the measurements points and showed a good reproduction of the GPP measurements, even if the relatively constant GPP in *Sphagnum* plots had a NRMSE close to 70.

3.4 Calibration and validation of the ER and CH_4 emissions models

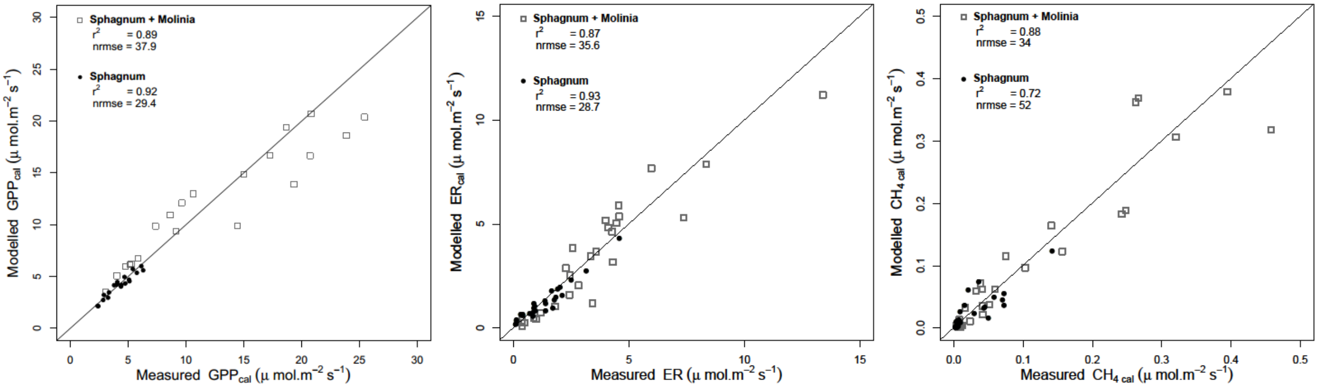

Figure 3: Calibration of the models by comparison of simulated and measured ecosystem respiration (ER), gross primary production (GPP), and CH_4 emission (CH_4) in *Sphagnum* and *Sphagnum* + *Molinia* plots. The diagonal lines represent the 1:1.

Calibration of the models showed a good agreement between the modelled and measured ER and CH_4 emissions with a high r^2 and low NRMSE for both plant communities (Fig. 3). Regarding the model evaluation, the validation data represented the ER measurements well, especially in *Sphagnum* plots with a r^2 of 0.82 and a NMRSE of 46.8 (Table 2). However, in *Sphagnum* + *Molinia* plots, the ER model validation showed a r^2 close to 0.6 but with the higher NMRSE. The validation of the CH_4 models explained a good proportion of the variance with a r^2 of 0.66 in *Sphagnum* plots and of 0.83 in *Sphagnum* + *Molinia* plots (Table 2).

		Validation	
		Sphagnum	*Sphagnum* + *Molinia*
ER			
	r^2	0.82	0.59
	NRMSE	46.8	94.7
	a	2.50	1.77
	b	0.33	0.0096
	c	1.49	1.43
GPP			
	r^2	0.56	0.77

	NRMSE	69.2	50.1
CH_4			
	r^2	0.66	0.83
	NRMSE	78.5	41.1
	d	0.041	-0.065
	e	0.001	0.092
	f	3.32	5.08

Table 2: r^2, Normalized Root Mean Square Errors (NRMSE) and adjusted model parameters for calibration of ecosystem respiration (ER), gross primary production (GPP), net ecosystem exchange (NEE) and CH_4 emissions (CH_4) in *Sphagnum* + *Molinia* and *Sphagnum* plots.

The model parameters a and c, respectively related to WTL and temperature sensitivity for ER models, were close for both plant communities, ranging for a from 2.50 to 1.77 and for c from 1.49 to 1.43 in *Sphagnum* and *Sphagnum* +*Molina* plots respectively (Table 2). Concerning the parameters of the CH_4 models, d and f differed between the two treatments. The parameter d connected to WTL was positive at 0.041 in *Sphagnum* plots but negative at -0.065 in *Sphagnum* + *Molinia* plots. The f value, representing the temperature sensitivity, rose from 3.32 in *Sphagnum* plots to 5.08 in *Sphagnum* + *Molinia* plots.

3.5 Greenhouse gases carbon budget and global warming potential

Table 3: Modeled annual gross primary production (GPP; g C m^{-2} y^{-1}), ecosystem respiration (ER; g C m^{-2} y^{-1}) and CH_4 emissions (CH_4; g C m^{-2} y^{-1}) in *Sphagnum* + *Molinia* and *Sphagnum* plots.

	GPP	ER	CH_4
Sphagnum	-414 ± 122	+ 376 ± 108	+ 7 ± 4
Sphagnum + *Molinia*	-1273 ± 482	+ 1018 ± 362	+ 33 ± 8

The modeled annual GPP over the studied period represented an input of 414 ± 122 g C m^{-2} y^{-1} in *Sphagnum* plots and of 1273 ± 482 g C m^{-2} y^{-1} in *Sphagnum* + *Molinia* plots (Table 3). The ER and CH_4 emissions showed, respectively, an output of 376 ± 108 and 7 ± 4 g C m^{-2} y^{-1} in *Sphagnum* plots and of 1078 ± 362 and 33 ± 8 g C m^{-2} y^{-1} in *Sphagnum* + *Molinia* plots (Table 3).

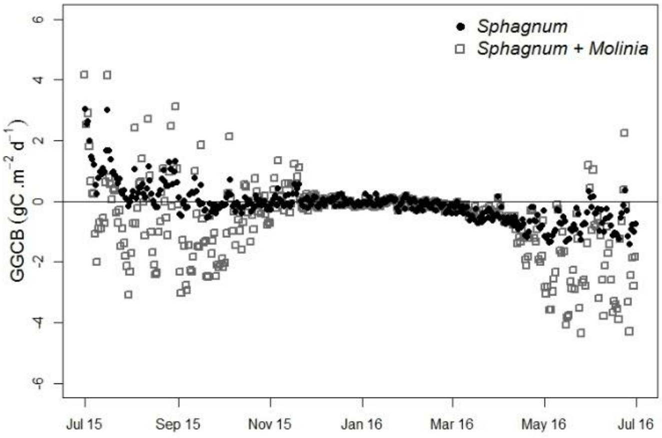

Figure 4: Greenhouse gases carbon budget (GGCB)) average per day in *Sphagnum* and *Sphagnum* + *Molinia* plots.

From July to December the GGCB was positive in *Sphagnum* plots which means that these plots released more C than they absorbed but the GGCB became negative from January to June (Fig. 4a). In contrast, the GGCB in *Sphagnum* + *Molinia* plots was mostly negative with positive values only in October and November. It results, the annual GGCB of *Sphagnum* plots absorbed 30 g C m^{-2} y^{-1} whereas the *Sphagnum* + *Molinia* plots absorbed 223 g C m^{-2} y^{-1}.The GWP_{100} for *Sphagnum* and *Sphagnum* + *Molinia* plots was, respectively, +195 and +547 g CO_2 eq m^{-2} y^{-1}.

4 Discussion

4.1 Gaseous C emissions

The presence of *Molinia caerulea* increased the gaseous C fluxes in the *Sphagnum*-dominated peat mesocosms. Compared to the latter, the GPP was higher with *Molinia caerulea*, with a C uptake close to 1300 g C m^{-2} y^{-1} against 400 g C m^{-2} y^{-1} with *Sphagnum* alone. This increase is linked to the large leaf area of *Molinia caerulea*, which increase the photosynthesizing plant material and so the GPP. The estimated GPP of *Sphagnum* mosses are consistent with studies conducted in boreal peatlands with a GPP close to 350 g C m^{-2} y^{-1} (Peichl et al., 2014; Trudeau et al., 2014). The GPP calculated with *Molinia caerulea* was higher than that measured in the site at La Guette peatland with an average of 1052 g C m^{-2} yr^{-1} (D’Angelo, 2015). Such a difference can be explained by the fact that in the field vegetation in collars contained other types of plants such as shrubs and woody chamephytes that exhibited lower GPP (D’Angelo, 2015). A higher GPP of vascular plants is expected to modify the belowground interactions that are not taken account into our models. Indeed, in comparison to *Sphagnum* mosses, vascular plants have an extensive root system which are able to release C and fuel microbial communities to optimize resource allocation (Fenner et al., 2007). It has been shown that up to 40 % of photosynthates can be allocated to root exudates in peatland (Crow and Wieder, 2005), with half that can be mineralized into CO_2 in a week and promote the ER (Kuzyakov et al., 2001) as the root decomposition (Ouyang et al., 2017). The higher ER in mesocosms with *Molinia caerulea* can also be linked to the metabolism of this vascular plant itself in which leaf respiration can account for more than 40% of the total assimilated C (Kuzyakov et al., 2001). Furthermore, after *Molinia caerulea* senescence, the leaves enhance CO_2 emissions through decomposition. Higher CH_4 emissions with graminoids compared to mosses or shrubs have been explained by the differences in root exudates quality and the aerenchyma of this plant type (e.g. Armstrong et al. 2015).

4.2 Models evaluation and sensitivities to parameters

Evaluation showed that our statistical models were efficient in representing ER and GPP for both plant communities. GPP in *Sphagnum* plots was the most difficult variable to represent (Table 2; Fig. 3). It was quite constant in time and only a small decrease was observed in winter when the solar radiation was low. In accordance with Tuittila et al. (2004), the *Sphagnum* growth or cover controlled the photosynthesis. These authors also reported that water saturation of *Sphagnum* govern it photosynthetic capacity and could further improve GPP models (Tuittila et al., 2004). However, with our stable *Sphagnum* moisture and *Sphagnum* cover, GPP in *Sphagnum* plots was mostly controlled by the photosynthetic active radiation. The ER models showed a similar sensitivity in both plant communities to abiotic factors with an empirical factor related to WTL at 2.1 and a temperature sensitivity close to 1.45 (Table 2). The parameters were similar for both plant communities and ER differences were mainly due to the contribution of *Molinia* leaves to aboveground and belowground respiration (Kandel et al., 2013). Modeling CH_4 explained a good proportion of the variance (between 70 and 80%). The parameters of the CH_4 models differed with vegetation cover. The presence of *Molinia caerulea* increased the temperature sensitivity of CH_4 emissions. Such increase of the temperature sensitivity could result from modification of methanogenesis pathways. Acetoclastic methanogenesis often dominated in minerotrophic peatlands, as La Guette peatland, and required less energy than hydrogenotrophic methanogenesis pathways (Beer and Blodau, 2007). An explication of vascular plants to influence the methane fluxes are often reported to their capacity to supply easily available substrates for the methanogenic microbes and with high variability in substrate quality and availability depending on plants species (Ström et al., 2012).Whilst roots exudates are source of acetate and thus suggested to favor acetoclastic methanogenesis (Saarnio et al., 2004), the roots exudates also stimulate the decomposition of recalcitrant organic matter favoring hydrogenotrophic methanogenesis (Hornibrook et al., 1997), and maybe more than acetates promoting acetoclastic methanogenesis. Shift from acetoclastic to hydrogenotrophic methanogenesis pathways could explain the increase of the temperature sensitivity observed here. Contributions of methanogens pathways to methane release could be explored by using mechanistic models. Such models could obtain new insight with additional measurements as substrate supply or microbial community response that could consider in future studies.

4.3 Annual C fluxes and GGCB

The shift from *Sphagnum* to *Molinia*-dominated peat mesocosms increased the C fixation through the GPP but also lead to an increase of the annual C output with CO_2 and CH_4 emissions. The gaseous C balance shows that both plant communities act as C-sinks with a storage of 30 g C m^{-2} y^{-1} in *Sphagnum* plots and 223 g C m^{-2} y^{-1} in *Sphagnum* + *Molinia* plots. These results contrast with the assumption mentioned in the introduction, that vascular plants could lead to a decrease in C-sequestration (Strakova et al., 2011). Nevertheless, the C-sink function of *Molinia*-dominated peat mesocosms can be questioned in view of the biomass production of *Molinia caerulea*. The root production, estimated by Taylor et al. (2001) at 1080 g m^{-2} y^{-1}, was produced with current-year photosynthates, meaning that the C-allocation in roots could account for 540 g C m^{-2} y^{-1}. Such an amount corresponds to a larger proportion than the C stored in *Sphagnum* + *Molinia* plots (223 g C m^{-2} y^{-1}) and could represent emission of the C already stored. Furthermore, C stored in roots, litters and leaves of *Molinia caerulea* could contribute to future C emissions by decomposition or respiration not taken into account here. Even with this C-sink function, GWP_{100} is positive for both vegetation covers. Although *Sphagnum* + *Molinia* plots act more as a C sink than *Sphagnum* ones, the higher GWP_{100} of CH_4 compared to CO_2 combined with the high emissions of CH_4 for *Sphagnum* + *Molinia* plots lead to a higher contribution of these plots to the greenhouse effect than in *Sphagnum* ones.

The shift from *Sphagnum* to *Molinia*-dominated peatlands enhanced CO_2 uptake by photosynthesis which led to higher CO_2 and CH_4 emissions. The application of models taking air temperature, water table level and vegetation index into account described these CO_2 fluxes and CH_4 emissions well. Respiration sensitivity to the two abiotic factors (temperature and WTL) was similar in both communities. However, the presence of *Molinia caerulea* seems to increase the sensitivity of CH_4 emissions to temperature. Modeling the C balance suggested that both *Sphagnum* and *Sphagnum* + *Molinia* plots acted as a C-sink. However, belowground C allocation as root C stocks needs further consideration due to their potential role as a substantial C source.

This study demonstrate the implications of Molinia caerulea colonisation in Sphagnum peatland on the C fluxes and on the parameters controlling it. The invasion of numerous peatlands by Molinia caeurlea will profondlly affect their C cycle at a mid term. However, a better understanding of these effect should be performed by propecting belowground C allocation as root C stocks needs further consideration due to their potential role as a substantial C source.

Author contribution.

FL, SG and FLD designed the experiment.

FL, SG, CG, XY, GB and WS collected data.

FL, SG, CG, LBJ and FLD performed model simulations and data analysis

FL prepared the manuscript with contributions from all co-authors

Acknowledgements This work was supported by the Labex VOLTAIRE (ANR-10-LABX-100-01). The authors gratefully acknowledge the financial support provided to the PIVOTS project by the Région Centre – Val de Loire (ARD 2020 program and CPER 2015 -2020). They thank A. Menneguerre for his contribution to gas measurements and P. Jacquet and C. Robert for their assistance in SPIRIT maintenance. We also thank E. Rowley-Jolivet for revision of the English version.

References

Armstrong, A., Waldron, S., Ostle, N. J., Richardson, H. and Whitaker, J.: Biotic and abiotic factors interact to regulate northern peatland carbon cycling, Ecosystems 18(8), 1395-1409, doi: 10.1007/s10021-015-9907-4, 2015.

Beer, J. and Blodau, C.: Transport and thermodynamics constrain belowground carbon turnover in a northern peatland, Geochimica et Cosmochimica Acta, 71(12), 2989-3002, doi: 10.1016/j.gca.2007.03.010, 2007.

Berendse, F., Van Breemen, N., Rydin, H., Buttler, A., Heijmans, M., Hoosbeek, M. R., Lee, J.A, Mitchell, E., Saarinen, T., Vasander, H., and Wallén, B.: Raised atmospheric CO2 levels and increased N deposition cause shifts in plant species composition and production in Sphagnum bogs. Global Change Biology, 7(5), 591-598, doi: 10.1046/j.1365-2486.2001.00433.x, 2001.

Chambers, F. M., Mauquoy, D., and Todd, P. A.: Recent rise to dominance of Molinia caerulea in environmentally sensitive areas: new perspectives from palaeoecological data, Journal of Applied Ecology, 36(5), 719-733, doi: 10.1046/j.1365-2664.1999.00435.x, 1999.

Berendse, F., Van Breemen, N., Rydin, H., Buttler, A., Heijmans, M., Hoosbeek, M. R., Lee, J., Mitchell, E., Saarinen, T., Vasander, H. and Wallén, B.: Raised atmospheric CO_2 levels and increased N deposition cause shifts in plant species composition and production in Sphagnum bogs, Global Change Biology, 7(5), 591-598, doi: 10.1046/j.1365-2486.2001.00433.x, 2001.

Bortoluzzi, E., Epron, D., Siegenthaler, A., Gilbert, D. and Buttler, A.: Carbon balance of a European mountain bog at contrasting stages of regeneration, New Phytologist, 172(4), 708-718, doi: 10.1111/j.1469-8137.2006.01859.x, 2006.

Bragazza, L., Buttler, A., Siegenthaler, A. and Mitchell, E. A.: Plant litter decomposition and nutrient release in peatlands, Carbon Cycling in Northern Peatlands, 99-110, doi: 10.1029/2008GM000815, 2009.

Buttler, A., Robroek, B. J., Laggoun-Défarge, F., Jassey, V. E., Pochelon, C., Bernard, G., Delarue, F., Gogo, S., Mariotte, P., Mitchell E. A. and Bragazza, L.: Experimental warming interacts with soil moisture to discriminate plant responses in an ombrotrophic peatland, Journal of Vegetation Science, 26(5), 964-974, doi: 10.1111/jvs.12296, 2015.

Chapin, F., Woodwell, G., Randerson, J., Lovett, G., Rastetter, E., Baldocchi, D., Clark, D., Harman, M., Schimel, D., Valentini, R., Wirth, C., Aber, J., Cole, J., Giblin, A., Goulden, M., Harden, J., Heimann, M., Howarth, R., Matson, P., McGuire, A., Melillo, J., Mooney, H., Neff, J., Houghton, R., Pace, M., Ryan, M., Running, S., Sala, O., Schlesinger, W. and Schulze, E.-D.: Reconciling carbon-cycle concepts, terminology, and methods, Ecosystems, 9(7), 1041-1050. doi: 10.1007/s10021-005-0105-7, 2006.

Crow, S. E. and Wieder, R. K.: Sources of CO_2 emission from a northern peatland: root respiration, exudation, and decomposition, Ecology 86(7), 1825-1834, doi: 10.1890/04-1575, 2005.

D'Angelo, B., Gogo, S., Laggoun-Défarge, F., Le Moing, F., Jégou, F. and Guimbaud, C.: Soil temperature synchronisation improves representation of diel variability of ecosystem respiration in Sphagnum peatlands, Agricultural and Forest Meteorology, 223, 95-102, doi: 0.1016/j.agrformet.2016.03.021, 2016.

D'Angelo, B.: Variabialité spatio-temporelle des émissions de GES dans une tourbière à Sphaignes: effets sur le bilan carbone, Doctoral dissertation, Université d'Orléans, 2015.

Dieleman, C. M., Branfireun, B. A., McLaughlin, J. W. and Lindo, Z.: Climate change drives a shift in peatland ecosystem plant community: implications for ecosystem function and stability, Global change biology, 21(1), 388-395, doi: 10.1111/gcb.12643, 2015.

Fenner, N., Ostle, N. J., McNamara, N., Sparks, T., Harmens, H., Reynolds, B. and Freeman, C.: Elevated CO_2 effects on peatland plant community carbon dynamics and DOC production, Ecosystems, 10(4), 635-647, doi: 10.1007/s10021-007-9051-x, 2007.

Gogo, S., Laggoun-Défarge, F., Merzouki, F., Mounier, S., Guirimand-Dufour, A., Jozja, N., Hughet, A., Delarue, F. and Défarge, C.: In situ and laboratory non-additive litter mixture effect on C dynamics of Sphagnum rubellum and Molinia caerulea litters, Journal of Soils and Sediments 16(1), 13-27, doi: 10.1007/s11368-015-1178-3, 2016.

Gogo, S., Laggoun-Défarge, F., Delarue, F. and Lottier, N.: Invasion of a Sphagnum-peatland by Betula spp and Molinia caerulea impacts organic matter biochemistry, Implications for carbon and nutrient cycling, Biogeochemistry, 106(1), 53-69, doi: 10.1007/s10533-010-9433-6, 2011.

Girkin, N. T., Turner, B. L., Ostle, N., Craigon, J., and Sjögersten, S.: Root exudate analogues accelerate CO2 and CH4 production in tropical peat. Soil Biology and Biochemistry, 117, 48-55, doi: 10.1016/j.soilbio.2017.11.008, 2018.

Green, S. M. and Baird, A. J.: A mesocosm study of the role of the sedge Eriophorum angustifolium in the efflux of methane—including that due to episodic ebullition—from peatlands, Plant and Soil, 351(1-2), 207-218, doi: 10.1007/s11104-011-0945-1, 2012.

Greenup, A. L., Bradford, M. A., McNamara, N. P., Ineson, P. and Lee, J. A.: The role of Eriophorum vaginatum in CH_4 flux from an ombrotrophic peatland, Plant and Soil, 227(1), 265-272, doi: 10.1023/A:1026573727311, 2000.

Guimbaud, C., Catoire, V., Gogo, S., Robert, C., Chartier, M., Laggoun-Défarge, F., Grossel, A., Albéric, P., Pomathiod, L., Nicoullaud, B. and Richard, G.: A portable infrared laser spectrometer for flux measurements of trace gases at the geosphere–atmosphere interface, Measurement Science and Technology, 22(7), 075601, doi: 10.1088/0957-0233/22/7/075601, 2011.

Guimbaud, C., Noel, C., Chartier, M., Catoire, V., Blessing, M., Gourry, J. C. and Robert, C.: A quantum cascade laser infrared spectrometer for CO_2 stable isotope analysis: Field implementation at a hydrocarbon contaminated site under bio-remediation, Journal of Environmental Sciences, 40, 60-74, doi: 10.1016/j.jes.2015.11.015, 2016.

Hornibrook, E. R., Longstaffe, F. J. and Fyfe, W. S.: Spatial distribution of microbial methane production pathways in temperate zone wetland soils: stable carbon and hydrogen isotope evidence, Geochimica et Cosmochimica Acta, 61(4), 745-753, doi: 10.1016/S0016-7037(96)00368-7, 1997.

Kao-Kniffin, J., Freyre, D. S. and Balser, T. C.: Methane dynamics across wetland plant species, Aquatic Botany, 93(2), 107-113, doi: 10.1016/j.aquabot.2010.03.009, 2010.

Kandel, T. P., Elsgaard, L. and Lærke, P. E.: Measurement and modelling of CO2 flux from a drained fen peatland cultivated with reed canary grass and spring barley, Gcb Bioenergy, 5(5), 548-561, doi: 10.1111/gcbb.12020, 2013.

Krab, E. J., Berg, M. P., Aerts, R., van Logtestijn, R. S. and Cornelissen, J. H.: Vascular plant litter input in subarctic peat bogs changes Collembola diets and decomposition patterns, Soil Biology and Biochemistry, 63, 106-115, doi: 10.1016/j.soilbio.2013.03.032, 2013.

Kuzyakov, Y., Ehrensberger, H. and Stahr, K.: Carbon partitioning and below-ground translocation by Lolium perenne, Soil Biology and Biochemistry 33(1), 61-74, doi: 10.1016/S0038-0717(00)00115-2, 2001.

Leroy, F., Gogo, S., Guimbaud, C., Bernard-Jannin, L., Hu, Z. and Laggoun-Défarge, F.: Vegetation composition controls temperature sensitivity of CO2 and CH4 emissions and DOC concentration in peatlands, Soil Biology and Biochemistry 107, 164-167, doi: 10.1016/j.soilbio.2017.01.005, 2017.

Mahadevan, P., Wofsy, S. C., Matross, D. M., Xiao, X., Dunn, A. L., Lin, J. C., Gerbig, C., Munger, J. W., Chow., V. Y. and Gottlieb, E. W.: A satellite-based biosphere parameterization for net ecosystem CO2 exchange: Vegetation Photosynthesis and Respiration Model (VPRM), Global Biogeochemical Cycles, 22(2), doi: 10.1029/2006GB002735, 2008.

Moore, T. R., Bubier, J. L. and Bledzki, L.: Litter decomposition in temperate peatland ecosystems: the effect of substrate and site, Ecosystems, 10(6), 949-963, doi: 10.1007/s10021-007-9064-5, 2007.

Myhre, G., Shindell, D., Bréon, F. M., Collins, W., Fuglestvedt, J., Huang, J., ., Koch, D., Lamarque, J.F., Lee, D., Mendoza, B., Nakajima, T., Robock A., Stephens, G., Takemura, T. and Nakajima, T.: Anthropogenic and Natural Radiative Forcing, In: Climate Change 2013: The Physical Science Basis, Contribution of Working Group 1 to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Table, 8, 714, 2013.

Neff, J. C. and Hooper, D. U.: Vegetation and climate controls on potential CO2, DOC and DON production in northern latitude soils, Global Change Biology, 8(9), 872-884, doi: 10.1046/j.1365-2486.2002.00517.x, 2002.

Noyce, G. L., Varner, R. K., Bubier, J. L. and Frolking, S.: Effect of Carex rostrata on seasonal and interannual variability in peatland methane emissions, Journal of Geophysical Research: Biogeosciences, 119(1), 24-34, doi: 10.1002/2013JG002474, 2014.

Ouyang, X., Lee, S. Y., and Connolly, R. M.: The role of root decomposition in global mangrove and saltmarsh carbon budgets. Earth-Science Reviews, 166, 53-63, doi: 10.1016/j.earscirev.2017.01.004, 2017.

Peichl, M., Öquist, M., Löfvenius, M. O., Ilstedt, U., Sagerfors, J., Grelle, A., Lindroth, A. and Nilsson, M. B.: A 12-year record reveals pre-growing season temperature and water table level threshold effects on the net carbon dioxide exchange in a boreal fen, Environmental Research Letters, 9(5), 055006, doi: 10.1088/1748-9326/9/5/055006, 2014.

R Core Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/, 2016.

Ritson, J. P., Brazier, R. E., Graham, N. J., Freeman, C., Templeton, M. R., and Clark, J. M.: The effect of drought on dissolved organic carbon (DOC) release from peatland soil and vegetation sources, Biogeosciences, doi: 10.5194/bg-2016-517, 2017.

Rydin, H. and Jeglum, J. K.: The biology of peatlands, 2e, Oxford university press, 2013.

Strakova, P., Niemi, R. M., Freeman, C., Peltoniemi, K., Toberman, H., Heiskanen, I., Fritze, H. and Laiho, R.: Litter type affects the activity of aerobic decomposers in a boreal peatland more than site nutrient and water table regimes, Biogeosciences 8(9), 2741-2755, doi: 10.5194/bg-8-2741-2011, 2011.

Taylor, K., Rowland, A. P. and Jones, H. E.: Molinia caerulea (L.) Moench, Journal of Ecology, 89(1), 126-144, doi: 10.1046/j.1365-2745.2001.00534.x, 2001.

Trudeau, N. C., Garneau, M. and Pelletier, L.: Interannual variability in the CO2 balance of a boreal patterned fen, James Bay, Canada, Biogeochemistry, 118(1-3), 371-387, doi: 10.1007/s10533-013-9939-9, 2014.

Tuittila, E. S., Vasander, H. and Laine, J.: Sensitivity of C Sequestration in Reintroduced Sphagnum to Water-Level Variation in a Cutaway Peatland, Restoration Ecology, 12(4), 483-493, doi: 10.1111/j.1061-2971.2004.00280.x, 2004.

Turetsky, M. R.: The role of bryophytes in carbon and nitrogen cycling, The Bryologist, 106(3), 395-409, doi: 10.1639/05, 2003.

Saarnio, S., Wittenmayer, L. and Merbach, W.: Rhizospheric exudation of Eriophorum vaginatum L.—potential link to methanogenesis, Plant and Soil, 267(1), 343-355, doi 10.1007/s11104-005-0140-3, 2004.

van Breemen, N.: How Sphagnum bogs down other plants, Trends in Ecology & Evolution, 10(7), 270-275, doi: 10.1016/0169-5347(95)90007-1, 1995.

Ward, S. E., Ostle, N. J., Oakley, S., Quirk, H., Henrys, P. A. and Bardgett, R. D.: Warming effects on greenhouse gas fluxes in peatlands are modulated by vegetation composition, Ecology letters, 16(10), 1285-1293, doi: 10.1111/ele.12167, 2013.

Wright, E. L., Black, C. R., Turner, B. L., and Sjögersten, S.: Environmental controls of temporal and spatial variability in CO2 and CH4 fluxes in a neotropical peatland. *Global change biology*, *19*(12), 3775-3789, doi: 10.1111/gcb.12330, 2013.

Yu, Z., Loisel, J., Brosseau, D. P., Beilman, D. W. and Hunt, S. J.: Global peatland dynamics since the Last Glacial Maximum, Geophysical Research Letters, 37(13), doi: 10.1029/2010GL043584, 2010.