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ARTICLE

Greenhouse Gas Emissions from Southward Transplanted Wetlands During Freezing-Thawing Periods in Northeast China

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Abstract Freezing-thawing in mid-high latitudes is an important factor controlling nutrient dynamics. We transplanted peatland columns (TQ) and freshwater marsh columns (SJ) in different latitudes into south seasonal frozen regions to determine the responses of greenhouse gas emissions from different wetlands to the freezing-thawing under climate warming. The decrease in CO_2 and CH_4 emissions during freezing stage were interrupted by a short emission peak. While N_2O uptake rate reduced with decreasing temperature. In the thawing stage, all the three greenhouse gases exhibited emission peaks. CO_2 were 159.83 mg m^{-2} h^{-1} (TQ) and 86.83 mg m^{-2} h^{-1} (SJ); CH_4 were 1.32 mg m^{-2} h^{-1} (TQ) and 4.07 mg m^{-2} h^{-1} (SJ); N_2O were 72.14 ug m^{-2} h^{-1} (TQ) and 22.15 ug m^{-2} h^{-1} (SJ). Meanwhile, N_2O transferred from sink into source. With temperature increase, the emission rate of CO_2 increased fast, while CH_4 and N_2O decreased. CO_2 emission during freezing-thawing periods was significantly correlated with soil temperature and CH_4 emission. Soil active organic carbon also played important roles in greenhouse gases emissions. Our study suggested that more greenhouse gases may release from wetlands into atmosphere in the context of global warming, and the potential release of CO_2 and N_2O during freezing-thawing periods was much higher in peatlands of permafrost zone.

Keywords Greenhouse gases · Freezing-thawing · Wetlands · Global warming · Active organic carbon

Introduction

Freezing-thawing is the fluctuations of soil temperature across the 0 °C isotherm (Hershfield 1979). It is the water transformation between liquid water and solid ice (Miller 1980). As one climate-driven pedoturbation, freezing-thawing regularly happens in mid-high latitude and high altitude regions (Grogan et al. 2004). It is the important meteorological event in boreal regions. Freezing-thawing can change the processes of soil nutrient dynamics, organic matter decomposition and affect carbon and nitrogen balance (Kidd et al. 2004). Recently, many studies focused on the effects of freezing-thawing on the key biogeochemical cycles of carbon and nitrogen, especially in the sensitive mid-high latitude regions (e.g., Grogan et al. 2004; Wang et al. 2011). And the greenhouse gas emission during seasonal freezing-thawing periods plays an important role in the atmosphere chemical change. For example, Some studies found that CO_2 emissions during freezing-thawing periods make up about 3–50 % of that of the whole year (Lafluer et al. 2001; Wickland et al. 2001); CH_4 emission rate in mires during thawing stage was about 2–3 times than that in summer, and is about 11 % of the whole year (Hargreaves et al. 2001); N_2O emission peaks during freezing-thawing periods were detected in agricultural, fallow and forest land, and the N_2O emissions during the entire winter period contributed to about 50 % of the annual N_2O emissions (Teepe et al. 2000; Wang et al. 2009). Meanwhile, Song et al. (2006) also found the high emission peaks of CO_2, CH_4 and N_2O during freezing-thawing periods in a freshwater marsh of Sanjiang Plain. Other ecosystems such as forest, farmland, temperate peatland, tundra and alpine meadow also exhibited emission peaks of greenhouse gas during freezing-thawing periods (Priemé and Christensen 2001; Bubier et al. 2002;

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Mikan et al. 2002; Kato et al. 2005). Therefore, the emission of greenhouse gas during freezing-thawing periods can't be ignored. However, their source and mechanism are far from certain (Song et al. 2006; Wang et al. 2009). And the existing studies of greenhouse gas emissions are mainly via indoor controlled experiments, but few studies consider the effect of global warming. In addition, the lack of consensus on freezing-thawing manipulations and variation in methodologies resulted in the inconsistent results (Henry 2007). Therefore, the conclusions from indoor controlled experiments are yet to be verified.

Wetlands store large amounts of organic carbon, and play an important role in the global carbon balance. In Northeast China, the area of wetlands is about 657.4×10^4 hm^2, and accounts for 48.3 % of total wetland area in China (Liu 2005). Freshwater marshes and peatlands are the two main wetland types in this region. Freshwater marshes are widely distributed in the Sanjiang plains, and peatlands are common in the Da and Xiao Xing'anling mountains. They are sensitive to climate change. Seasonal freezing-thawing is an important event in Northern China, and it impacts the evolution process of the ecosystem, controls the soil development, and affects the chemistry process of mass and energy cycles in the global ecosystems (Song et al. 2006). At present, global warming and human activity are changing the wetland ecosystem structure and function. They can affect greenhouse gas emissions during freezing-thawing periods by changing physical properties, freezing time, freezing depth and thawing process (Henry 2007). However, there was no study of emissions of CO_2, CH_4 and N_2O in the wetlands of China during freezing-thawing periods in the context of climate warming. Therefore, we transplanted the peatland columns in permafrost zone (TQ) and freshwater marsh columns in seasonal frozen regions (SJ) into a southern seasonal frozen ground to simulate the plots under climate warming. The objectives of this study are to reveal the characters of greenhouse gas emissions from different wetlands during freezing-thawing periods in the context of climate warming, and to discuss the associated mechanisms impacts by seasonal freezing-thawing.

Materials and Methods

Study Areas and Sampling

In order to study the effects of warmer climate on the greenhouse gas emission during freezing-thawing periods, we chose the two important kinds of wetlands in Northeast China: a peatland in Da Xing'anling Mountains, and a freshwater marsh in Sanjiang Plain. Their characteristics are shown in Table 1. In October 2010, using a polypropylene tube (diameter 10 cm; height 60 cm), we took seven soil columns (diameter 10 cm; soil height 30 cm) from peatland and freshwater marsh respectively, and transplanted them into the seasonal frozen ground at the Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences (43°48′N, 125°14′E). The climate is continental monsoon, with an average altitude of 211-m, mean annual temperature of 5.6 °C, and annual precipitation ranging from 522 mm to 615 mm. The soil columns from different latitudes make two treatments. Every treatment has four replicates. The bottoms of the tubes were sealed with caps and buried in the ground in the late October 2010. The distance between the soil surface and the upper of the tube is 30 cm. Meanwhile, the thermometers, whose sensitivity is ±0.3 °C, were set at depths of 0, 10, 20, 30, 40, and 60 cm. The PT1000 data logger measures the outputs of thermometer every 10 min, and the format of data is the same as the recording of meteorological data. Because the soil in the polypropylene tube is only 30 cm thick and the tubes are 60 cm long, the thermometers were set at 60 cm. The soil columns were covered with a foam box to avoid precipitation and reduce evaporation (Fig. 1). Additionally, we analyzed the active organic carbon fractions in the other soil columns as the control.

Table 1 Site descriptions

	TQ	SJ
Location	52°56′ N, 122°52′ E	47°35′ N, 133°29′ E
Temperature	−5.5 °C	1.9 °C
Precipitation	400 mm	558 mm
Altitude	467–472 m	55–65 m
Wetland type	Peatland	Freshwater marsh
Frozen soil type	Continuous permafrost	Seasonal frozen ground
Climate	Cold temperate monsoon	Humid and sub-humid monsoon
Vegetation	*ASS.Ledum palustre-Vaccinium uliginosum-Sphagnum*	*ASS.Calamagrostis angustifolia*

TQ, soil column from peatland in permafrost zone; *SJ*, soil column from freshwater marsh in seasonal frozen regions

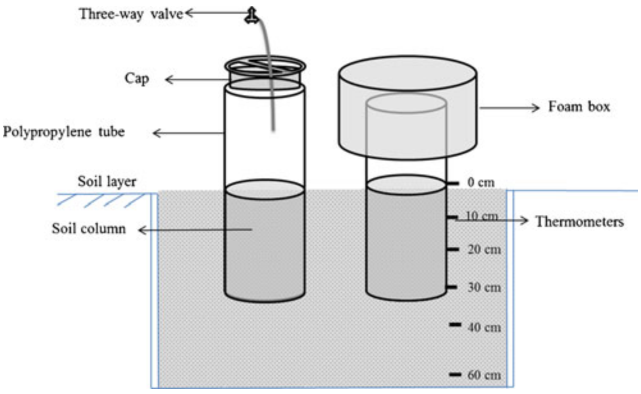


Fig. 1 The schematic of soil columns for freezing-thawing cycles

Sampling and Analyzing

After the soil equilibrated for about one month, we observed CO_2, CH_4 and N_2O emissions in the soil columns once per week during winter and twice per week during freezing-thawing periods from late November 2010 to April 2011. Soil and air temperature were recorded simultaneously. When collecting gas samples, the upper caps with tree-way valves were screwed tightly into the permanently polypropylene tubes, and sealed with vaseline and plastic film to avoid leaks. 50 ml nylon syringes were connected with the three-way valves to collect gas at 10 min interval over 30 min. The samples were measured by a modified gas chromatography (GC Agilent 7820A) within 12 h. CH_4 and CO_2 were separated with a 2 m stainless-steel column with inner diameter of 2 mm column (80/100 mesh). FID works at 200 °C using highly pure nitrogen as a carrier gas at a flow rate of 30 ml min^{-1}. N_2O was separated using a 1 m stainless-steel column with inner diameter 2 mm Porapak Q (80/100 mesh) and measured using the ECD, which was set at 330 °C using highly pure nitrogen as a carrier gas at a flow rate of 35 ml min^{-1}. The column temperatures were maintained at 55 °C for separation (Song et al. 2006). The GC was standardized using a CO_2, CH_4 and N_2O standard gas after approximately every eight samples.

The flux was calculated according to the following equation (Song et al. 2006):

$$J = \frac{dc}{dt} \cdot \frac{M}{V_0} \cdot \frac{P}{P_0} \cdot \frac{T_0}{T} \cdot H \tag{1}$$

Where $\frac{dc}{dt}$ is the slope of the curve of gas concentration variation with time; M is the mole mass of gas, P is the atmospheric pressure in sampling site, T is the absolute temperature during sampling, and H is the relative height of column above the water surface. V_0, T_0, P_0 are gas mole volume, air absolute temperate and atmospheric pressure under standard conditions. When the linear regression with coefficient $R^2>0.90$ occurred, the data are available.

Sample Analyses

Soil organic carbon (SOC) (using potassium dichromate-external heating method) and total nitrogen (TN) (using Kjeldahl digests method) were determined following the laboratory methods described by Zhang (2000). Soil light fraction organic carbon (LFOC) was determined using the density fractionation method (Gregorich and Ellert 1993). Soil particle organic carbon (POC) was measured by particle size (Cambardella and Elliott 1992). Soil microbial biomass carbon (MBC) was determined by a fumigation-extraction method (Vance et al. 1987). Soil dissolved organic carbon (DOC) was determined by the method of Jones and Willett (2006).

Statistical Analysis

One-way analysis of variance (ANOVA) was performed to assess the differences in active organic carbon fractions before and after freezing-thawing periods and gas emission in two kinds of wetlands (LSD). Correlation analysis was used to examine the relationships among CO_2, CH_4 and soil temperature. SPSS (13.0) software package for windows performed all statistical analysis. The Origin (7.5) software drew figures.

Results and Discussion

Seasonal Variations of Freezing-Thawing Characteristics

Northeast Institute of Geography and Agroecology, Chinese Academy of Sciences belongs to the seasonal frozen ground. From the Fig. 2a, we know that the freezing-thawing curve was separated by freezing and thawing in two stages. The first stage is freezing period. It is about from the beginning of November 2010 that the soil columns began to freeze. With decreasing temperature, the freezing process proceeded from the upper part of the column to the bottom part. And until 9 January 2011, the soil columns were fully frozen. But the lowest temperature in the 10 cm soil layer was not more than −6 °C (Fig. 2b). The second stage is thawing period. It is about from the beginning of March 2011 that the soil columns began to thaw. With increasing temperature, the thawing process proceeded from both the upper and bottom parts of soil column to the middle. And by 5 April 2011, soil columns were fully thawed. Meanwhile, the 10 cm soil temperature continues to increase, but it increased slowly near 0 °C, and then increased quickly.

Characteristics of CO_2 and CH_4 Emissions During Freezing-Thawing Periods

During freezing period, CO_2 and CH_4 emission rates in TQ and SJ gradually reduced with decreasing temperature but the decrease in CO_2 and CH_4 emissions were interrupted by short emission peaks before the soil fully froze. The short peaks of CO_2 were 232.99 mg m^{-2} h^{-1} (TQ) and 46.32 mg m^{-2} h^{-1} (SJ). The CH_4 were 0.89 mg m^{-2} h^{-1} (TQ) and 1.66 mg m^{-2} h^{-1} (SJ). This result was consistent with the findings of CO_2 peak in agriculture (Teepe et al. 2001) and CH_4 burst in tundra (Mastepanov et al. 2008). This emission peak was possibly caused by water soluble CO_2 and CH_4 being forced out of the growing ice structure (Teepe et al. 2001; Mastepanov et al. 2008). Even though the soil columns were fully

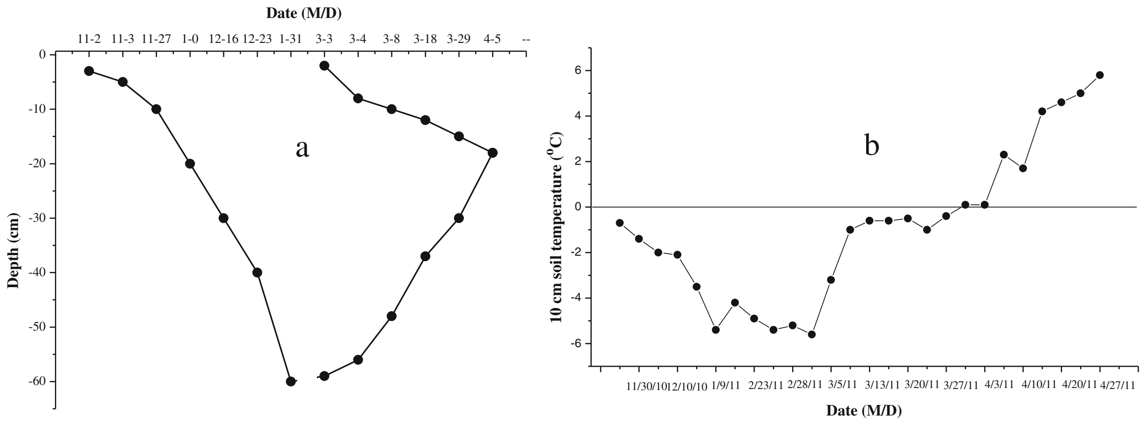


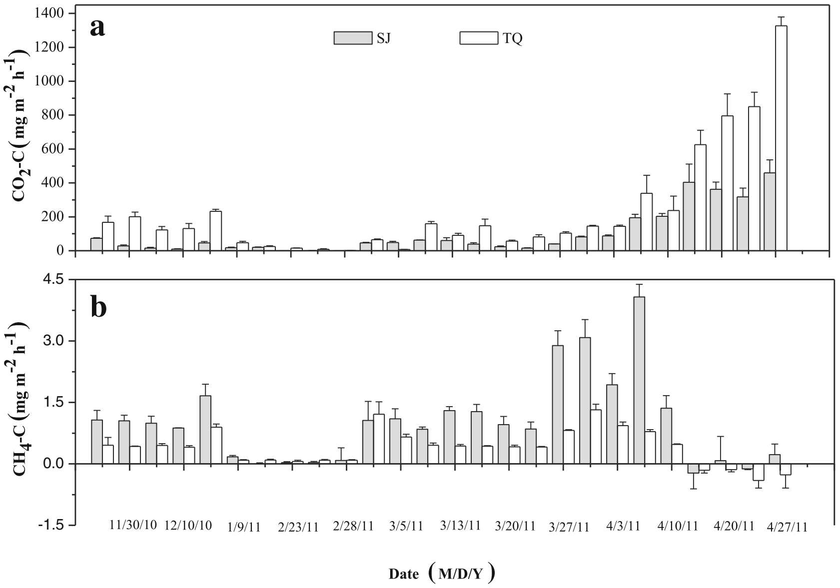
Fig. 2 The seasonal freezing-thawing curve of the wetland soil and 10 cm soil temperature

frozen during winter, there were still gas emissions: about 0.90 mg m^{-2} h^{-1}(TQ) and 0.35 mg m^{-2} h^{-1} (SJ) for CO_2, and 0.084 mg m^{-2} h^{-1} (TQ) and 0.012 mg m^{-2} h^{-1} (SJ) for CH_4 (Fig. 3). It suggested that microbes which produce CO_2 and CH_4 were activated even in winter, and the gas can escape through frost-induced cracks (Teepe et al. 2001; Sharma 2006).

During the thawing period, there was obvious emission peaks in CO_2 and CH_4. The peaks of CO_2 were 159.83 mg m^{-2} h^{-1} (TQ) and 86.83 mg m^{-2} h^{-1} (SJ). While there were two peaks in CH_4 emissions, the highest values were 1.32 mg m^{-2} h^{-1} (TQ) and 4.07 mg m^{-2} h^{-1} (SJ). It is possible that the thawing process proceeded from upper and bottom to middle, and resulted in the two peaks. When the soil columns were fully thawed, the CO_2 emission rate increased rapidly with soil temperature. The significant positive correlation between CO_2 emission and soil temperature (Fig. 4b) suggested that temperature as an indirect factor controlled CO_2 emission by adjusting microbial activities. However, CH_4 emission rate gradually decreased after the peak, and exhibited absorption in the late thawing stage. That was because there was not external water supply during freezing-thawing periods, and soil water might be the important factor to limit CH_4 emission (Song et al. 2003). Meanwhile, methanotrophs are concentrated in the upper soil layer (Schimel 1995). CH_4 from the underlying soil layer will be oxidized by methanotrophs during the diffusion, which resulted in a massive CO_2 release and CH_4 uptake in the late thawing stage (Fig. 3a).

The emission peaks of CO_2 and CH_4 emission during the thawing stage were consistent with other studies (Priemé and Christensen 2001; Teepe et al. 2001; Song et al. 2006; Mastepanov et al. 2008). The causes of high emission peaks during thawing periods might be as follows. Firstly, with temperature increase, the activity of dormant microorganisms might be recovered and even elevated due to the repeatedly freezing-thawing cycles (Wagner et al. 2005; Sharma et al. 2006). Secondly, freezing-thawing resulted in much more soil

Fig. 3 CO_2 and CH_4 fluxes during freezing-thawing periods. Values are means and standard deviation bars (n=3); TQ, soil column from peatland in permafrost zone; SJ, soil column from freshwater marsh in seasonal frozen region



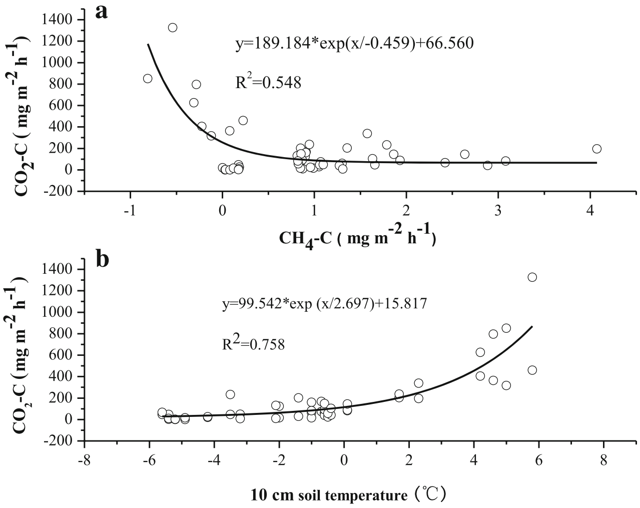


Fig. 4 Relationship between CO_2 fluxes and soil temperature, CH_4 fluxes during freezing-thawing periods

Table 3 The accumulative greenhouse gases emissions from the peatland and freshwater marsh during the freezing-thawing periods

Site	CO_2 (g m^{-2} season^{-1})	CH_4 (mg m^{-2} season^{-1})	N_2O (mg m^{-2} season^{-1})
TQ	598.514^a	1273.243^b	33.503^a
SJ	255.345^b	2930.676^a	14.691^b

TQ, soil column from peatland in permafrost zone; *SJ*, soil column from freshwater marsh in seasonal frozen regions. The different letter in the same column indicates significant differences at $P<0.05$

active organic carbon release, and the released active organic carbon can supply enough substrate for microbial activity (Feng et al. 2007). From Table 2, we know that the accumulated LFOC, POC, DOC and MBC in fall decreased after the long freezing-thawing cycles. It suggested that these active organic carbon fractions might play important roles in CO_2 and CH_4 emission peaks during thawing stages. It is possible that the micromolecule like DOC and MBC will be utilized by microbe directly, but the macromolecule like LFOC and POC as the indirect carbon source. Lastly, with soil columns thawing, the diffusion barriers have been eliminated, and then the accumulated gas in the soil below the frozen soil surface immediately emitted (Herrmann and Witter 2002).

From the mean flux and cumulative CO_2 and CH_4 emissions during freezing-thawing periods (Table 3, Fig. 3), we know that at the same freezing-thawing periods, the emission of CO_2 in SJ was significantly lower than that in TQ, which was contrary to CH_4 emission. But all of them are the sources of CO_2 and CH_4. The different emissions of CO_2 and CH_4 in freshwater marsh and peatland were mainly due to the differences in soil microbial activities, active organic matter and soil physical properties. Compared to the in situ observations of CO_2 and CH_4 emission during snow covered season (Miao et al. 2012), our carbon emission rates were much higher. And the CO_2 emission in TQ was higher than that in SJ, which was different from the in situ observations. It suggested that the potential release of CO_2 during freezing-thawing periods was much higher in peatlands of permafrost zone than that in freshwater marsh of seasonal frozen regions. However, the lower temperature in Da Xing'anling Mountains restricted the carbon emission (Wang et al. 2010). Therefore, under global warming, more CO_2 and CH_4 will be released during freezing-thawing periods and their roles cannot be ignored.

Characteristics of N_2O Emission During Freezing-Thawing Periods

From Fig. 5, we know that during freezing period, all the soil columns were the sink of N_2O and the uptake rate decreased from 24.68 ug m^{-2} h^{-1} (TQ) and 11.98 ug m^{-2} h^{-1} (SJ) into 0.24 ug m^{-2} h^{-1} (TQ) and 0.15 ug m^{-2} h^{-1} (SJ). In our study, there is no emission peak of N_2O during freezing period, which was different from the findings of Teepe et al. (2001). But the uptake capacity of N_2O decreased with soil column freezing. It suggested that microbes in freezing soil were still active. And the anaerobic environment due to the ice barrier supported favorable conditions for denitrification. But the ice layers prevent the escape of soluble N_2O into the liquid water film and may result in supersaturated soil solutions (Teepe

Table 2 The properties of active organic carbon before and after freezing-thawing periods

		SOC (g kg^{-1})	TN (g kg^{-1})	C/N	LFOC (g kg^{-1})	POC (g kg^{-1})	DOC (mg kg^{-1})	MBC (mg kg^{-1})
before	SJ	57.23^c	2.68^b	21.40^{bc}	7.38^b	17.59^c	38.01^c	1971.05^c
	TQ	445.77^a	19.51^a	22.92^{ab}	355.14^a	186.86^a	462.46^a	4192.26^a
after	SJ	53.26^c	2.53^b	21.06^c	6.02^b	13.99^c	47.67^c	719.60^d
	TQ	426.03^b	18.39^a	23.61^a	347.64^a	162.87^b	339.66^b	3193.70^b

SOC soil organic carbon; *TN* total nitrogen; *LFOC* light fraction organic carbon; *POC* particle organic carbon; *DOC* dissolved organic carbon; *MBC* microbial biomass carbon. *TQ* soil column from peatland in permafrost zone; *SJ* soil column from freshwater marsh in seasonal frozen regions. The different letter in the same column indicates significant differences at $P<0.05$

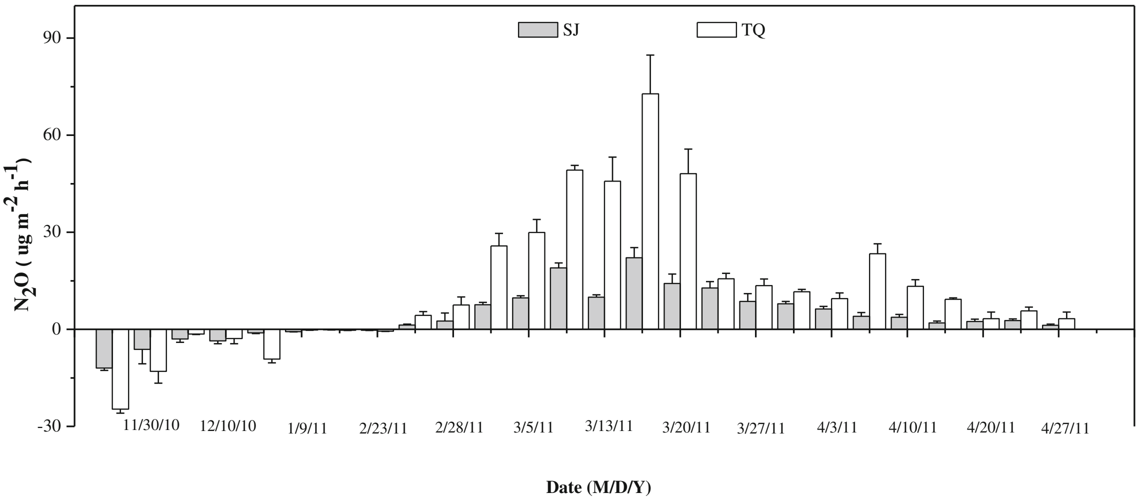


Fig. 5 N_2O fluxes during freezing-thawing periods. Values are means and standard deviation bars (n=3); TQ, soil column from peatland in permafrost zone; SJ, soil column from freshwater marsh in seasonal frozen region

et al. 2001). However, part of the trapped N_2O may still escape through cracks in the ice layer into the air filled pore space (Teepe et al. 2001). Therefore, the capacity of soils for N_2O uptake became smaller. However, when the soil thawed, all the soil columns transferred from N_2O sink to source. The emission rate gradually increased with temperature increase, and the peak were 72.14 ug m^{-2} h^{-1} (TQ) and 22.15 ug m^{-2} h^{-1} (SJ). Our emission peak of N_2O during thawing stage was consistent with other studies (Teepe et al. 2001; Koponen and Martikainen 2004; Ludwig et al. 2006; Song et al. 2006). When the soil columns were fully thawed, the emission rate began to decrease but they were always the N_2O source. Usually, N_2O production in soil is mainly from nitrification and denitrification by microbial activity (Bouwman 1994). Whether ecosystems acted as source or sink of N_2O depended on the balance of N_2O production and consumption. Our high N_2O emissions during soil thawing may be the burst emission of accumulated N_2O in the soil below the frozen soil surface due to the disappeared diffusion barriers (Burton and Beauchamp 1994). Meanwhile, denitrification is the main cause of N_2O production during thawing periods. Ludwig et al. (2004) found that immediately after the beginning of the thawing, denitrification contributed by 83 % to the N_2O production. That was because the enzyme reductase activity and active organic matter released by broken aggregates or from microorganisms killed by freezing-thawing cycles play an important role in controlling the N_2O emissions during freezing-thawing periods (Wang et al. 2005).

From the mean flux and cumulative N_2O emissions during freezing-thawing periods (Table 3, Fig. 5), the emission of N_2O in TQ was significantly higher than that in SJ, which was contrary to the in situ observation of N_2O emission during snow covered season (Miao et al. 2012). It suggested that under global warming, the potential emission capacity of N_2O during thawing periods was much higher in the peatlands of permafrost zone than that in the freshwater marsh of seasonal frozen regions. Therefore, available nitrogen will be activated and more N_2O will be emitted from wetlands during freezing-thawing periods, which intensify the greenhouse effect combined with CO_2 and CH_4.

Conclusion

In our study, we found that the emission rates of CO_2 and CH_4 during freezing stage decreased with soil freezing but the short peaks appeared before soil columns were fully frozen. However, all the soil columns were a N_2O sink during freezing stage and the capacity of the sink reduced with temperature decrease. During the thawing stage, all the three greenhouse gases exhibited obvious peaks and N_2O transferred from sink into source. Meanwhile, there was significant correlation between CO_2, CH_4 and 10 cm soil temperature. Soil active organic carbon also plays an important role in greenhouse gases emissions during freezing-thawing periods. The high CO_2 and N_2O emissions in the peatland of the permafrost zone suggested that their potential releases during freezing-thawing periods were much higher than that in the freshwater marsh of seasonal frozen regions. Therefore, under global warming, greater amounts of CO_2, CH_4 and N_2O will release into atmosphere, and intensify the greenhouse effect.

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