The fluxes and controlling factors of N_2O and CH_4 emissions from freshwater marsh in Northeast China

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Nitrous oxide (N_2O) and methane (CH_4) emissions were measured using a static chamber method in two adjacent plots of freshwater marsh predominated by *Calamagrostis angustifolia*, one is seasonal waterlogged (SW) and the other without surface water accumulation (NW), in Sanjiang Plain wetland (47°35′N, 133°31′E), northeast China, during 2002−2004. The diurnal and seasonal flux variations of both gases were significantly correlated with 5-cm-soil temperature. The NW marsh is a source of N_2O and sink of CH_4, while the SW marsh is sink of N_2O and source of CH_4. Remarkably, we observed a N_2O emission peak under Eh of −300 to −100 mV, and CH_4 emission peak under Eh of +300 to +400 mV, which indicate additional sources of N_2O and CH_4 for the freeze-thaw induced emission peaks of N_2O and CH_4 observed between late July and early August. Further study shows that the additional N_2O and CH_4 were emitted under the frozen soil after thawing.

Nitrous oxide (N_2O) and methane (CH_4) are two important greenhouse gases behind carbon dioxide (CO_2) in their contributions to radiative forcing of the Earth's atmosphere, which are about 300 and 20–30 times more effective in global warming than CO_2, respectively [1]. The atmospheric concentrations of N_2O and CH_4 have increased by 49 ppb (18.2%) and 1059 ppb (148.1%) between 1750 and 2005, respectively, and continue to increase [1–4]. In addition to greenhouse effects, N_2O also participates in the destruction of the ozone layer through its oxidation to NO in the stratosphere. Therefore, N_2O and CH_4 have been the subjects of

much concern especially regarding to the mechanisms involved in its formation and emission from the soil and other sources, as well as its loss in the atmosphere.

Wetlands are among the most important ecosystems in the world in terms of greenhouse gas emission, accounting 20% and 25% of the current global annual emission of N_2O and CH_4, respectively [5, 6], although they make up only 5% of Earth's land surface. General consensus is that the N_2O and CH_4 emissions from soil are affected by various factors, such as temperature, soil moisture, redox potential, etc [7–13]. Zhang et al. [7] investigated the effects of exogenous nitrogen on ecosystem respiration, CH_4 and N_2O emissions from freshwater marshes *in situ* and found that

the seasonal patterns of N_2O and CH_4 emission were significantly influenced by the exogenous nitrogen. Several studies found that the standing water depth and temperature greatly governed the spatial variation of CH_4 and N_2O emissions from different marshes [13–15]. Some researchers even observed the CH_4 emission from freshwater marshes in winter in Sanjiang Plain [16–18].

In this study, we monitored the emission patterns of N_2O and CH_4 during plant growing season of 2002–2004, and the N_2O and CH_4 concentrations at different depths during the freeze-thaw period from October 2003 to July 2004, in freshwater marsh predominated by *Calamagrostis angustifolia* in Sanjiang Plain of China. The objectives of this study are to (1) measure N_2O and CH_4 emissions from freshwater marsh ecosystems in temperate climate zone; (2) assess the effect of temperature, biomass, pH and Eh on emissions of N_2O and CH_4; and (3) understand the mechanism of N_2O and CH_4 seasonal emission under freeze-thaw condition.

1 Material and methods

1.1 Studied region

The studied region is located at the Sanjiang Plain (45°01′N to 48°28′N, 130°13′E to 135°05′E) in Heilongjiang Province, northeast China, which is the largest continuous freshwater marsh of plain in China [19], covering an area of about 14800 km^2 [20]. The mean annual precipitation is 500–650 mm, concentrated in July and August, and the mean annual temperature is 1.9°C for a whole year, −20°C in January and 22°C in July in this region. The freeze-thaw cycle lasts about 9 months a year in the Sanjiang Plain. The soil starts to freeze in early November, while the frozen soil starts to thaw in early March, and is ultimately melted thoroughly around mid-July. The marshes in the Sanjiang Plain are divided into four major types according to plant species, i.e., *Carex lasiocarpa*, *Carex pseudocuraica*, *Carex meyeriana* and *Calamagrostis angustifolia* [19]. The *Calamagrostis angustifolia* freshwater marsh covers about 34% of the total marsh [21]. This type of freshwater marsh is further classified into two types, seasonally waterlogged (SW) marsh and non-waterlogged (NW) marsh according to hydrological regime of the marsh. There is about 0–10 cm depth of standing water, which comes from snow and precipitation in SW marsh from early March to middle July, while from middle July to early November, there is no standing water after the frozen soil is melted thoroughly. The soil of both SW and NW marsh is water-saturated dur-

ing July and August because of precipitation. The topsoil (0–5 cm) is relatively dry except in July and August during plant growing season in NW marsh.

The plants are pure *Calamagrostis angustifolia* in the SW marsh, and 90% *Calamagrostis angustifolia* with 10% shrubs in NW marsh. The soil in studied plots is gley soil. In general, the profile is composed of root layer, peat layer and gley layer. The depth of the dead/live root layer is about 15–20 cm in NW marsh and 20–30 cm in SW marsh, respectively. The thickness of peat layer ranged 10–20 cm in NW marsh and 15–30 cm in SW marsh, respectively. The gley layer is the bottom of soil underneath peat layer. The nutrient contents in soil profiles were shown in Table 1 [22].

1.2 Sample collection

Two adjacent plots (10 m×25 m) of *Calamagrostis angustifolia* freshwater marsh, representing SW and NW, respectively, were selected to monitor N_2O and CH_4 emissions through the Sanjiang Experimental Station of Marsh Wetland Ecology, Chinese Academy of Sciences, at approximately 47°35′N, 133°31′E. Five monitoring sites for N_2O and CH_4 fluxes, six monitoring sites for N_2O and CH_4 concentrations at different soil depths under the freezing soil layer were set for each plot. Boardwalks were established for each site in order to minimize disturbance to the marsh during sampling.

Gas flux was monitored in static chambers made of Plexiglas, similar to that used by Lindau [23]. The gas collection chamber consisted of permanently installed metal base units (50 cm×50 cm×5 cm) with four fixed metal pegs, open bottoms and removable clear Plexiglas tops (50 cm×50 cm×70 cm). Four pegs were installed about 10 cm into the soil to support the chamber prior to sampling. A thin rubber tube with clamp (sampling port), a thermometer, and a battery-operated fan were installed on the top of each chamber. Chambers were placed in each of the 10 monitoring sites in early May.

The N_2O and CH_4 concentrations at different soil depths under freezing soil layer were monitored using perforated PVC pipes (Figure 1). Two sets of PVC pipes (6 pieces each) with same diameters (7.5 cm) but different lengths (25, 35, 55, 80, 100 and 140 cm, respectively) were buried in both plots next to the static chambers, respectively, which were designed to collect gases at 10–25, 25–35, 40–55, 60–80, 80–100, 120–140 cm soil depths, respectively. Both ends of

Table 1 The nutrient contents in soil profiles of studied marsh

Soil profile	TN (g kg^{-1})	NH$_4$-N (ppm)	NO$_3$-N (ppm)	TP (ppm)	TOC (g kg^{-1})	TS (ppm)	pH
Root layer	17.03–19.78	50.96–73.27	2.43–6.21	1356.23–2673.44	50.56–64.61	476.32–524.76	5.12–6.25
Peat layer	20.20–22.94	31.40–82.02	2.94–3.39	1987.43–2064.79	60.57–80.76	452.12–512.34	5.14–5.97
Gley layer	7.04–8.05	16.92–28.25	0.57–1.26	364.85–759.05	7.44–15.99	299.34–401.43	5.67–6.26
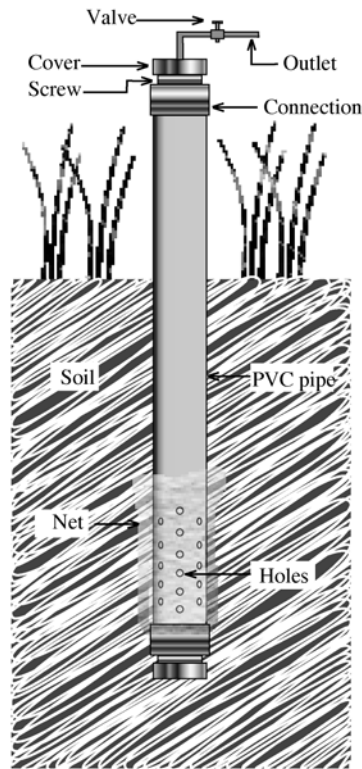
Figure 1 Illustration PVC pipes used to monitor the concentrations of N_2O and CH_4 at the different soil depths.

the pipes were sealed with a thin rubber tube with clamp installed on top of each pipe as sampling port, whereas the lower portion has 36 to 48 holes of 0.8 cm in diameter for gas collection (Figure 1).

The sampling was carried out during the growing seasons of 2002 to 2004. The N_2O and CH_4 fluxes were measured twice each Saturday, at 8:30–9:30 and 14:30–15:30, and 8 times (with 3 hour intervals) on the 18th of each month. For each sampling, the chamber was sealed and three replicate samples of the chamber air were manually collected through the sampling port with gas-tight 50 mL syringes at 0, 30 and 60 min after closure. Each sample was injected into a vacuum bag immediately to prevent exchange or contamination by atmospheric gases.

Gases in different soil depths were sampled three times each month, at about 9:00–10:00 on the 6th, 16th and 26th, respectively, during November 2003 to August 2004. At each sampling, the pipes were sealed after inlet air was pumped out. The samples of the soil air in different depth were manually collected through the sampling port with gas-tight 50 mL syringes after 30 min of balancing, and then each sample was injected into a vacuum bag immediately. All gas samples were analyzed at the Sanjiang Experimental Station of Marsh Wetland Ecology within 10 hours after sampling.

The biomass of vegetation was determined in the middle of each month in six 50 cm×50 cm plots at two sites during the growing season. Live plants and plant litter in each plot

were clipped to ground level, then the plots were excavated to a depth of 60 cm, and then the roots were separated from the soil.

1.3 Sample analysis

The N_2O and CH_4 concentrations were analyzed using Agilent 6820 Gas Chromatography with dual channel system, a ^{63}Ni electron capture detector (ECD) and a 3 m Poropak Q (60/80 mesh) column for N_2O measurement, and a flame ionization detector (FID) and a 2 mL 3X molecular sieve (80/100 mesh) for CH_4 measurement. The temperatures were 55, 250 and 375°C for the oven, the injector and the detector, respectively for N_2O, and 55, 200 and 330°C for CH_4. The carrier gases were 99.9995% N_2 for N_2O measurement and 99.9995% He for CH_4 measurement, respectively. The flow rates of carrier gases (N_2 and He) were 60 mL min^{-1}. Each gas analysis was calibrated against corresponding certified standards. Standard gases of CH_4 and N_2O were provided by National Research Institute of Standard Material, China.

Live plant material and litter were separated manually in the laboratory, dried at 80°C in an oven for ~72 h and dried to a constant weight. The biomass was calculated on a dry weight basis.

Air and 5-cm depth soil temperatures were measured in duplicate while monitoring N_2O and CH_4 emission. Soil pH was measured *in situ* using pHB-4 portable pH meter (Shanghai Scientific Instrument Factory of Radium Magnetism, China) at each sampling time. Soil redox potential (Eh) was measured *in situ* in the field using pHB-4 portable redox meter with Pt electrodes (2 replicates: 5 cm) and an Ag-AgCl reference electrode. The data were corrected to standard hydrogen half-cell by adding 199 mV to the field measurements [24].
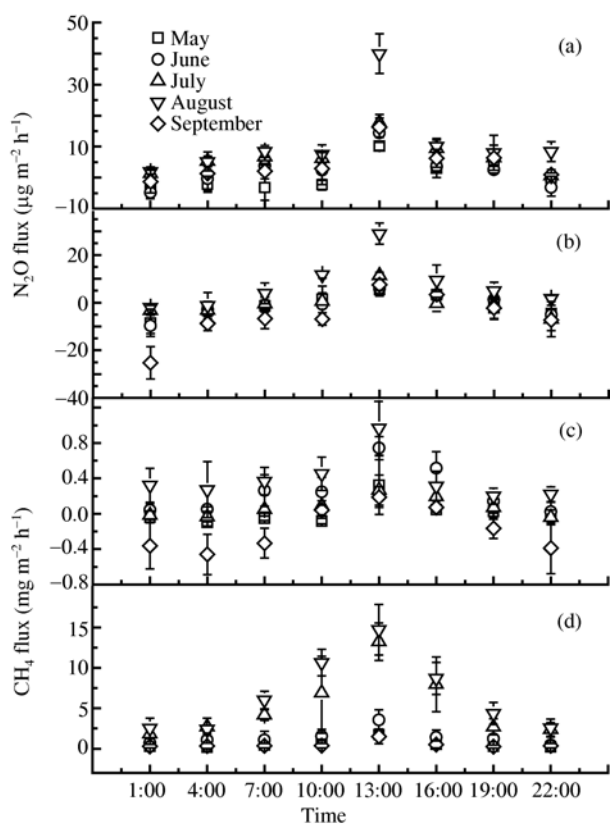
1.4 Fluxes calculation

The fluxes of N_2O or CH_4 emission were calculated from the equation: $F = \rho \times H \times (\Delta C/\Delta t) \times 273/(273+T)$, where, F is the flux of N_2O (µg m^{-2} h^{-1}) or CH_4 (mg m^{-2} h^{-1}), ρ is N_2O or CH_4 density under standard state (N_2O: 1.96 kg m^{-3}, CH_4: 0.71 kg m^{-3}), H is the height of the static chamber (m), $\Delta C/\Delta t$ is the rate of concentration-change of N_2O (ppb h^{-1}) or CH_4 (ppm h^{-1}) within the chamber, and T is the temperature in the chamber (°C). The value of $\Delta C/\Delta t$ is determined by using the least squares regression.
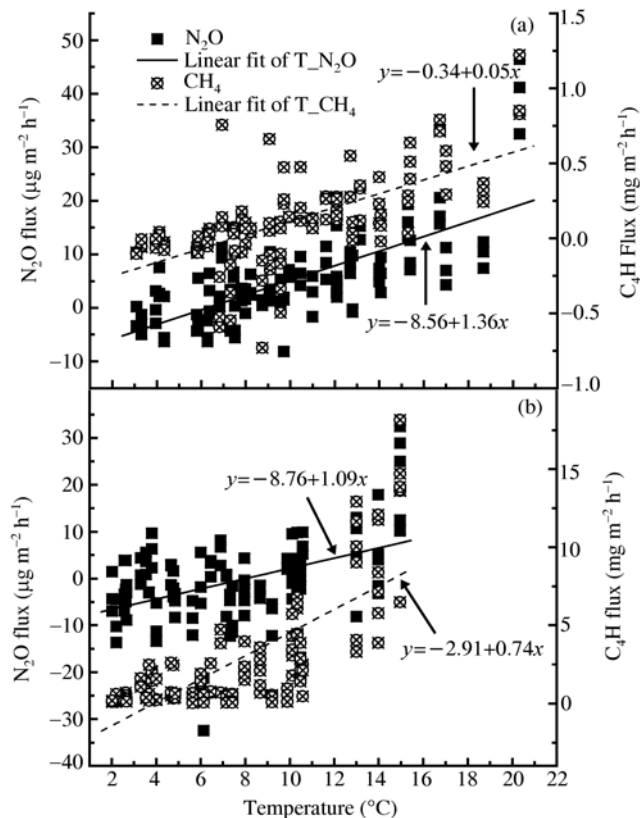
2 Results and discussion

2.1 The diurnal variations of N_2O and CH_4 flux*es*

For both plots, the N_2O and CH_4 emission fluxes in *Calamagrostis angustifolia* marsh were low in early morn-

ing, reached a maximum value at 13:00, and then decreased (Figure 2(a)–(d)). These are likely due to the impacts of temperature on the emission. This however, does not well agree with daily temperature variation (generally peaked at 14:00), probably because of the low resolution of our non-continuous monitoring (with 3 hour intervals). The 5-cm-soil temperature in the NW marsh ranged from 3.09 to 20.31°C, and those in the SW marsh ranged from 2.02 to 14.96°C, respectively. The daily variation trends of 5-cm-soil temperature in the NW and the SW marshes were similar: increase in the morning, reach the peaks at 13:00 and then drop gradually in the afternoon. The correlation coefficients (α=0.01) of N_2O and CH_4 fluxes to 5-cm-soil temperature in the NW plots were 0.71 and 0.65 (Figure 3(a)) and those in the SW plots were 0.46 and 0.76 (Figure 3(b)), respectively. The correlation between N_2O/CH_4 fluxes and soil temperature is significant at the 0.01 level. These facts can be plausibly interpreted by the effect of temperature on microbial activity, e.g., the numbers of zymogenic bacteria, CH_4 oxidizers, nitrifiers, and especially denitrifiers increased with an increase in temperature [10]. Alternatively, they may simply reflect the dependence of physical release of N_2O and CH_4 on temperature. For the SW marsh, from May to September, the emission of N_2O occurs at daytime around 13:00, while it acts as a sink of N_2O during the rest of the day and particularly at night. The

Figure 3 The relationship between temperature and fluxes of N_2O and CH_4. (a) NW; (b) SW.

emission and absorption patterns of the NW march are similar to those of the SW marsh, except in July and August when continuous emission of N_2O in the NW marsh was observed (Figure 2(a) and (b)).

In contrast, CH_4 was emitted all the day from May to August in the SW marsh, with minor absorption in September, whereas continuous emission of CH_4 was observed in the NW marsh only in July and August. During the rest of the year, the emission of CH_4 occurs at daytime around 13:00 in the NW marsh, while it absorbs CH_4 during the rest of the day (Figure 2(c) and (d)). The main reasons of this phenomenon are seasonal variation of temperature and the freeze-thaw cycle of the soil (see discussion below) [25]. The diurnal changes of N_2O and CH_4 fluxes from the marshes were not significantly correlative with soil pH and Eh because of small diurnal pH and Eh change.
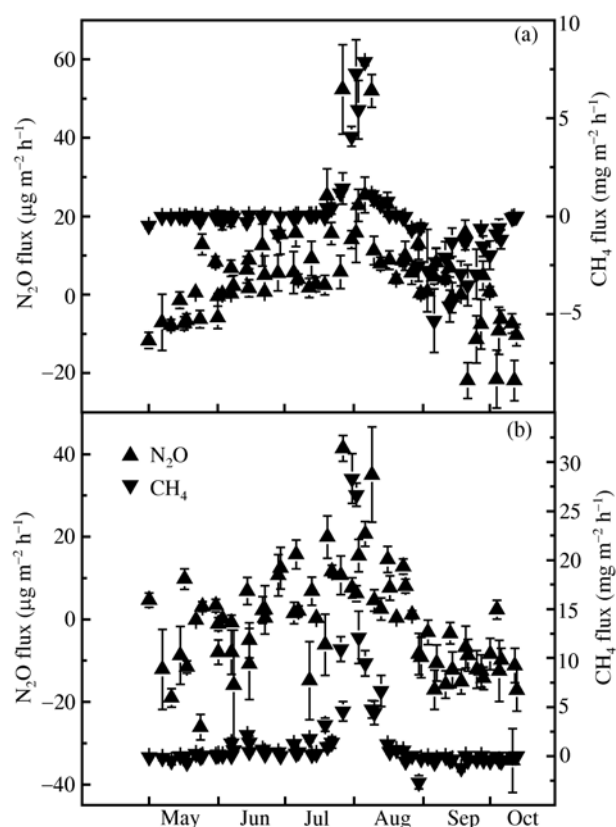
2.2 The seasonal variations of N_2O and CH_4 fluxes

The seasonal variations of N_2O and CH_4 fluxes are shown in Figure 4. The N_2O and CH_4 emission rates reached a peak in the SW and the NW marshes from late July to early August. The maximum values of N_2O fluxes were 66.34 $\mu g\ m^{-2}\ h^{-1}$ in the NW marsh and 46.88 $\mu g\ m^{-2}\ h^{-1}$ in the SW marsh, while those values of CH_4 fluxes were 8.99

Figure 2 The diurnal variation of N_2O and CH_4 emission. (a) and (c) NW; (b) and (d) SW.

mg m^{-2} h^{-1} in the NW marsh and 31.21 mg·m^{-2}·h^{-1} in the SW marsh. The NW plots continuously released N$_2$O gas during the middle June to early September and released CH$_4$ in a short period of late July to early August. Nitrous oxide emission from the SW sites fluctuated more with periods of both emission and absorption because of seasonal waterlog on soil surface, while CH$_4$ was nearly continuously released during plant growth period in this marsh (Figure 4). The N$_2$O fluxes in the NW marsh were obviously higher, while CH$_4$ fluxes were significantly lower than that in the SW marsh. The average and the median values of N$_2$O fluxes were 4.65 μg m^{-2} h^{-1} and 3.34 μg m^{-2} h^{-1} in the NW marsh and −1.24 μg m^{-2} h^{-1} and 0.02 μg m^{-2} h^{-1} in the SW marsh, respectively, and those values of CH$_4$ fluxes were −0.16 and −0.03 mg m^{-2} h^{-1} in the NW marsh and 1.71 and 0.07 mg m^{-2} h^{-1} in the SW marsh, respectively, in whole growth period. The results showed that surface accumulative water promoted the production and emission of CH$_4$ but restrained those of N$_2$O. The NW marsh is a source of N$_2$O and sink of CH$_4$, while the SW marsh is sink of N$_2$O and source of CH$_4$. These support that it was hydrological regime that made the big differences of N$_2$O and CH$_4$ fluxes between the NW marsh and the SW marsh [14, 26–28]. Comparison of our results with previous reports in wetland of different regions (Table 2) shows that the N$_2$O and CH$_4$ fluxes in growth season is obvious higher than those in winter [16]. The N$_2$O flux from marsh of Sanjiang Plain is much lower than that from rice fields, peatland and constructed wetland, but slightly higher than Riparian ecosystem (Table 2). The CH$_4$ flux in the study is lower than those from rice fields, subalpine wetland and bog, and similar to reed marsh and constructed wetland (Table 2).

The seasonal changes of N$_2$O and CH$_4$ fluxes were obviously impacted by 5-cm-soil temperature (Figure 5). The ranges of temperature at 5-cm-soil depth were 5.4 to 24.4°C in the NW marsh and 4.2 to 23.7°C in the SW marsh during growing season in the monitored period. The mean values of temperature were 15.1°C in the NW marsh and 14.1°C in the SW marsh. Soil temperature of both marshes increased gradually from mid-May and reached a maximum in August. Temperature has important effects on the seasonal varia-

tions of N$_2$O and CH$_4$ fluxes. The N$_2$O and CH$_4$ emission rates reached maximum values when soil temperatures reached a peak in August. The correlation coefficients (α=0.05) of N$_2$O and CH$_4$ fluxes to soil temperature were 0.66 and 0.39 in the NW marsh (Figure 5(a)) and were 0.58 and 0.42 in the SW marsh (Figure 5(b)). The results show that the soil temperature plays an important role in seasonal emissions of N$_2$O and CH$_4$ from marshes. That is because decomposition and mineralization increase with increasing temperature [36, 37], which consequently enhanced the CH$_4$ and N$_2$O emissions [38]. Moreover, numbers and activities of microorganism such as denitrifiers, zymogenicbacteria, and CH$_4$ oxidizers increase with an increasing temperature


Figure 4 The seasonal variation of N$_2$O and CH$_4$ emission. (a) NW; (b) SW.

Table 2 Reported N$_2$O and CH$_4$ fluxes from wetland of different regions

| Location	Wetland	N$_2$O flux (μg m^{-2} h^{-1})	CH$_4$ flux (mg m^{-2} h^{-1})	Reference
Finland	Peatland	5.78−17.36		[29]
Northeast China Southern Rocky	Rice field	−39−164	0−4.98	[30]
Southern Rocky Mountains	Subalpine Wetland		0.2−21.9	[31]
West Siberian	Bog		0.88−9.7	[5]
Liaohe Delta, Northern China	Reed marsh		−1−3	[32]
Southern Estonia	Constructed wetlands	−0.4−58	0−0.265	[33]
Sanjiang Plain, Northern China[a]	Marsh	<0	0.5	[16]
Southern Appalachia	Riparian ecosystem	0.28		[34]
West Java	Irrigated rice	22.65		[35]
Sanjiang Plain, Northern China	Marsh	−1.24−4.65	−0.16−1.71	This study

a) Measured in winter seasons.
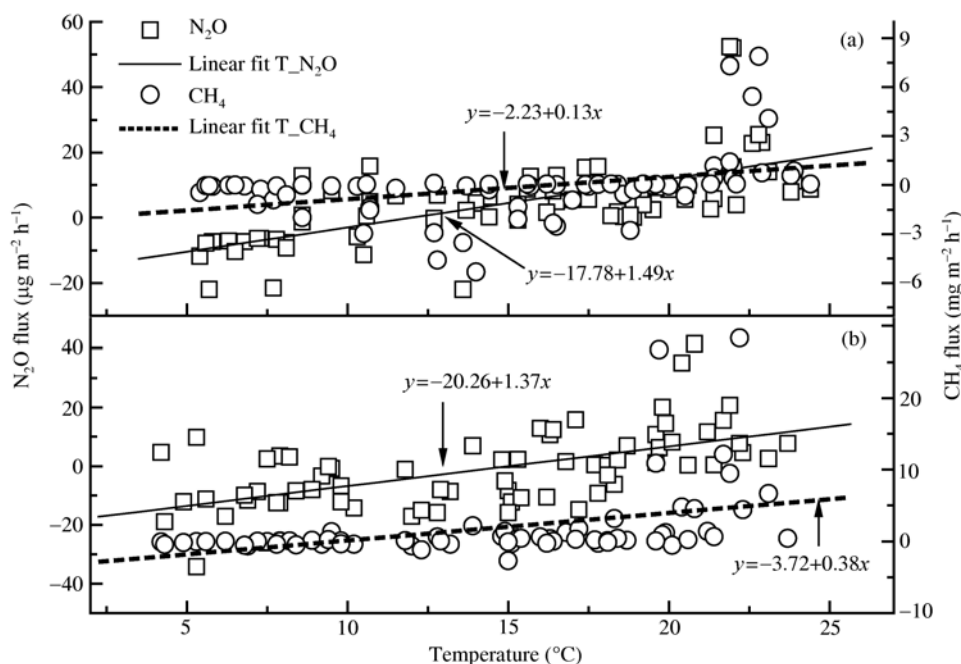
Figure 5   The relationship between temperature and N$_2$O and CH$_4$ fluxes. (a) NW; (b) SW.

[10, 39], which also accelerate N$_2$O and CH$_4$ production. Meanwhile, increasing temperature stimulates microbial respiration i.e., O$_2$ consumption, the volume of the anaerobic fraction of the soil increases, enhancing the denitrification activity [40, 41].

Another potential factor for the emissions is the redox of the soil. A well-oxidized soil has a redox potential range up to +400 to +700 mV, whereas flooded soils may reach redox potential values of lower than −300 mV due to the absence of O$_2$ and the activity of facultative and obligate anaerobic bacteria [42]. We observed that the ranges of Eh value in the NW marsh and the SW marsh were +30 to +510 mV and −430 to +390 mV, respectively (Figure 6). The redox potential was under +400 mV in most plots in the marsh, indicating anaerobic conditions. The change trend of Eh value in the NW marsh increases gradually with time during growing season, and the lowest value appeared in May. The variation of Eh in the SW marshes was significant. The soil Eh dropped sharply when waterlogged on the soil surface. The Eh value in the NW marsh was obviously higher than that in the SW marsh because of the different hydrological regime. We found that Eh was a sensitive factor in seasonal N$_2$O and CH$_4$ emissions from both types of marshes (Figure 6). The moderately oxidizing Eh range of +200 to +400 mV appeared to be optimum for N$_2$O flux for both conditions, especially for the NW marsh in August (Figure 6(a)). The Eh range of −300 to −100 mV was beneficial for CH$_4$ emission from the SW marsh (Figure 6(b)). This is because that most of the N$_2$O is produced from denitrification under moderately anaerobic conditions in natural ecosystem [43]. The highest N$_2$O emission rate from soil
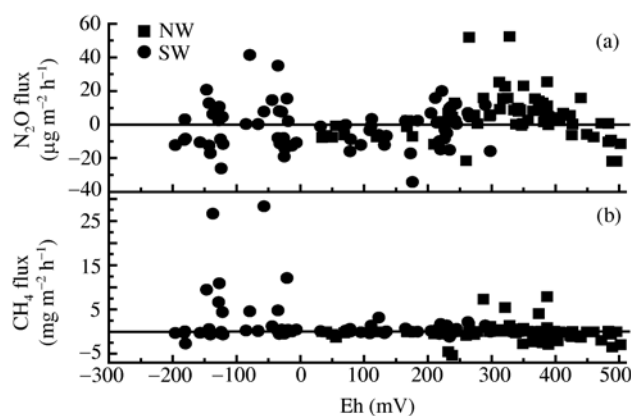
Figure 6   The fluxes of N$_2$O and CH$_4$ under different soil redox conditions. (a) N$_2$O; (b) CH$_4$.

was observed during denitrification reactions at a redox level of 400 mV in a laboratory study [44], while CH$_4$ is produced under low redox potential conditions by obligate anaerobes through either carbon dioxide reduction or transmethylation processes [45].

Remarkably, we observed a second N$_2$O emission peak under Eh range −300 to −100 mV (Figure 6(a)) and a second CH$_4$ emission peak under Eh range +300 to +400 mV (Figure 6(b)). These contradict the laboratory results, which have well demonstrated that little N$_2$O was produced under condition of Eh<−100 mV, whereas little CH$_4$ was produced under condition of Eh>0 mV [9, 10, 46]. One plausible explanation is that these emission peaks were due to additional sources of N$_2$O and CH$_4$ underneath the soil. These ghost emission peaks are related to the emission burst

Table 3   Correlation of biomass and fluxes of N_2O and CH_4 from marshes with different hydrological regime[a]

Biomass	Marsh	Mean N_2O	Highest N_2O	Mean CH_4	Highest CH_4
Aboveground	NW	0.294	0.250	0.045	0.478
Aboveground	SW	0.299	0.323	0.425	0.446
belowground	NW	0.403	0.384	0.222	0.523
belowground	SW	0.276	0.306	0.264	0.265
Total	NW	0.387	0.417	0.108	0.421
Total	SW	0.306	0.332	0.341	0.355

a) N=18. The relationships between N_2O and CH_3 are not signifisant at 0.05 level

of N_2O and CH_4 in late July to early August, several days after the soil is completely thawed out. Therefore, they strongly support that the freeze-thaw related emission bursts of N_2O and CH_4 come from underneath [25].

The average dry weight of total, aboveground and belowground live plant material in August was significantly higher than that in other months. The means of total biomass were 2100 and 3770 g m^{-2} in the SW and the NW plots in August, respectively. The belowground biomass was higher than aboveground biomass in the same month under same site. In natural ecosystem, N_2O and CH_4 mainly come from biological and chemical processes and it is demonstrated that N_2O and CH_4 emissions were strongly correlated with biomass [47]. We did not find very good relationship between N_2O and CH_4 fluxes and biomass (Table 3), although N_2O and CH_4 fluxes from both the NW and the SW marshes reached a peak in August, when the total and the belowground biomass of marshes also reached a peak.

The pH was relatively stable in both marshes soils, ranging from 5.20 to 6.20 (soil/water ratio of 1/5). For our data, the significantly correlation of seasonal changes of N_2O and CH_4 fluxes from the marshes and soil pH were not observed because of small seasonal pH change.

2.3   The changes of N_2O and CH_4 concentrations beneath frozen layer during freeze-thaw process

We observed significant emission burst of N_2O and CH_4 in late July to early August, several days after the soil is thawed out thoroughly [25]. The N_2O emission burst in temperate climates has been reported long ago and has been ascribed as one of the most striking phenomena. It has been estimated that up to 70% of the total annual N_2O flux occurred during thawing [16, 48], which usually lasted for only a few days [49]. The nature of this remarkable burst of emission is controversial, particularly the question of whether this is due to the increased amount of microbially available organic carbon [50, 51] and/or (NO_3^-) [50, 52] liberated during freezing and metabolized during subsequent thawing [50, 51], to chemical reactions with nitrite (NO_2^-) [52, 53], or to biological processes [48], etc. Our results show that the emission burst of N_2O is closely coupled with that of CH_4 [25].

Most previous studies on greenhouse gases emission from soil under low temperature have been concentrated on the period of thawing, when emission peaks are observed [49, 54, 55]. To track down the major sources of N_2O and CH_4 for the emission bursts in later July to early August, we monitored the N_2O and CH_4 concentrations at different depths under the frozen soil during the freeze-thawing period from 2003 to 2004. The results showed that the highest concentrations of N_2O and CH_4 at different soil depth underneath frozen layer were increased with increasing frozen depth during freezing process (Figure 7). The highest concentrations of N_2O and CH_4 were about 1600 ppb and 5.15 ppm in NW marsh and 1267 ppb and 5.50 ppm in the SW marsh, respectively, which were observed at depths of 90–100 cm in early February when the frozen layer reached a maximum depth of about 90 cm. During the early stage of freezing, the N_2O and CH_4 were concentrated within 20 cm underneath the frozen layer (Figure 7). The depth of the N_2O and CH_4 enriched layer was continuously depressed downward during the development of the frozen cover in winter. All these indicate that significant amounts of N_2O and CH_4 were produced underneath the frozen layer, but not likely within the frozen soil. The highest concentrations of N_2O and CH_4 remained roughly constant at 90–100 cm depth from early March to middle June during thawing process because the soil at this depth is subsoil with very low organic matters. The highest concentrations of N_2O and CH_4 in different soil depth decreased abruptly after frozen soil thawed thoroughly from middle July (Figure 7). The concentrations of N_2O and CH_4 remained the highest at the depths of 80–100 cm before the frozen soil thickness reduced to 20 cm (Figure 8). We did not observe that N_2O and CH_4 migrated upward at the early stage of thawing probably because of the low resolution of our device (Figure 1, 15–20 cm), and the faster thawing rate from the top. The migrations of the greenhouse gases were first observed when the thickness of the frozen layer reduced to ~15 cm at depths of about 50–70 cm. When the frozen soil thawed completely, the concentrations of N_2O and CH_4 underneath the frozen layer dropped down rapidly due to upward migrations (Figures 7 and 8). Correspondingly, the N_2O and CH_4 emission bursts appeared about one week later.

Given that N_2O and CH_4 can be produced in anoxic microsites even in the frozen soil because the activities of mi-
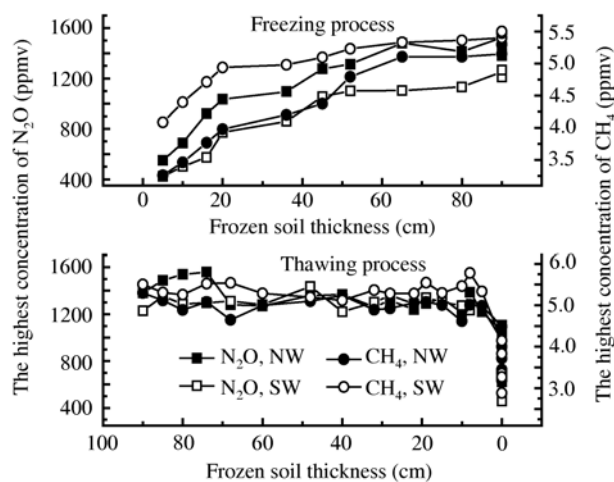
Figure 7 The variations of highest concentration of N_2O and CH_4 in different soil depths underneath frozen layer during freeze-thaw process.
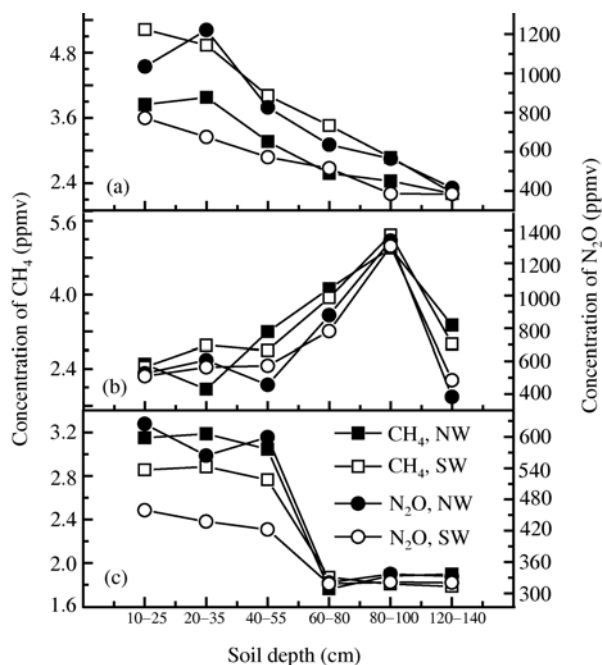
Figure 8 The changes of N_2O and CH_4 concentration in different soil depth under different frozen soil depths or thicknesses. (a) Freezing process, frozen soil depth at 20 cm; (b) thawing process, frozen soil thickness was 20 cm; (c) thawing completely.

cro-organisms were still active under very low temperature [56–58], a plausible interpretation for the high concentrations of N_2O and CH_4 is that the frozen layer prevented transportation of oxygen from the atmosphere to soil, which subsequently produced an anoxic environment underneath the frozen layer as oxygen was consumed due to biological activities [25], and consequently promoted the formation of N_2O and CH_4 through denitrification [52, 59] and anoxic digestion of organic matters [60], respectively. In addition, freezing can increase $NO_3^- + NO_2^-$ supplies [52, 61] and concentrate water solvable organic carbon [50, 51]. As

freezing develops, nutrients might be expelled downward to the unfrozen soil, which leads to better nutrient supply underneath and consequently enhanced gas production.

This model is supported by results in this paper. First, although there is a fairly good relationship between soil temperature and fluxes in general, the emission bursts cannot be feasibly explained by soil temperature, because most of data points of N_2O and CH_4 fluxes during the late July to early August were obviously above the fit line of temperature and fluxes (Figure 5). Second, the emission burst is not correlated with biomass, and therefore it cannot be explained by biomass either. More importantly, we found that some of the peak emissions of N_2O occurred under 5-cm-soil Eh range of −300 to −100 mV, whereas those of CH_4 under Eh range of +300 to +400 mV (Figure 6), far away from the favorable Eh for these greenhouse gases [9, 10, 46]. All these imply additional N_2O and CH_4 supplied after thawing.

3   Conclusions

Our data suggest that the NW marsh is a source of N_2O and sink of CH_4, while the SW marsh is sink of N_2O and source of CH_4. The maximum values of N_2O fluxes were 66.34 $\mu g\ m^{-2}\ h^{-1}$ in the NW marsh and 46.88 $\mu g\ m^{-2}\ h^{-1}$ in the SW marsh, while those values of CH_4 fluxes were 8.99 $mg\ m^{-2}\ h^{-1}$ in the NW marsh and 31.21 $mg\ m^{-2}\ h^{-1}$ in the SW marsh. The diurnal and seasonal flux variations of N_2O and CH_4 were well correlated with 5-cm-soil temperature, indicating the significant effects of temperature on emission. The redox at 5 cm depth was not well correlated with emissions, which is in contrast to previous results [9, 46]. Remarkably, we observed a N_2O emission peak under Eh range of −300 to −100 mV, and CH_4 emission peak under Eh range of +300 to +400 mV. These can be plausibly interpreted by additional sources of N_2O and CH_4 for the freeze-thaw induced emission peaks of N_2O and CH_4 observed between late July and early August. We have found considerable accumulations of N_2O and CH_4 underneath the frozen soil. The concentrations of N_2O and CH_4 underneath the frozen layer increased with frozen soil depth during freezing process and reached maximum concentrations at depths of 90–100 cm in early February when the frozen layer reached a maximum depth of about 90 cm. The cumulated gasses released abruptly shortly after thawing, which can plausibly explain the mismatch between Eh and N_2O, CH_4 emissions.

1 Intergovernmental Panel on Climate Change. Synthesis Report. Contribution of Working Group Ⅰ to the Fourth Assessment Report of the Intergoverment Panel on Climate Change. Cambridge and New York: Cambridge University Press, 2007

2 Dlugokencky E J, Houweling S, Bruhwiler L, et al. Atmospheric methane levels off: Temporary pause or a new steady-state? Geophys Res Lett, 2003, 30, doi: 10.1029/2003GL018126

3 Dlugokencky E J, Myers R C, Lang P M, et al. Conversion of NOAA atmospheric dry air CH_4 mole fractions to a gravimetrically prepared standard scale. J Geophys Res, 2005, 110(D18), doi: 10.1029/2005JD006035

4 Meure C M, Etheridge D, Trudinger C, et al. Law Dome CO_2, CH_4 and N_2O ice core records extended to 2000 years BP. Geophys Res Lett, 2006, 33, doi: 10.1029/2006GL026152

5 Takeuchi W, Tamura M, Yasuoka Y. Estimation of methane emission from West Siberian wetland by scaling technique between NOAA AVHRR and SPOT HRV. Remote Sens Environ, 2003, 85: 21–29

6 Whalen S C. Biogeochemistry of methane exchange between natural wetlands and the atmosphere. Environ Eng Sci, 2005, 22: 73－94

7 Zhang L H, Song C C, Zheng X H, et al. Effects of nitrogen on the ecosystem respiration, CH_4 and N_2O emissions to the atmosphere from the freshwater marshes in northeast China. Environ Geol, 2007, 52: 529–539

8 Lindau C W, Delaune R D, Jiraporncharoen S, et al. Nitrous-oxide and dinitrogen emissions from panicum-hemitomon S fresh-water marsh soils following addition of N-15 labeled ammonium and nitrate. J Freshw Ecol, 1991, 6: 191–198

9 Yu K W, Patrick W H. Redox range with minimum nitrous oxide and methane production in a rice soil under different pH. Soil Sci Soc Am J, 2003, 67: 1952–1958

10 Hou A X, Chen G X, Wang Z P, et al. Methane and nitrous oxide emissions from a rice field in relation to soil redox and microbiological processes. Soil Sci Soc Am J, 2000, 64: 2180–2186

11 Abao E B, Bronson K F, Wassmann R, et al. Simultaneous records of methane and nitrous oxide emissions in rice-based cropping systems under rainfed conditions. Nutr Cycl Agroecosys, 2000, 58: 131–139

12 Ding W X, Cai Z C, Tsuruta H. Cultivation, nitrogen fertilization, and set-aside effects on methane uptake in a drained marsh soil in Northeast China. Glob Change Biol, 2004, 10: 1801–1809

13 Yu J B, Liu J S, Wang J D, et al. Nitrous oxide emission from Deyeuxia angustifolia freshwater marsh in northeast China. Environ Manage, 2007, 40: 613–622

14 Ding W X, Cai Z C. Methane emission from natural wetlands in China: Summary of years 1995–2004 studies. Pedosphere, 2007, 17: 475–486

15 Ding W X, Cai Z C, Tsuruta H, et al. Key factors affecting spatial variation of methane emissions from freshwater marshes. Chemosphere, 2003, 51: 167–173

16 Zhang J B, Song C C, Yang W Y. Cold season CH_4, CO_2 and N_2O fluxes from freshwater marshes in northeast China. Chemosphere, 2005, 59: 1703–1705

17 Song C C, Wang Y S, Wang Y Y, et al. Emission of CO_2, CH_4 and N_2O from freshwater marsh during freeze-thaw period in Northeast of China. Atmos Environ, 2006, 40: 6879–6885

18 Song C C, Zhang J B, Wang Y Y, et al. Emission of CO_2, CH_4 and N_2O from freshwater marsh in northeast of China. J Environ Manage, 2008, 88: 428–436

19 Zhao K Y. Mires in China (in Chinese). Beijing: Science Press, 1999. 88–98

20 Liu X T, Ma X H. Effect of large-scale reclamation on natural environment and regional environmental protection in the Sanjiang Plain (in Chinese). Sci Geogr Sin, 2000, 20: 14–19

21 He L. Chinese Sanjiang Plain (in Chinese). Harbin: Heilongjiang Science Press, 2000

22 Yu J B, Liu J S, Wang J D. The distribution law of nutrient materials in peat Sediments in Sanjiang Plain (in Chinese). Wetland Sci, 2004, 2: 31–35

23 Lindau C W. Methane emissions from louisiana rice fields amended with nitrogen fertilizers. Soil Biol Biochem, 1994, 26: 353–359

24 Patrick W H, Gambrell R P, Faulkner S P. Redox measurements of soils. In: Sparks D L, ed. Methods of Soil Analysis. Madison, WI: SSSA Book Ser. 5, 1996. 1255–1273

25 Yu J B, Sun W D, Liu J S, et al. Enhanced net formations of nitrous oxide and methane underneath the frozen soil in Sanjiang wetland, northeastern China. J Geophys Res, 2007, 112(D7), doi: 10.1029/2006JD008025

26 Hargreaves K J, Fowler D. Quantifying the effects of water table and soil temperature on the emission of methane from peat wetland at the field scale. Atmos Environ, 1998, 32: 3275–3282

27 Regina K, Silvola J, Martikainen P J. Short-term effects of changing water table on N_2O fluxes from peat monoliths from natural and drained boreal peatlands. Glob Change Biol, 1999, 5: 183–189

28 Heikkinen J E P, Elsakov V, Martikainen P J. Carbon dioxide and methane dynamics and annual carbon balance in tundra wetland in NE Europe, Russia. Glob Biogeochem Cycle, 2002, 16: 62-1–62-9

29 Martikainen P J, Nykanen H, Crill P, et al. Effect of a lowered water-Table on nitrous-oxide fluxes from Northern Peatlands. Nature, 1993, 366: 51–53

30 Chen G X, Huang G H, Huang B, et al. Nitrous oxide and methane emissions from soil-plant systems. Nutr Cycl Agroecosys, 1997, 49: 41–45

31 Wickland K P, Striegl R G, Schmidt S K, et al. Methane flux in subalpine wetland and unsaturated soils in the southern Rocky Mountains. Glob Biogeochem Cycle, 1999, 13: 101–113

32 Huang G H, Li X Z, Hu Y M, et al. Methane (CH_4) emission from a natural wetland of Northern China. J Environ Sci Heal A, 2005, 40: 1227–1238

33 Mander U, Teiter S, Augustin J. Emission of greenhouse gases from constructed wetlands for wastewater treatment and from riparian buffer zones. Water Sci Technol, 2005, 52: 167–176

34 Walker T J, Geron D C, Vose M J, et al. Nitrogen trace gas emissions from a riparian ecosystem in southern Appalachia. Chemosphere, 2002, 49: 1389–1398

35 Suratno W, Murdiyaso D, Suratmo G F, et al. Nitrous oxide flux from irrigated rice fields in West Java. Environ Pollut, 1998, 102: 159–166

36 Kirschbaum M U F. The Temperature-dependence of soil organic-matter decomposition, and the effect of global warming on soil organic-C storage. Soil Biol Biochem, 1995, 27: 753–760

37 Er F, Ogut M, Mikayilov F D, et al. Important factors affecting biosolid nitrogen mineralization in soils. Commun Soil Sci Plan, 2004, 35: 2327–2343

38 Renger M, Wessolek G, Schwarzel K, et al. Aspects of peat conservation and water management. J Plant Nutr Soil Sc, 2002, 165: 487–493

39 Hellmann B, Zelles L, Palojarvi A, et al. Emission of climate-relevant trace gases and succession of microbial communities during open-window composting. Appl Environ Microbiol, 1997, 63: 1011–1018

40 Grant R F, Rochette P. Soil microbial respiration at different water potentials and temperatures—Theory and mathematical-modeling. Soil Sci Soc Am J, 1994, 58: 1681–1690

41 Conrad R. Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4, OCS, N_2O, and NO). Microbiol Rev, 1996, 60: 609–640

42 Patrick W H, Mahapatra I C. Transformation and availability to rice of nitrogen and phosphorus in waterlogged soils. Adv Agron, 1968, 20: 323–359

43 Rice C W, Rogers K L. Denitrification in subsurface environments: Potential source for atmospheric nitrous oxide. In: Rolston D E, Duxbury J M, Harper L A, et al, eds. Agricultural Ecosystem Effects on Trace Gases and Global Climate Change. ASA Special Publication, 1993. 121–132

44 Masscheleyn P H, Delaune R D, Patrick W H. Methane and nitrous-oxide emissions from laboratory measurements of rice soil suspension-effect of soil oxidation-reduction status. Chemosphere, 1993, 26: 251–260

45 Vogels G D, Keltjens J T, van der Drift C. Biochemistry of CH_4 production. In: Zehnder A J B, ed. Biology of Anaerobic Microorganisms. Chichester: Wiley, 1988. 707–717

46 Yu K W, Wang Z P, Vermoesen A, et al. Nitrous oxide and methane emissions from different soil suspensions: Effect of soil redox status. Biol Fert Soils, 2001, 34: 25–30

47 Vann C D, Megonigal J P. Elevated CO_2 and water depth regulation of methane emissions: Comparison of woody and non-woody wetland plant species. Biogeochemistry, 2003, 63: 117–134

48 Rover M, Heinemeyer O, Kaiser E A. Microbial induced nitrous oxide emissions from an arable soil during winter. Soil Biol Biochem, 1998, 30: 1859–1865

49 Christensen S, Tiedje J M. Brief and vigorous N_2O production by soil at spring thaw. J Soil Sci, 1990, 41: 1–4

50 Muller C, Martin M, Stevens R J, et al. Processes leading to N_2O emissions in grassland soil during freezing and thawing. Soil Biol Biochem, 2002, 34: 1325–1331

51 Sehy U, Dyckmans J, Ruser R, et al. Adding dissolved organic carbon to simulate freeze-thaw related N_2O emissions from soil. J Plant Nutr Soil Sc, 2004, 167: 471–478

52 Usui T, Koike I, Ogura N. N_2O production, nitrification and denitrification in an estuarine sediment. Estuar Coast Shelf Sci, 2001, 52: 769–781

53 Christianson C B, Cho C M. Chemical denitrification of nitrite in frozen soils. Soil Sci Soc Am J, 1983, 47: 38–42

54 Koponen H T, Martikainen P J. Soil water content and freezing temperature affect freeze-thaw related N_2O production in organic soil. Nutr Cycl Agroecosys, 2004, 69: 213–219

55 Kammann C, Grunhage L, Muller C, et al. Seasonal variability and mitigation options for N_2O emissions from differently managed grasslands. Environ Pollut, 1998, 102: 179–186

56 Holtan-Hartwig L, Dorsch P, Bakken L R. Low temperature control of soil denitrifying communities: Kinetics of N_2O production and reduction. Soil Biol Biochem, 2002, 34: 1797–1806

57 Oquist M G, Nilsson M, Sorensson F, et al. Nitrous oxide production in a forest soil at low temperatures—Processes and environmental controls. FEMS Microbiol Ecol, 2004, 49: 371–378

58 Kotsyurbenko O R, Nozhevnikova A N, Soloviova T I, et al. Methanogenesis at low temperatures by microflora of tundra wetland soil. Antonie Van Leeuwenhoek, 1996, 69: 75–86

59 Stein L Y, Yung Y L. Production, isotopic composition, and atmospheric fate of biologically produced nitrous oxide. Annu Rev Earth Planet Sci, 2003, 31: 329–356

60 Le Mer J, Roger P. Production, oxidation, emission and consumption of methane by soils: A review. Eur J Soil Biol, 2001, 37: 25–50

61 Grogan P, Michelsen A, Ambus P, et al. Freeze-thaw regime effects on carbon and nitrogen dynamics in sub-arctic heath tundra mesocosms. Soil Biol Biochem, 2004, 36: 641–654