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Nitrous oxide emissions from an agro-pastoral ecotone of northern China depending on land uses

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ABSTRACT

Overgrazing and intensive farming have led to severe land degradation in the past half century in the agro-pastoral ecotone of northern China. Currently, complete and periodical exclusions of grazing are commonly adopted for the restoration of these degraded grasslands. However, little is known about the effects of such land uses on nitrous oxide (N_2O) emission in this region. Using static chamber technique, we quantified annual N_2O emissions (from May 2012 to September 2013) from four land uses: summer-grazed grassland (SG), winter-grazed grassland (WG), ungrazed grassland since 1997 (UG) and oat cropland (OC). N_2O emissions occurred mainly after farmyard manure fertilization and during spring thaw periods. Annual N_2O fluxes from the SG, WG, UG and OC were 0.19, 0.15, 0.43 and 0.98 kg N ha^{-1} yr^{-1}, respectively. The spring–thaw N_2O emissions from UG and OC dominated the annual emission and accounted for 70% and 65% of the annual fluxes, respectively. In contrast, the contributions of spring thaw fluxes to total annual N_2O emissions for SG and WG were only 32%. N_2O fluxes during spring thaw season were positively related to soil NH_4^+ + NO_3^- content accounting for 80% of N_2O flux variability across all land uses. Land use conversion from the native grassland to cropland increased N_2O flux both during growing and spring thaw seasons due to farmyard manure application. Instead, grazing has the potential to decrease annual N_2O losses mainly through reducing spring–thaw N_2O emissions.

1. Introduction

Nitrous oxide (N_2O) is one of the important greenhouse gases with a global warming potential 265 times that of CO_2 and an atmospheric lifetime of about 121 years (IPCC, 2013). Moreover, N_2O plays a role in the destruction of ozone in the stratosphere. In viewed of atmospheric N_2O concentration increase of about 0.3% per year, it can be expected that the contribution of N_2O to global warming will further increase in the future (Wu et al., 2010). Soils are the dominant source of N_2O worldwide, releasing an estimated 9.5 Tg N yr^{-1} to the atmosphere (65% of global N_2O emissions), of which 3.5 Tg N yr^{-1} originate in agricultural soils and 1 Tg N yr^{-1} in temperate grasslands (Flechard et al., 2007).

Land use change is one of the major factors regulating soil N_2O emission (Skiba and Smith, 2000). Crop cultivation and grazing, main land uses, could profoundly impact N_2O emissions of grassland ecosystem through altering abiotic and biotic characteristics of soil (Holst et al., 2007; Mosier et al., 1997; Rafique et al., 2011; Ri et al., 2003). It has been generally recognized that conversion of grassland to croplands increases the emission of N_2O due to the impacts of agricultural practices, especially organic and mineral nitrogen (N) fertilization (Mosier et al., 1997; Wang et al., 2001). However, effects of grazing on N_2O emissions still remain controversial, with increases (Rafique et al., 2011; Saggar et al., 2007), decreases (Wolf et al., 2010; Xu et al., 2008), and no changes (Holst et al., 2007; Li et al., 2012) all being reported. The discrepancies between studies could be attributable to different grazing history, grassland type, climate regime and type of soil. Therefore, it is important to investigate N_2O emissions under site-specific land use patterns in order to draw regionally specific conclusions.

Although N_2O emissions from grasslands have been investigated worldwide, there are still high uncertainties in estimates of annual soil-atmosphere N_2O exchange of grassland ecosystem because most investigations have focused on the growing season (Holst et al., 2007;

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Xu et al., 2008). Several studies have revealed that winter or spring–thaw N_2O loss can be of major importance for the annual N_2O loss in temperate ecosystems (Röver et al., 1998; Teepe et al., 2000; Wagner-Riddle et al., 2007; Wolf et al., 2010). In some cases up to 80% of the annual N_2O emissions were found in the spring–thaw period (Holst et al., 2008; Wolf et al., 2010). This phenomenon has been attributed to physical release of N_2O produced in unfrozen part of the soil and accumulated below the frozen soil layer (Burton and Beauchamp, 1994; Teepe et al., 2001) and/or enhanced microbial metabolism by substrate supply (Röver et al., 1998; Wolf et al., 2010). Moreover, the magnitude of spring–thaw N_2O emission may differ between land uses even at similar weather (Holst et al., 2008; Wagner-Riddle and Thurtell, 1998; Wolf et al., 2010). Clearly, long-term studies of at least one year or more are necessary for reliable estimates of annual N_2O release from soil.

The agro-pastoral ecotone in northern China covers 6.2×10^5 km^2 from the North China Plain to the Inner Mongolia Plateau (Liu and Gao, 2008). It is a transitional land use from livestock-grazing to farming in between semi-arid temperate steppe and semi-humid cropland. This region plays an important role in livestock farming and environmental conservation. However, overgrazing and intensive farming have led to severe land degradation in the past half century in this region. Currently, improved grassland management practices, complete and periodical exclusions of grazing are commonly adopted for the restoration of these degraded grasslands. Quantifying the effects of cultivation and grazing regimes on the greenhouse gas emissions is critical for the understanding of consequences of land use conversion including that on N_2O emissions. However, previous studies of N_2O emissions in the semi-arid grassland in China have primarily focused on the growing season (Holst et al., 2007; Xu et al., 2008) and on grazing management (Wolf et al., 2010). Limited evaluations of annual N_2O emissions and land uses including both cropland and grassland underscore the need for additional research.

In present study, we measured soil N_2O emissions, temperature, soil moisture and mineral N content ($NH_4^+ + NO_3^-$) over a 16-month period from four land uses in the agro-pastoral zone of northern China. The objectives were to: (1) investigate seasonal variations of N_2O fluxes depending on land uses; (2) quantify annual N_2O emissions depending on land uses and evaluate the contribution of spring–thaw N_2O emissions to annual N_2O losses; (3) examine the effects of soil temperature, water-filled pore space (WFPS) and mineral N content ($NH_4^+ + NO_3^-$) on N_2O fluxes from land uses.

2. Materials and methods

2.1. Study site

The study was carried out at the National Grassland Ecosystem Observation and Research Station (41°46′N, 115°40′E, 1460 m above sea level), which lies in the typical agro-pastoral ecotone in the Guyuan county, Hebei province, Northern China. The region has a semi-arid and temperate continental monsoon climate, with a frost-free period of 80–110 days. The 30 year (1979–2009) annual mean precipitation is 380 mm with 80% falling during the growing season from May to September. The annual mean temperature is 1.4 °C with the minimum monthly mean of −18.6 °C in January and the maximum of 17.6 °C in July. The soil is classified as a Kastanozem according to the FAO system.

Four land uses were selected for the study: a summer-grazed grassland (SG), a winter-grazed grassland (WG), an ungrazed grassland (UG), and a cropland (OC). The 15-ha SG has been moderately grazed (4–5 sheep ha^{-1}) from June to September since 2009. Before 2009, the grassland was mown at mid or late September once a year. A majority of the species in the SG site was *Leymus chinensis* (73% of the species composition) but *Stipa krylivii* (10%) and *Potentilla acaulis* (8%) also made significant contributions to the species composition. The remaining species were *Iris lactea* Var. *chinesis* and *Saussurea runcinata*. The 10-ha WG has been grazed from November to March by 5–6 sheep ha^{-1} since 2007. At 80% of the relative species composition, *L. chinensis* was the dominant species in the WG site. The remaining species composition was comprised of *S. krylivii* (12%), *Artemisia frigida* and *P. acaulis* (8%). The 3-ha UG was fenced in 1997 and since then grazing has been forbidden in this fenced site. There is a thin litter layer (about 4–5 cm) covering the ground surface because of long-term enclosure. The UG site was dominated by *L. chinensis* (90% of the species composition) while the remainder of the species were *S. krylivii* (8%), *Hordeum brevisubulatum* and *P. acaulis* (2%). Vegetation coverage was 45%, 60% and 90% for SG, WG and UG, respectively. The three grasslands have been extensively managed consistently without fertilizer, herbicides or irrigation since 1995. The 5-ha cropland has been reclaimed in part of the *L. chinensis* grassland since 1995. Oat (*Avena sativa*) was usually sown in late May and harvested in late September. Oat was grown under rainfed condition. The cropland was plowed to a depth of 15–20 cm using a mouldboard plough before oat sowing. A limited amount of farmyard manure (about 675 kg ha^{-1}, corresponding to 30 kg N ha^{-1}) was applied as the base fertilizer before sowing. After harvest, most of the crop residue was removed, and only a small amount of standing stubble of about 5–10 cm in height remained. Live aboveground biomass was measured by clipping live plants from five representative 1m x 1m quadrats in each land use in late August 2013. Live aboveground biomass was 56, 307, 426 and 336 g m^{-2} for SG, WG, UG and OC, respectively. Root biomass at 50 cm depth was taken with soil core method in the same quadrats that were used for aboveground biomass measurement. Root biomass was 1392, 1277, 1933 and 737 g m^{-2} for SG, WG, UG and OC, respectively. The OC, UG and SG sites were adjacent to each other and the WG site lay about 1800 m west of these sites.

2.2. N_2O flux measurements

N_2O fluxes were measured with an opaque static closed chamber method (Wang and Wang, 2003) from 25 May 2012 to 29 September 2013. Four gas flux measurement plots within each land use were established randomly. Stainless steel base frames (0.5 m × 0.5 m, height 0.1 m) were inserted 10 cm into the soil on 1st May 2012 and left there through the experiment. During sampling, an open-bottom stainless steel chamber (0.5 m × 0.5 m, height 0.5 m) was placed over the base frames, which had rubber seal in the upper end to ensure air-tightness. N_2O fluxes were generally measured twice per week during the growing season from May to September and during spring thaw from March to April, and twice per month from October to next February. The gas samplings were normally carried out between 8:00–11:00, because a preliminary experiment investigating diurnal variations in N_2O fluxes showed that the fluxes at this time represent average daily flux. Gas samples were taken with 60 ml plastic syringes attached to a three-way stopcock at 0, 15, 30, 45, 60 min following chamber closure, respectively. N_2O concentrations in gas samples were analyzed within 8 h after sampling with a gas chromatograph (GC, Agilent 7890A, Santa Clara, CA, USA) equipped with an electron capture detector (ECD). Details of the gas chromatograph configurations for N_2O analysis are referred to Wang et al. (2010) and Zheng et al. (2008). N_2O flux was calculated jointly from the linear or non-linear change in gas concentrations (Wang et al., 2013).

2.3. Auxiliary measurements

Weather variables (precipitation, air temperature, and atmospheric pressure) were measured continuously from the meteorological station at the experimental site. While the N_2O fluxes were being measured, chamber air temperature, soil temperatures and water content were simultaneously observed. Soil (5 cm depth) and chamber air temperatures were measured with portable digital thermometers (JM624, JinMing Instrument Co. Ltd., Tianjin, China). Soil volumetric water contents (0-6 cm) were monitored with a portable frequency domain reflectometry probe (FDR, ThetaKit, Delta-T Devices, Cambridge, UK). Soil moisture (0–5 cm) was determined gravimetrically when the soil was frozen. The water-filled pore space (WFPS) was calculated as follows (Zhang and Han, 2008):

$$\text{WFPS}(\%) = \frac{\text{Soil volumetric water content}(\%)}{(1 - \text{Soil bulk density}/2.65)} \quad (1)$$

For determination of topsoil (0–10 cm) mineral N content ($NH_4^+ + NO_3^-$), soil samples were taken at weekly or biweekly intervals with four replicates in each land use field. Mineral N was extracted with 1 M KCl solution. Extracts were frozen until analyzed for NH_4^+ and NO_3^- with a continuous flow analyzer (TRAACS2000, Bran and Luebbe, Norderstedt, Germany).

Soil samples were collected at the beginning of the experiment to measure physiochemical properties of topsoil (0–10 cm) under each land use. Four subplots (20 m × 20 m, 4 replicates) were randomly established within each land use. Twelve soil cores were obtained in each subplot with a 4 cm diameter soil auger. Soil cores within each subplot were well mixed and combined to a composite sample. All together, there were 16 composite samples representing four land uses and four field replicates. Soil samples were air-dried and passed through a 2 mm sieve. Soil pH was determined with a PHS-3C pH meter (REX Instrument Factory, Shanghai, China) by mixing 10 g of soil with 25 ml of 0.01 M $CaCl_2$ solution. Soil texture was obtained by the pipette method (Gee and Bauder, 1986). Soil organic carbon (SOC) and total nitrogen (TN) contents were determined by dry combustion (vario Macro CNS Analyzer, elementar, Germany). Soil bulk density samples (0–10 cm) were taken by the core method (Blake and Hartge, 1986) with five replicates from each land use filed.

Linear or non-linear regression was used to examine the relationship between N_2O fluxes with soil variables (SPSS 17.0, Chicage, IL, USA).

3. Results

3.1. Environmental variables

During the period studied (from May 2012 to September 2013), the mean daily air temperature ranged from −32.1 °C (6 February 2013) to 23.6 °C (23 June 2013) with a mean of 2.8 °C (Fig. 1). Total precipitation for the sampling period was 654 mm (Figs. 2–5b). From October 2012 to September 2013, the annual mean air temperature (−1.7 °C) was lower than the 30-year average of 1.4 °C, while annual precipitation (415 mm) was greater than the long time average of 380 mm. Precipitation during the growing season accounted for 88% of total precipitation. During the no-growing season, snowfall was approximately 42 mm.

Soil temperature showed clear seasonal patterns, ranging from −12.3 °C in February 2013 to 28.0 °C in July 2012 across all four land uses (Figs. 2–5c). During the study period, mean soil temperatures were 12.0, 14.0, 8.1 and 9.9 °C for SG, WG, UG and OC, respectively. The main period of spring thaw was observed in the field and lasted for about six weeks (from 13 March to 24 April). Soil WFPS varied in phase with rainfall and were always below 60% in all sites except UG site (Figs. 2–5b). During the spring thaw, WFPS increased sharply and reached 80% at the UG site, but no remarkable increases were observed at the rest three sites. Over the entire study period, the mean soil WFPS was the highest at the UG site, ranging from 25 to 80% (mean 49%), and the lowest at the WG site, varying from 11 to 53% (mean 30%).

Soil mineral N contents varied 0.5–5.8 mg N kg^{-1} for NH_4^+ (Figs. 2–5d) and 2.3–20.7 mg N kg^{-1} for NO_3^- (Figs. 2–5e). The seasonal variability of NH_4^+ and NO_3^- contents was primarily regulated by freeze–thaw events in the three grasslands and both freeze–thaw and fertilization events in the cropland. During the spring–thaw period, both the NH_4^+ and NO_3^- contents increased rapidly in all land uses. During this period, soil mineral N content was highest in the OC site, lowest in the WG and SG sites, and intermediate in the UG site. NH_4^+ and NO_3^- contents peaked within 5–7 weeks after farmyard manure application in the middle of May.

Soils were neutral to slightly alkaline in all the four land uses, with pH values ranging from 7.63 to 8.07 (Table 1). Except for the soil in the SG site, which is a loam soil, all the other soils are sandy loam. Bulk density ranged from 1.11 to 1.45 g m^{-3}. Soil organic C and TN contents were highest in the SG site, lowest in the UG and OC sites, and intermediate in the WG site. The C:N ratio was similar across all land uses.

3.2. Hourly N_2O fluxes

The hourly N_2O fluxes of SG, WG, UG and OC during the study period ranged from −3.0 to 10.7, −2.3 to 7.9, −2.4 to 40.7 and −2.2 to 72.3 μg N m^{-2} h^{-1}, respectively (Figs. 2–a). The means during this period were 3.3, 2.0, 5.2 and 13.5 μg N m^{-2} h^{-1}, respectively.

During the spring thaw, large pulses of N_2O emissions were observed at the UG and OC sites (Figs. 4 and 5a). The spring–thaw

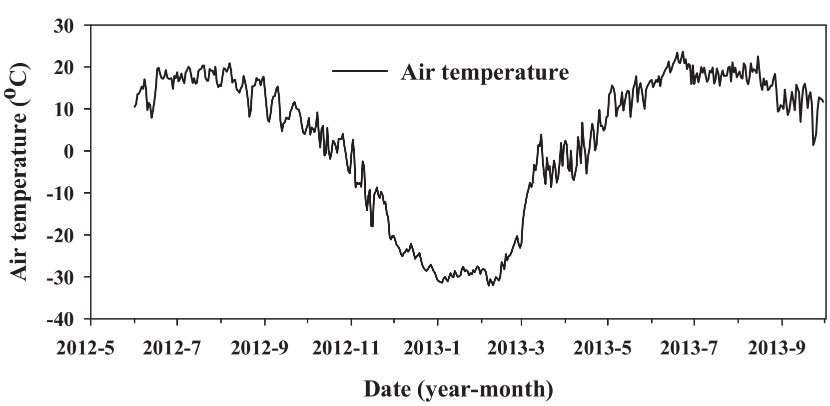

Fig. 1. Seasonal variations of air temperature from 25 May 2012 to 29 September 2013 in the agro-pastoral ectone of northern China.

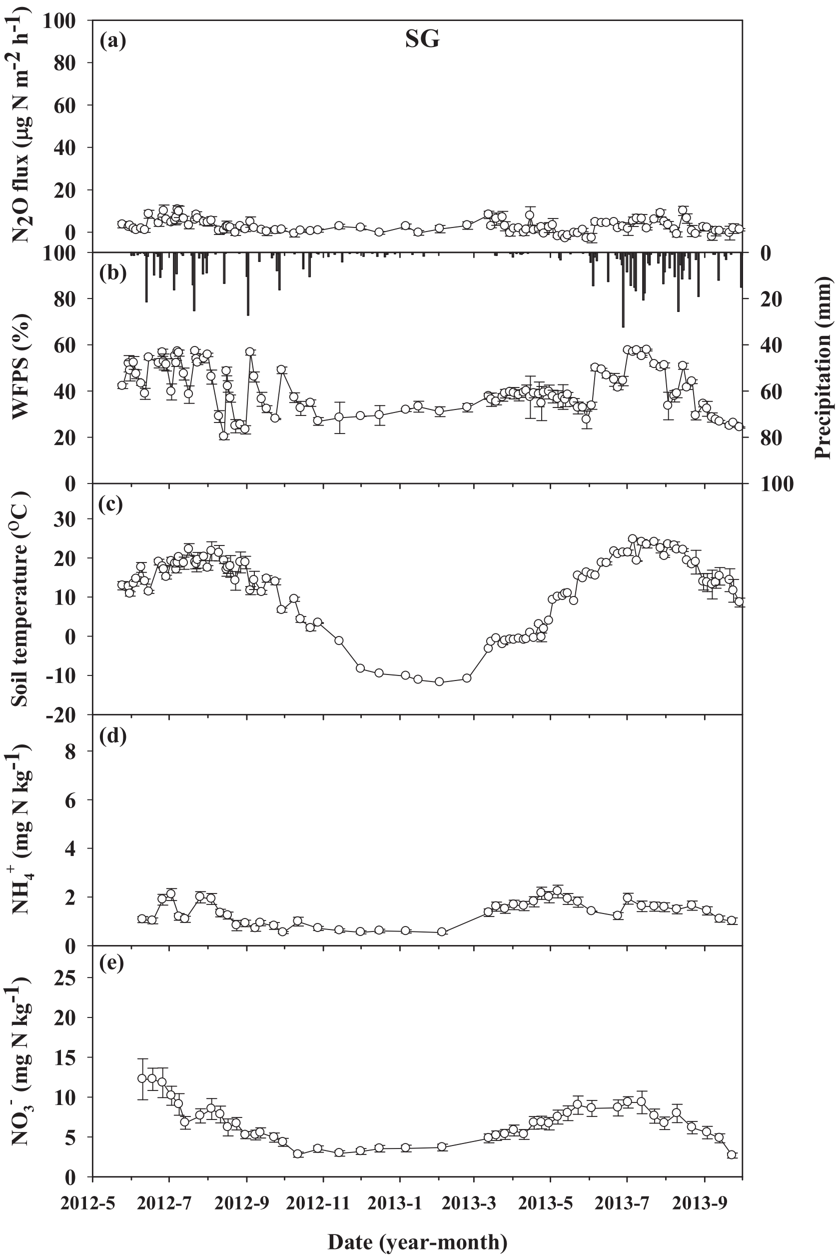

Fig. 2. Seasonal variations of (a) N_2O flux, (b) water-filled pore space (%WFPS, 0–6 cm) and precipitation, (c) soil temperature at 5 cm depth, (d) soil NH_4^+ content and (e) soil NO_3^- content (0–10 cm) at summer-grazed grassland (SG) from 25 May 2012 to 29 September 2013 in the agro-pastoral ectone of northern China. Values are mean ± S.E (standard error) ($n = 4$).

N_2O peaks reached up to 40.7 for UG and 72.3 μg N m^{-2} h^{-1} for OC, respectively. However, there were no matching pulses of N_2O emissions at the SG or WG sites (Figs. 2 and 3a). Mean N_2O fluxes were 4.4, 6.8, 24.1 and 53.8 μg N m^{-2} h^{-1} for SG, WG, UG and OC, respectively, during the spring–thaw period.

In the cropland, farmyard manure application stimulated N_2O emission. Emission peaks (which were 15.6 and 38.4 μg N m^{-2} h^{-1} in 2012 and 2013, respectively) were observed within 5–7 weeks following manure application in the middle of May (Fig. 5a).

3.3. Seasonal and annual N_2O emissions

Annual N_2O emissions were highest for OC, intermediate for UG and lowest for SG and WG (Table 2). The spring–thaw N_2O emissions of UG and OC dominated the total annual N_2O emission and accounted for 70% and 65% of the annual fluxes, respectively. In contrast, the contributions of spring thaw fluxes to total annual N_2O emissions were only 31% and 33% for SG and WG, respectively. The growing-season emissions accounted for 45%, 53%, 22% and 31% of annual fluxes at SG, WG, UG and OC sites, respectively. The winter emissions (measured from October to the middle of March) accounted for 24%, 14%, 8% and 4% of annual fluxes at SG, WG, UG and OC sites, respectively.

3.4. Relationships between N_2O fluxes and environmental parameters

The relationships between N_2O fluxes and environmental conditions were analyzed across the entire period studied. For all sites, a significant positive correlation existed between N_2O emissions and WFPS ($P < 0.001$, Fig. 6). Changes in WFPS explained 35%, 15%, 28% and 23% of the temporal variability in N_2O emissions, for SG, WG, UG and OC, respectively. Soil N_2O fluxes positively

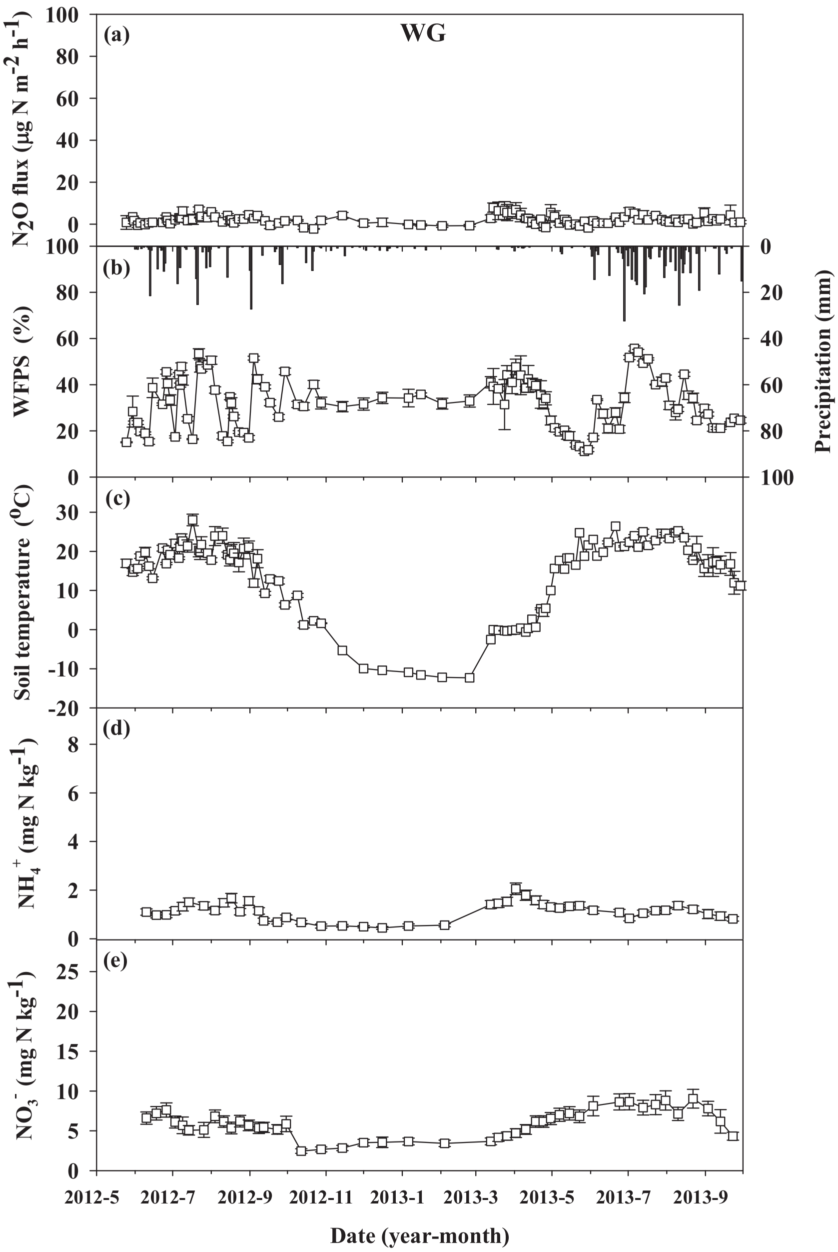

Fig. 3. Seasonal variations of (a) N_2O flux, (b) water-filled pore space (%WFPS, 0–6 cm) and precipitation, (c) soil temperature at 5 cm depth, (d) soil NH_4^+ content and (e) soil NO_3^- content (0–10 cm) at winter-grazed grassland (WG) from 25 May 2012 to 29 September 2013 in the agro-pastoral ectone of northern China. Values are mean ± S.E (standard error) (n = 4).

correlated to the total soil mineral N contents ($NH_4^+ + NO_3^-$) for all land uses except WG (Fig. 7). Soil mineral N contents accounted for 16%, 30% and 57% of N_2O flux variability for SG, UG and OC, respectively. There was no significant correlation between N_2O fluxes and soil temperature (figures not shown).

4. Discussion

4.1. Annual N_2O emissions

The annual N_2O emissions from three grassland sites ranged from 0.15 to 0.43 kg N ha^{-1} yr^{-1} (Table 2), indicating that the investigated grassland soils functioned as a source of atmospheric N_2O. On average, grassland soils released about 0.25 kg N ha^{-1} yr^{-1} (arithmetic average of three sites) into the atmosphere. The annual N_2O emissions observed here were within the range of emissions observed from temperate semi-arid grassland (0.01–0.73 kg N ha^{-1} yr^{-1}) in Inner Mongolia (Du et al., 2006; Wang et al., 2005; Wolf et al., 2010) and from different shortgrass steppe and shrub-steppe ecosystems (0.13–0.44 kg N ha^{-1} yr^{-1}) in North America (Epstein et al., 1998; Matson et al., 1991; Mosier et al., 2002; Mummey et al., 1997). Our results were close to those from extensive pasture (0.32–0.48 kg N ha^{-1} yr^{-1}) in a temperate region of Western and Central Europe, but were lower compared to intensive pasture (0.95–1.77 kg N ha^{-1} yr^{-1}) which received N fertilizer (Flechard et al., 2007), as higher N inputs may have enhanced N_2O emission (del Prado et al., 2006; Stehfest and Bouwman, 2006). Our observed annual N_2O emissions were lower than the agricultural background value of 1 kg N ha^{-1} yr^{-1} reported by IPCC (2006), demonstrating the potential for low N_2O emissions from unfertilized and unirrigated grasslands of the agro-pastoral ectone of northern China.

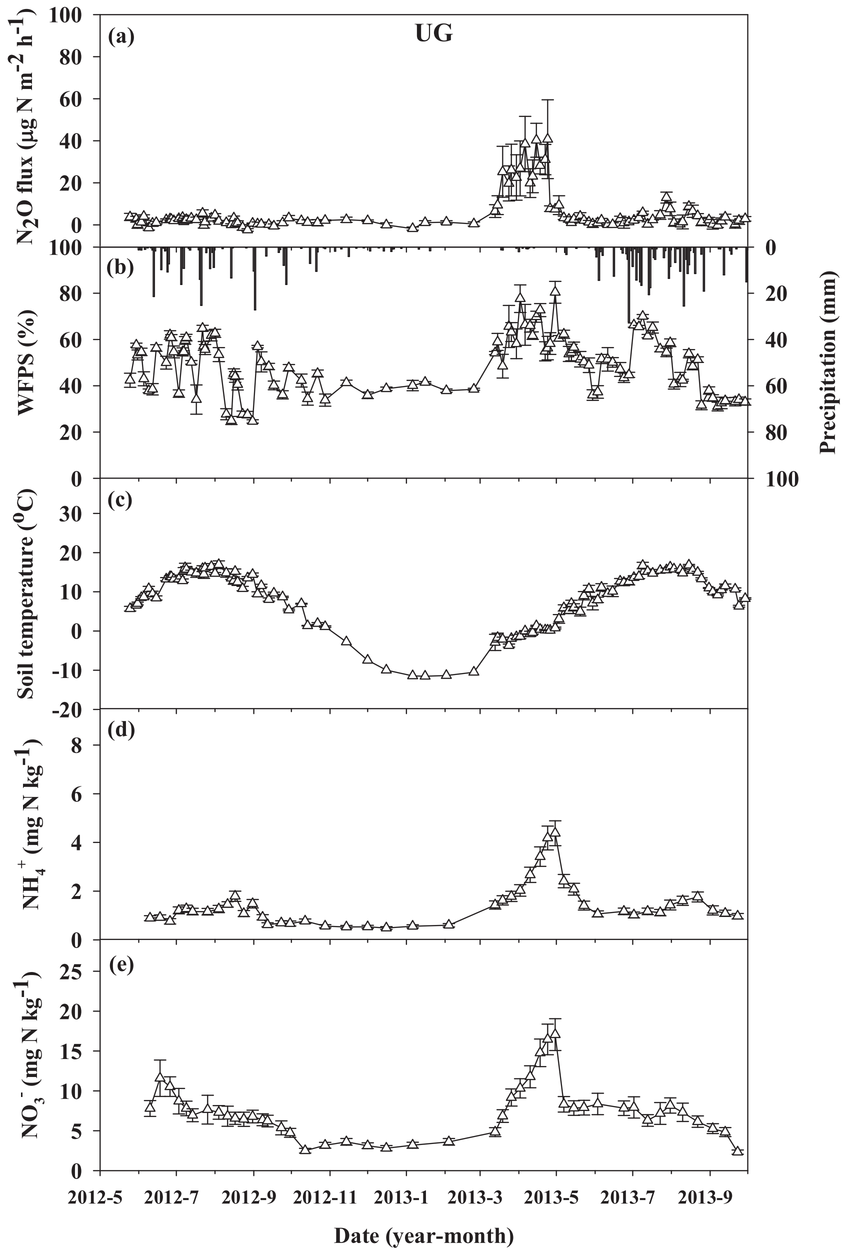

Fig. 4. Seasonal variations of (a) N_2O flux, (b) water-filled pore space (%WFPS, 0–6 cm) and precipitation, (c) soil temperature at 5 cm depth, (d) soil NH_4^+ content and (e) soil NO_3^- content (0–10 cm) at ungrazed grassland (UG) from 25 May 2012 to 29 September 2013 in the agro-pastoral ectone of northern China. Values are mean ± S.E (standard error) ($n = 4$).

Annual N_2O emission from OC site was 0.98 kg N ha^{-1} yr^{-1}, which was higher than the values reported from rain-fed croplands in semi-arid regions of Western Australia (0.09–0.11 kg N ha^{-1} yr^{-1}) (Barton et al., 2008) and South-eastern Australia (0.20–0.27 kg N ha^{-1} yr^{-1}) (Barker-Reid et al., 2005). The higher N_2O emission in our study might have been partly attributed to higher N_2O loss during spring–thaw season. In contrast, the study sites in Western and South-eastern Australia were not subject to freeze–thaw cycles. On the other hand, the N_2O emission reported in this study was lower than the emissions from intensively fertilized cropland soils in the North China Plain (4.6–5.4 kg N ha^{-1} yr^{-1}, Dong et al., 2000; 2.54–5.26 kg N ha^{-1} yr^{-1}, Yan et al., 2013). The higher N_2O emissions were most likely due to more favored soil water-heat conditions and higher N fertilizer inputs in the North China Plain. Our findings fell in the range from 0.3 to 16.8 kg N ha^{-1} yr^{-1} in cropped mineral soils across a variety of climatic regions as reported by Stehfest and Bouwman (2006).

Annual N_2O emissions from cropland site were 1–6 times higher than those from grassland sites, suggesting that land use change from grassland to cropping increased N_2O flux. Our result confirmed the notion that the conversion from native vegetable to agriculture significantly increased soil N_2O loss (Hadi et al., 2000; Mosier et al., 1997; Ri et al., 2003). Soil N_2O emissions from OC site were 1–11 times and 2–3 times higher than those from grassland sites in the spring thaw and growing season, respectively (Table 2). N_2O emissions were similar among the four land uses in the winter time. Therefore, the annual flux variation was mainly induced by spring thaw (61–73% of total difference) and growing season flux (27–38% of total difference).

Fertilizer application generally increases N_2O emissions (Flessa et al., 2002; Rafique et al., 2011; Scheer et al., 2008). In this study

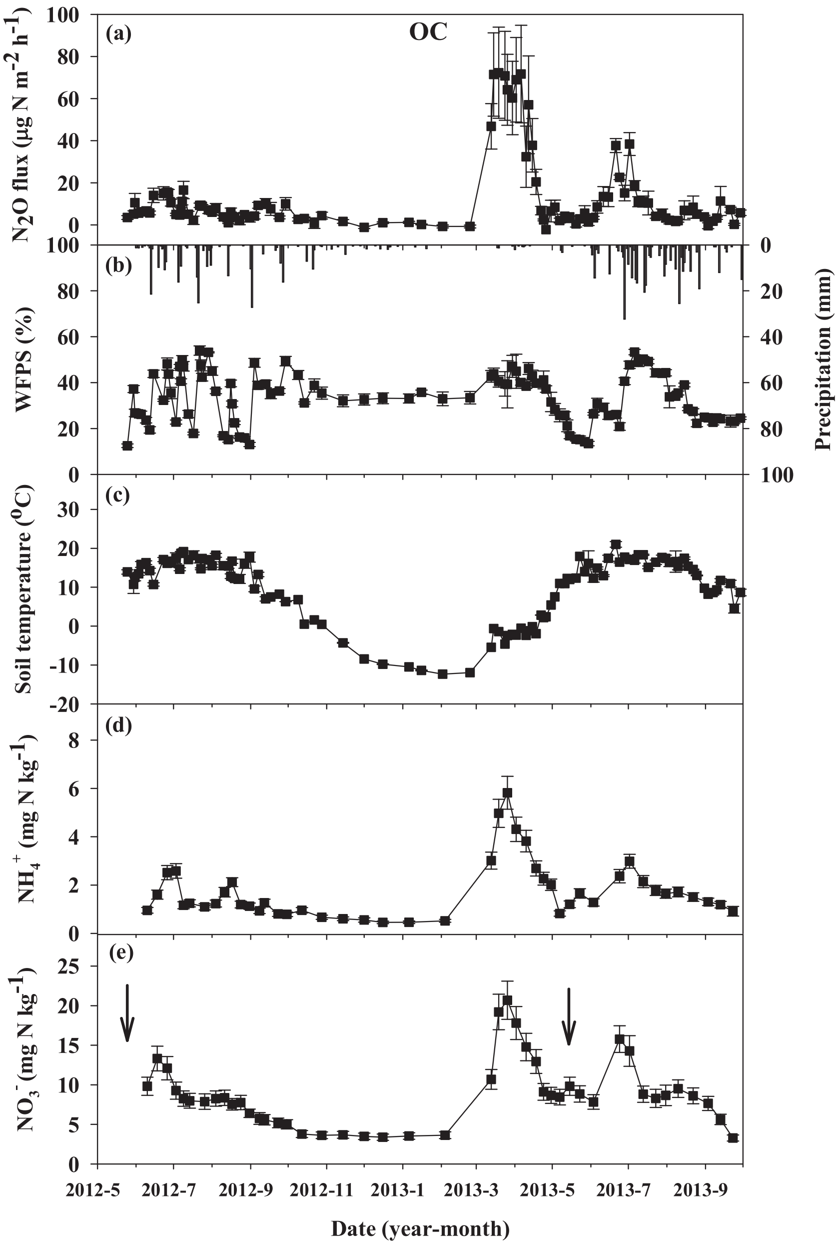

Fig. 5. Seasonal variations of (a) N_2O flux, (b) water-filled pore space (%WFPS, 0–6 cm) and precipitation, (c) soil temperature at 5 cm depth, (d) soil NH_4^+ content and (e) soil NO_3^- content (0–10 cm) at cropland (OC) from 25 May 2012 to 29 September 2013 in the agro-pastoral ectone of northern China. Values are mean ± S.E (standard error) (n = 4). Arrows indicate times of farmyard manure application (17 May 2012 and 13 May 2013).

we found increased N_2O emissions in the cropland soil compared with the unfertilized grassland soils during the growing season. Farmyard manure application in the cropland site increased the amount of N available (NH_4^+ and NO_3^-). Soil mineral N content reached maximum values of 3.0 mg N kg^{-1} for NH_4^+ and 15.7 mg N kg^{-1} for NO_3^- (Fig. 5) five to seven weeks following manure application in the middle of May. High N substrate availability and favored soil WFPS (averaged 38%) stimulated nitrification and denitrification process, and thus the amount of N_2O emitted. When accumulated, the N_2O loss by fertilizer effect accounted for 53% of the total N_2O loss over the growing season (0.16 vs. 0.30 kg N ha^{-1}). This led to greater N_2O loss from cropland soil compared to grassland soils during the growing season.

Annual N_2O emissions at grazed sites (SG and WG) were on average 60% lower than those at UG, which might indicate that grazing had a suppressive effect on annual N_2O emissions. Grazing management had little impact on N_2O emissions during the growing and winter seasons (Table 2), suggesting that most of the difference between ungrazed site and grazed sites was a result of spring thaw emissions. Strategies that reduce N_2O flux during spring thaw could reduce annual N_2O emissions. Similarly, Wolf et al. (2010) reported that annual emissions from ungrazed sites were higher than those from heavily grazed sites, suggesting that grazing decreases rather than increases N_2O emissions. However, our result was in contrast to other findings (Rafique et al., 2011; Saggar et al., 2007). These studies have shown that grazing stimulated soil N_2O emission by soil compaction as a result of animal treading and/ or the return of N in excreta patches. In our study, the similar mineral N contents between grazed and ungrazed sites contributed to similar N_2O emissions both during growing and winter seasons. The effects of grazing on N_2O emissions seem to vary in different grassland ecosystems.

Table 1
Soil physico-chemical properties depending on land uses at 0–10 cm depth in the agro-pastoral ectone of northern China.

Land use	SG	WG	UG	OC
pH	8.07 ± 0.09	7.70 ± 0.04	7.63 ± 0.04	7.86 ± 0.08
Bulk density ($g\,m^{-3}$)	1.11 ± 0.02	1.23 ± 0.08	1.45 ± 0.01	1.25 ± 0.01
SOC ($g\,kg^{-1}$)	28.25 ± 3.01	23.24 ± 1.59	13.03 ± 2.50	14.72 ± 1.32
Total N ($g\,kg^{-1}$)	3.18 ± 0.31	2.70 ± 0.23	1.47 ± 0.32	1.64 ± 0.20
C/N	8.86 ± 0.30	8.63 ± 0.30	8.89 ± 0.30	8.83 ± 0.56
Soil texture	Loam	Sandy loam	Sandy loam	Sandy loam
Sand (%)	45.3 ± 1.1	50.6 ± 6.7	71.9 ± 1.7	61.0 ± 8.0
Silt (%)	35.9 ± 3.9	27.6 ± 7.6	17.7 ± 1.0	22.9 ± 5.2
Clay (%)	18.8 ± 3.1	21.8 ± 2.0	10.4 ± 1.0	16.1 ± 2.9

Values are mean ± S.D (standard deviation).
Sand: 2–0.05 mm, Silt: 0.05–0.002 mm, Clay: <0.002 mm.
SG: summer-grazed grassland; WG: winter-grazed grassland; UG: ungrazed grassland; OC: cropland

4.2. N_2O fluxes during spring thaw season

Land use types had a great effect on N_2O fluxes during spring–thaw periods. Pulse emissions of N_2O were most pronounced at the OC site, followed by UG, but were hardly detectable at the SG or WG (Table 2). Grazing decreased N_2O emissions and conversion of grasslands to croplands promoted N_2O emissions during spring–thaw. Our results confirm the idea, developed in previous studies that grazing decreases spring–thaw N_2O emissions in temperate grassland in Inner Mongolia (Holst et al., 2008; Wolf et al., 2010). The higher spring–thaw N_2O emissions in the UG site were probably caused by a combination of higher soil moisture and increased substrate availability compared to the SG and WG sites. In the UG site, the standing dead grasses were taller and denser and there were more litter covering on the ground, which could collect more winter snow and accumulate more C and N substrates in the soil than the grazed sties. On the other hand, in the SG and WG sites, grazing reduced aboveground plant biomass and mean canopy height, which could weaken snow-holding capacity and

Table 2
Seasonal and annual cumulative N_2O emissions depending on land uses from 29 September 2012 to 29 September 2013 in the agro-pastoral ectone of northern China.

Land use	Number of chambers	Cumulative N_2O emission ($kg\,N\,ha^{-1}$)			
		AE ± S.E	GE ± S.E	WE ± S.E	STE ± S.E
SG	4	0.19 ± 0.03	0.08 ± 0.01	0.05 ± 0.01	0.06 ± 0.02
WG	4	0.15 ± 0.03	0.08 ± 0.01	0.02 ± 0.00	0.05 ± 0.02
UG	4	0.43 ± 0.07	0.09 ± 0.01	0.04 ± 0.00	0.30 ± 0.07
OC	4	0.98 ± 0.09	0.30 ± 0.02	0.04 ± 0.01	0.64 ± 0.09

AE: annual emissions; GE: growing season emissions; WE: winter emissions; STE: spring thaw emissions; S.E: standard error.
SG: summer-grazed grassland; WG: winter-grazed grassland; UG: ungrazed grassland; OC: cropland.

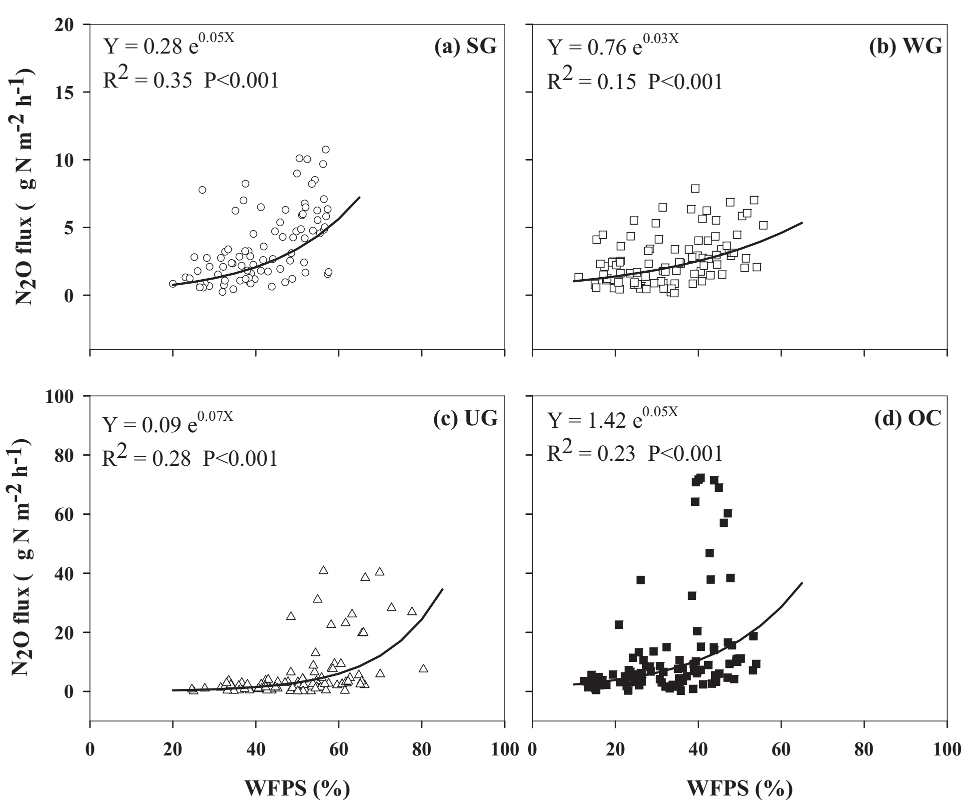

Fig. 6. Relationship between soil N_2O flux and water-filled pore space (WFPS) at 0–6 cm depth depending on land uses: (a) summer-grazed grassland (SG), (b) winter-grazed grassland (WG), (c) ungrazed grassland (UG) and (d) cropland (OC).

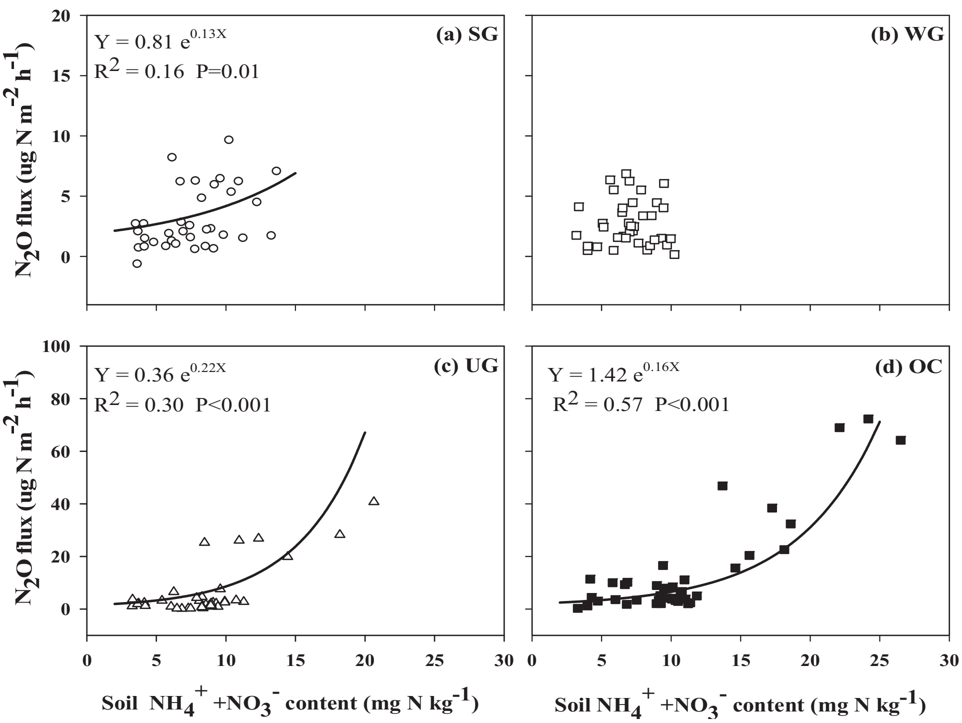

Fig. 7. Relationship between soil N_2O flux and soil mineral N content ($NH_4^+ + NO_3^-$) at 0–10 cm depth depending on land uses: (a) summer-grazed grassland (SG), (b) winter-grazed grassland (WG), (c) ungrazed grassland (UG) and (d) cropland (OC).

reduce releases of available C and N into soils. These interpretations were further supported by the field observations of WFPS and mineral N contents. Melting of snow markedly increased WFPS in the UG site and WFPS values were on average 63%, whereas at SG and WG sites, WFPS were only 38% during spring thaw (Figs. 2–4b). The NH_4^+ and NO_3^- contents at UG site (Fig. 4d and e) were 0.6–1.2 times greater than those in the grazed sites (Figs. 2 and 3d and e) during spring thaw. Therefore, the increased availability of NH_4^+ and NO_3^- and high WFPS in the UG site led to a general increase in nitrification and denitrification activity resulting in enhanced N_2O emissions. While less mineral N and relative lower WFPS in the grazed sites during spring thaw season might have inhibited N_2O production. In the OC site, the removal of crop residue after harvest decreased the capture of snow. Accordingly, WFPS at the OC site was on average 34% during spring thaw season. However, the observed soil mineral N content was the highest due to manure application. The highest spring–thaw N_2O pulses in the OC site were probably related to the highest N availability. Our results showed that changes in soil mineral N content could explain 80% of N_2O variability (Fig. 8), demonstrating that the magnitude of spring–thaw N_2O emission under different land uses might be primary controlled by N substrate availability.

N_2O emission during spring thaw season accounted for 31–70% in the grassland soils and 65% of the annual N_2O budget in the cropland soil (Table 2). Wolf et al. (2010) reported that the spring–thaw N_2O pulses on average accounted for 72% of the annual emission for ungrazed sites and 33% of the annual emission for the grazed sites in Inner Mongolia steppe. Wagner-Riddle et al. (2007)

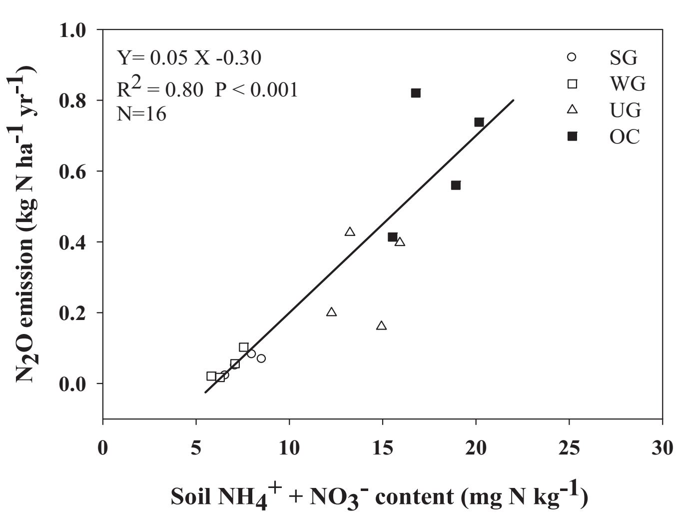

Fig. 8. Regression analysis between cumulative N_2O emissions (kg N ha^{-1} yr^{-1}) and mean soil $NH_4^+ + NO_3^-$ content (mg N kg^{-1}) at 0–10 cm soil depth during the spring thaw season.

observed that no-growing season (November-April) emissions, comprised between 30% and 90% of the annual emissions, mostly due to increased N_2O fluxes during soil thawing, in a 5-yr study in Ontario, Canada, from a corn–soybean–wheat rotation. Röver et al. (1998) suggested that approximately 70% of N_2O was emitted during the winter with freeze–thaw cycle occurrences for arable soils in Lower Saxony, Germany. These data confirmed the importance of the no-growing season, particularly spring thaw season for the assessment of annual N_2O budget at the temperate climate zones, especially in locations where soils undergo freeze–thaw cycles. Thus, more measurements during spring thaw are required for reliable estimations of N_2O inventories.

4.3. Effects of environmental variables on N_2O fluxes

Many studies have shown that soil temperature, soil moisture, and mineral N content were the key variables controlling N_2O emissions (Dobbie and Smith, 2003; Jones et al., 2007; Rudaz et al., 1999; Wang et al., 2005). Soil moisture controlled N_2O emissions through its effect on activity of both nitrifiers and denitrifiers and gas transport within the soil (Burger et al., 2005; Skiba and Smith, 2000). At all investigated sites, we observed an exponential correlation between WFPS and N_2O emissions (R^2 = 0.15–0.35, $P < 0.001$, Fig. 7). Liu et al. (2011) also found a positive linear correlation between soil WFPS and N_2O emissions for spring maize in semi-arid northern China (R^2 = 0.25–0.57, $P < 0.01$). Similar positive relationship between soil moisture and N_2O emissions has been reported in semi-arid grassland in Inner Mongolia (Wang et al., 2005; Xu et al., 2008; Zhang and Han, 2008). Low precipitation combined with course soil texture prevented WFPS from exceeding 60% for all land uses in most of days during the study period except UG site in the spring–thaw (Figs. 2–5). The previous study indicated that denitrification increased rapidly when WFPS exceeded 60%, whereas nitrification was the dominant source of N_2O in the range of 30–70% of WFPS (Davidson, 1992). It can be assumed that nitrification was the predominant source of N_2O at our study sites.

Soil emissions of N_2O are often positively correlated with inorganic N availability in many ecosystems (Jones et al., 2007; Yao et al., 2010). Soil mineral N content could explain 16–57% of N_2O variability except WG site. High N_2O emissions coincided with high N availability (NH_4^+ and NO_3^-) due to fertilization or spring thawing in our study.

It is well established that the rate of N_2O emission usually increases with soil temperature (Li et al., 2012; Smith et al., 1998; Wang et al., 2005). The dependence of N_2O on soil temperature can be attributed to sensitivity of microbial activity to temperature as N_2O production was mainly from microbial mediated nitrification and denitrification. However, soil temperature was not significantly correlated with N_2O emissions in the present study, as was also found by other studies (Corre et al., 1999; Parsons et al., 1991). The absence of a significant statistical relationship between soil temperature and N_2O emissions might be explained in two ways. First, high N_2O fluxes occurred even at below-zero temperature during spring thaw. Second, soil temperature showed clear seasonal patterns, whereas there was little variation in N_2O emissions.

5. Conclusions

We quantified annual N_2O emissions depending on land uses in a semi-arid agro-pastoral ecotone of northern China. Emissions of N_2O occurred mainly after farmyard manure fertilization and during spring thaw periods. The spring–thaw N_2O pulses dominated the annual emission for UG and OC, whereas only one third of the annual N_2O emission for SG and WG. Our results stressed the importance of spring–thaw N_2O losses for the annual balance. Conversion from grassland to cropland increased N_2O flux both during growing and spring thaw seasons. Grazing reduced annual N_2O losses through decreasing spring–thaw N_2O emission, suggesting a practicable mitigation option.

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