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Effects of sunlight on tundra nitrous oxide and methane fluxes in maritime Antarctica

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Abstract The relationships of nitrous oxide (N_2O) and methane (CH_4) emissions to other environmental parameters have been studied extensively in Antarctic terrestrial ecosystems. However, the effects of sunlight on soil N_2O and CH_4 fluxes are neglected across the Antarctic tundra. Here, fluxes of N_2O and CH_4 from maritime Antarctic tundra soils were measured in the absence and presence of sunlight during three summers. The N_2O fluxes averaged -4.6 ± 1.2 $\mu g\cdot m^{-2}\cdot h^{-1}$ in the absence of sunlight and 5.7 ± 1.5 $\mu g\cdot m^{-2}\cdot h^{-1}$ in its presence; CH_4 fluxes averaged 119.8 ± 24.5 $\mu g\cdot m^{-2}\cdot h^{-1}$ (absence) and -40.5 ± 28.3 $\mu g\cdot m^{-2}\cdot h^{-1}$ (presence). The correlations between N_2O and CH_4 fluxes and other environmental variables (e.g., soil moisture, temperature, organic and inorganic material) were not statistically significant ($P>0.05$) at all sites. On average, sunlight significantly increased N_2O emissions and CH_4 uptake by 10.3 $\mu g\cdot m^{-2}\cdot h^{-1}$ and 160.3 $\mu g\cdot m^{-2}\cdot h^{-1}$, respectively. This study indicates that sunlight is critical for accurately estimating N_2O and CH_4 budgets from maritime Antarctica and necessary for constraining the role of their emissions from tundra soil.

Keywords **sunlight, methane, nitrous oxide, greenhouse gas, soil, wetland, Antarctica**

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1 Introduction

Nitrous oxide (N_2O) and methane (CH_4) are two active greenhouse gases (GHGs) that together comprise approximately one third of the causes of global warming (IPCC, 2013; Bao et al., 2018). Although N_2O and CH_4 concentrations are much lower than CO_2 in the atmosphere, their global warming potential is 298 times and 25 times that of CO_2 on a century scale, respectively. Soils can act as sources or sinks of GHGs (Vieira et al., 2013). Over the past 2 decades, N_2O and CH_4 fluxes and factors affecting them have been recognized and studied extensively in temperate, tropical/subtropical and boreal soils of terrestrial ecosystems (Christensen et al., 2004; Repo et al., 2009; Marushchak et al., 2011; Ullah and Moore, 2011; Kirschke et al., 2013; Drewer et al., 2017; Pereira, 2017). Relatively high CH_4 emission rates have been reported in subarctic wetlands and high tundra N_2O emissions were recorded after Arctic permafrost thaw (Repo et al., 2009; Elberling et al., 2010; Marushchak et al., 2011). Previous studies of Antarctic GHG fluxes mainly reported soil CO_2 fluxes in dry valleys (Barret et al., 2006; Gregorich et al., 2006; Ball

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et al., 2009) and maritime tundra (Zhu et al., 2013, 2014; Drewer et al., 2015; Neufeld et al., 2015; Bao et al., 2016, 2018). However, studies of N_2O and CH_4 fluxes remain scarce in Antarctic terrestrial ecosystems compared with other global regions.

The ice-free areas of maritime Antarctica are characterized by high spatial–temporal heterogeneity in environmental variables and landform configurations and are vulnerable to climate change (Vieira et al., 2013; Zhu et al., 2014). Climate change is also expected to affect tundra N_2O and CH_4 production and emission rates as soil water content and temperature are related to soil carbon (C) and nitrogen (N) balance and microbial activity (Carvalho et al., 2010; Zhu et al., 2014; Bao et al., 2018). Previous studies in the region have demonstrated that microtopography, oxygen (O_2) and substrate availability and interactions, soil water content, and soil temperature are crucial to N_2O and CH_4 fluxes (Carvalho et al., 2010; Vieira et al., 2013; Zhu et al., 2013, 2014; Drewer et al., 2015; Neufeld et al., 2015; Bao et al., 2018). Additionally, relatively high N_2O and CH_4 fluxes are present in the natural habitats of penguins and seals because of highly mobile and readily available C and N fractions in their excreta (Zhu et al., 2013; Drewer et al., 2015; Neufeld et al., 2015). Despite all this information, the effects of sunlight on tundra N_2O and CH_4 emissions are unknown because of a lack of relevant studies in maritime Antarctica.

In tundra, N_2O production is predominantly biological and takes place primarily through the activity of microorganisms during denitrification and nitrification. The dominance of these two processes is linked to O_2 availability from photosynthesis by terrestrial plants (Wrage et al., 2001). Moreover, the predominance of N_2O consumption over production occurs in tundra soils under constant, totally anoxic conditions (Stewart et al., 2012). Sunlight plays an important role in photosynthesis because more N_2O can be consumed under highly anoxic soil conditions in the total absence of sunlight (Chapuis-Lardy et al., 2007; Stewart et al., 2012). It has been reported that the responses of several environmental variables to vegetation N_2O fluxes differed under complete darkness and sunlight exposure, which suggests that N_2O release might depend on sunlight (Li et al., 2011). Significant differences in the N_2O flux have been identified in tundra vegetation under sunlight and darkness, and observed N_2O fluxes from individual plants and communities have switched between acting as sinks and sources depending on different sunlight conditions in High-Arctic ecosystems (Stewart et al., 2012). Sunlight can significantly inhibit CH_4 release from lake ecosystems because of O_2 production from submerged aquatic vegetation photosynthesis, and both CH_4 production and oxidation are partially inhibited by O_2 availability (Frenzel and Karofeld, 2000). Moreover, sunlight can stimulate plant growth and development, and high vegetation cover is conducive to producing autochthonous dissolved organic matter, which in turn could supply appropriate nutrient substrates for methanogenic bacteria (Ding et al., 2013). Additionally, tundra CH_4 production is stimulated by the release of newly photo-assimilated C in the form of compounds (e.g., hydrogen, acetate and propionate) regarded as prerequisites for CH_4 production (von Fischer et al., 2010; Dorodnikov et al., 2011). It has been suggested that sunlight could strongly affect tundra N_2O and CH_4 emissions and uptake based on O_2 release via photosynthesis in Ny-Ålesund (Svalbard, Norway; Li et al., 2016). Compared with the Arctic and other parts of the world, Antarctic tundra must have not only adapted to fluctuating and higher light and ultraviolet radiation regimes during the austral summer, but also have acclimated to efficiently capture and use the limited light available during winter (La Rocca et al., 2015; Bao et al., 2018). Therefore, it is important to investigate the effects of sunlight on tundra N_2O and CH_4 emissions in Antarctica.

In this study, we report data from three summers (2011/2012, 2013/2014 and 2014/2015) of soil N_2O and CH_4 flux measurements in the tundra ecosystem of maritime Antarctica. Our objective was to test the hypothesis that the presence of sunlight stimulates tundra N_2O emissions and CH_4 uptake.

2 Materials and methods

2.1 Study area and sample collection

Ardley Island (62°13′S, 58°56′W) and Fildes Peninsula (61°51′–62°15′S, 57°30′–59°00′W) are situated in the southwestern portion of King George Island, and encompass an area of about 33 km^2 (Figure 1). In general, mosses (*Bryum Pseudotriquetrum* and *B. muelenbeckii*) and lichen (*Usnea* spp.) dominate the vegetation in these areas. Ardley Island is connected to Fildes Peninsula by a sandbar. The eastern coast of Ardley Island is affected by penguin (including Adelie, gentoo and chinstrap) activities while the western part of the tundra has no penguins. More information about the study area is given in Appendix 1.

During Chinese Antarctic Expeditions over the austral summers of 2011/2012, 2013/2014 and 2014/2015, six flux measurement sites were established in three tundra areas (Figure 1). Specifically, two measurement sites were set up in each of the tundra areas: the eastern tundra (ET, sites EA and EB) and western tundra (TM, sites WA and WB) on Ardley Island, and the upland tundra (UT, sites GA and GB) on Fildes Peninsula. Each site was equipped with two chamber collars (one for the transparent chamber and one for the opaque chamber), and the N_2O and CH_4 fluxes from the collars in each tundra site were measured at roughly the same time. There were no differences in the dominant plant species at the two sites in each tundra area. Because tertiary lava, pyroclastic rock and volcanic sedimentary rock structure the main body of these areas, volcanic rock erosion and weathering residues have generated pristine sandy soils (Zhu et al., 2014; Bao et al., 2018).

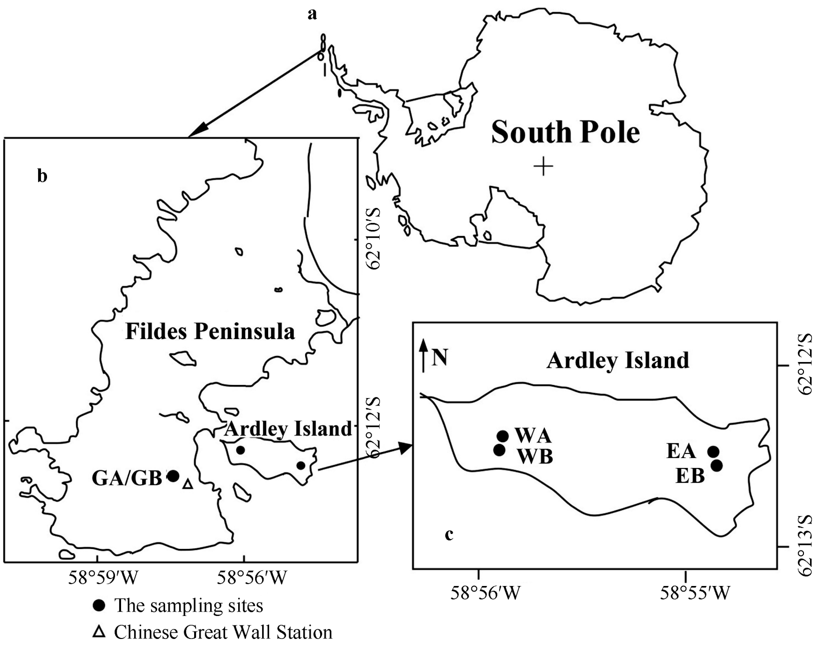

Figure 1 Study area and N_2O and CH_4 observation sites. **a**, The dot indicates the location of the study area in maritime Antarctica. **b**, Site locations on Fildes Peninsula and Ardley Island. Two upland tundra sites (GA and GB) are shown. **c**, The flux chamber sites in the eastern and western tundra on Ardley Island, including four regular sites EA, EB and WA, WB. The map was drawn using CorelDRAW×7.

We used a static chamber technique (Zhu et al., 2014; Bao et al., 2018, 2020) to measure tundra N_2O and CH_4 emissions. A more detailed description of *in situ* flux measurements is given in Appendix 2. From 24 December 2011 to 8 February 2012, eight N_2O flux measurements each were made at all six sites. From 17 February 2014 to 7 March 2014, eight N_2O and CH_4 flux measurements were made at WA and WB, and nine measurements were taken at GA and GB. Finally, from 18 December 2014 to 10 February 2015, eight N_2O and CH_4 flux measurements were taken at WA and WB, and six at GA and GB.

2.2 Analysis of N_2O and CH_4 concentrations and flux calculations

Concentrations of N_2O and CH_4 were simultaneously analyzed by gas chromatography (GC; HP5890, Hewlett Packard); the GC was equipped with an electron capture detector for N_2O and a flame ionization detector for CH_4. The N_2O and CH_4 flux rates were calculated from the slope of the temporal change in gas concentrations within the static chamber. A detailed description of the flux analysis and calculation was previously published (Zhu et al., 2013, 2014; Bao et al., 2016, 2018).

2.3 Environmental variables

Soil temperatures at depths of 0, 5 and 10 cm were determined *in situ* using soil thermometers inserted to a corresponding depth inside the chambers. Daily variations in meteorological parameters were recorded at Great Wall Station. Soils were sampled (0–15 cm) using a PVC tube (6 cm diameter) after the completion of N_2O and CH_4 flux measurements in summer 2011/2012 and 2014/2015, then sealed and stored at 4℃ until analysis. Soil moisture (SM) was estimated by drying the fresh soil for 24 h at 105℃. Soil NO_3^--N and NH_4^+-N contents were determined by the Griess–Ilosvay colorimetric method (Zhu et al., 2013, 2014). Total nitrogen (TN) was determined using a CNS elemental analyzer (Elementar Vario EL, Hanau, Germany). Total organic carbon (TOC) was measured using the chemical volumetric method (Bao et al., 2018). Soil pH was measured in deionized water with a 1:3 soil to solution ratio.

2.4 Statistical analysis

All statistical analyses were performed with ORIGIN Pro 8.5 software (OriginLab Corp., Northampton, MA, USA) and SPSS 20.0 software (IBM Corp., Armonk, NY, USA). For each observation plot, the uncertainty of individual fluxes was represented as the standard error of the mean. Analysis of variance (ANOVA, LSD multiple comparison) was performed to test the significant difference between tundra N_2O or CH_4 emissions in the absence and presence of sunlight. Correlation analysis was used to investigate the relationships between N_2O and CH_4 fluxes and environmental variables (e.g., soil temperature, NO_3^--N, NH_4^+-N, TOC and TN). The contribution of sunlight to tundra N_2O or CH_4 flux was calculated as: $CS=M_A-M_B$. In this equation, CS indicates the contribution of sunlight to tundra N_2O or CH_4 flux, and M_A and M_B indicate mean N_2O or CH_4 flux in the presence and absence of sunlight, respectively.

3 Results

3.1 Environmental variables

During the three sampling periods, ground and air temperatures showed large fluctuations. The daily maximum and minimum ground/air temperatures were generally above 5 ℃ and below 0 ℃, respectively. The total precipitation did not vary significantly ($P<0.01$) among the three sampling seasons. Diurnal sunlight time (ST) showed large fluctuations. The mean ST increased gradually from the end of November to February, which was followed by a rapid drop; the daily maximum ST was generally above 15 h (Appendix Figure A1 and Table A1). Overall, soil pH, SM, TOC and TN were similar between WA and WB, EA and EB, and GA and GB. However, soil physiochemical properties among the tundra areas showed differences. The mean soil pH on Ardley Island was 5.95, which was lower than that on Fildes Peninsula (7.05). The upland tundra soils at GA and GB were more alkaline and had higher C∶N ratios than the eastern tundra soils (EA and EB; Table 1). The SM (42.8%–45.7%) in upland tundra soils was lower than in the marsh soils (83.8%–88.9%). Particularly high soil inorganic nitrogen (NO_3^--N and NH_4^+-N) was present in eastern tundra soils (mean = 61.4 μg·g^{-1} (NH_4^+-N) and 103.6 μg·g^{-1} (NO_3-N)). Soil TOC and TN ranged from 2.26% to 6.05% and 0.27% to 0.58%, respectively, in tundra marsh soils; TOC (15.06%–16.56%) and TN (2.01%–2.05%) contents in eastern tundra soils were 2–3 times higher than in western marsh soils. Additional details regarding climate conditions are given in Appendix 3 and Table A1.

Table 1 Soil physiochemical properties at the observation sites of maritime Antarctica

Tundra sites		pH	SM/%	TOC/%	TN/%	NH_4^+-N /(μg·g^{-1})	NO_3^--N /(μg·g^{-1})	C/N
Lowland tundra marsh (western tundra) on Ardley Island (TM)	WA	6.5	85.8	2.26	0.27	9.84	15.61	8.4
	WB	6.8	88.9	6.05	0.58	4.18	15.18	10.4
Eastern tundra on Ardley Island (ET)	EA	5.2	83.8	16.56	2.05	43.62	74.89	8.1
	EB	5.3	86.2	15.06	2.01	79.20	132.23	7.5
Upland tundra on Fildes Peninsula (UT)	GA	7.3	45.7	1.86	0.08	1.26	0.53	9.4
	GB	6.8	42.8	1.08	0.12	1.17	0.44	8.5

Note: SM, TOC, TN, and C/N indicate soil moisture, total organic carbon, total nitrogen, and the ratios of soil carbon and nitrogen, respectively.

3.2 Tundra N_2O fluxes in the absence and presence of sunlight

During the three sampling periods, tundra N_2O fluxes showed similar fluctuations among the sites in terms of sunlight absence and presence (Figure 2). In tundra area TM, N_2O emissions at WA were enhanced significantly in the presence of sunlight (mean flux range of 3.7–6.6 μg·m^{-2}·h^{-1}), whereas WB showed extremely low N_2O emissions and negative fluxes in the absence of sunlight (Figure 2a). Similarly, EB acted as a stronger N_2O sink in the absence of sunlight (mean flux of −12.4±3.7 μg·m^{-2}·h^{-1}) than EA with sunlight (mean flux of −3.2±5.2 μg·m^{-2}·h^{-1}) in summer 2011/2012 (Figure 2b). For tundra area UT, GA was a strong N_2O emission source with sunlight (mean flux range of 6.8−13.8 μg·m^{-2}·h^{-1}), whereas GB was a weak N_2O sink (mean flux of −2.7±2.0 μg·m^{-2}·h^{-1}) without sunlight (Figure 2c).

A high degree of variability in the N_2O fluxes was observed among the three tundra areas in the absence or presence of sunlight (Table 2). Additionally, tundra N_2O emissions showed no significant annual changes ($P>0.05$) in maritime Antarctica (Table 3). For the western, eastern and upland tundra sites, statistically significant differences ($P<0.05$) were found between mean N_2O fluxes in the absence and presence of sunlight (Figure 3a). By extension, these results revealed that the presence of sunlight significantly ($P=0.000$) increased N_2O fluxes by a mean value of 10.3 μg·m^{-2}·h^{-1} (Table 3).

3.3 Tundra CH_4 fluxes in the absence and presence of sunlight

The CH_4 fluxes at WB ranged from 26.3 to 359.4 μg·m^{-2}·h^{-1} (mean of 170.9±28.3 μg·m^{-2}·h^{-1}), with most fluxes higher than 60 μg·m^{-2}·h^{-1} in the absence of sunlight (Figure 4a). In the presence of sunlight, the CH_4 fluxes at WA varied between acting as a strong source (up to 255.3 μg·m^{-2}·h^{-1}) and a strong sink (up to −324.9 μg·m^{-2}·h^{-1}) with a mean CH_4 emission rate of −11.4±41.2 μg·m^{-2}·h^{-1}. Similarly, for the upland tundra, a strong CH_4 sink was present at GA (−51.0±31.0 μg·m^{-2}·h^{-1} in 2013/2014 and −24.8±78.9 μg·m^{-2}·h^{-1} in 2014/2015) with sunlight, whereas GB was a strong CH_4 emission source (70.2±33.3 μg·m^{-2}·h^{-1} in 2013/2014 and 58.0±81.5 μg·m^{-2}·h^{-1} in 2014/2015) without sunlight (Figure 4b).

The CH_4 fluxes showed no significant ($P>0.05$) spatial and temporal variations among the three tundra areas (Tables 2 and 3). For the western and upland tundra sites, statistically significant differences ($P<0.05$) were found between mean CH_4 fluxes in the absence and presence of sunlight (Figure 3b). By considering all the measurement data, we found that the presence of sunlight significantly ($P=0.000$) increased CH_4 uptake by 160.3 μg·m^{-2}·h^{-1} (Table 3).

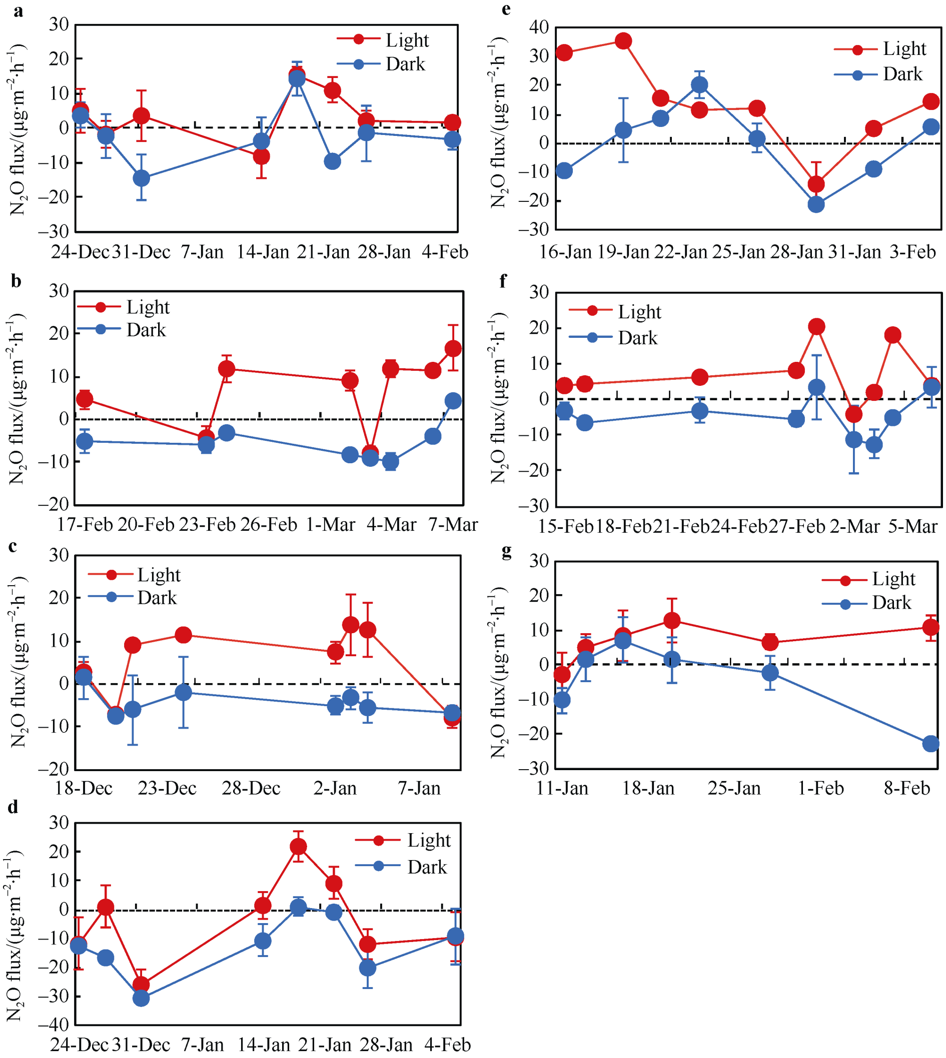

Figure 2 N_2O fluxes from the western, eastern and upland tundra sites in the presence and absence of sunlight during the summers of 2011/2012, 2013/2014 and 2014/2015. Western tundra N_2O fluxes in 2011/2012 (**a**), 2013/2014 (**b**) and 2014/2015 (**c**). Eastern tundra N_2O flux in summer 2011/2012 (**d**). Upland tundra N_2O fluxes in 2011/2012 (**e**), 2013/2014 (**f**) and 2014/2015 (**g**). The red lines indicate fluxes in the presence of sunlight, and blue lines indicate fluxes in the total absence of sunlight.

Table 2 Comparisons of N_2O and CH_4 fluxes from the tundra observation sites in the presence or absence of sunlight during the observation period

Tundra types		In presence of sunlight		In absence of sunlight		Difference
		Range	Mean ± SE	Range	Mean ± SE	CS (M_A–M_B)
N_2O flux/(μg·m^{-2}·h^{-1})	TM	−8.1 – 16.6	5.2±1.6a	−14.3 – 14.2	−3.8±1.1a	9.0
	ET	−26.2 – 21.7	−3.2±5.2a	−30.9 – 1.1	−12.4±3.7b	9.2
	UT	−14.0 – 35.5	9.3±2.2a	−22.5 – 20.2	−2.7±2.0a	12.0
CH_4 flux/(μg·m^{-2}·h^{-1})	TM	−324.9 – 255.3	−11.4±41.2a	26.3 – 359.4	170.9±28.3a	−182.3
	ET	-	-	-	-	-
	UT	−520.1 – 55.9	−71.6±38.6a	−196.1 – 279.7	65.3±36.5a	−136.9

Note: The CS indicated the contribution of sunlight to tundra N_2O or CH_4 fluxes. The M_A and M_B indicated the mean N_2O or CH_4 fluxes in the presence and absence of sunlight, respectively. Within the columns, the different suffix letters (a and b) indicate that the mean N_2O and CH_4 fluxes between tundra sites for a given measurement type (i.e. in presence of sunlight or in absence of sunlight) are significantly different (ANOVA and LSD, $P<0.05$) whereas the same suffix letters indicate that the mean fluxes between the sites have no significant difference (ANOVA and LSD tests, $P>0.05$). CH_4 flux was not obtained from ET during the observation period.

Table 3 Comparisons of tundra N_2O fluxes and CH_4 fluxes from all the observation sites in the presence or absence of sunlight in the summers of 2011/2012, 2013/2014 and 2014/2015

	Observation period	In presence of sunlight		In absence of sunlight		Difference
		Range	Mean±SE	Range	Mean±SE	CS (M_A–M_B)
N_2O flux/ ($\mu g \cdot m^{-2} \cdot h^{-1}$)	2011/2012	−26.2 – 35.5	4.8±2.9a	−30.9 – 20.2	−4.7±2.4a	9.5
	2013/2014	−7.8 – 16.6	6.8±1.9a	−12.5 – 3.4	−4.8±1.2a	11.6
	2014/2015	−7.8 – 12.7	6.0±1.9a	−22.5 – 1.6	−4.2±1.9a	10.2
	Comprehensive	−26.2 – 35.5	5.7±1.5	−30.9 – 20.2	−4.6±1.2	10.3
CH_4 flux/ ($\mu g \cdot m^{-2} \cdot h^{-1}$)	2011/2012	-	-	-	-	-
	2013/2014	−229.1 – 255.3	−23.6±30.1a	−95.7 – 334.0	99.3±25.9a	−122.9
	2014/2015	−520.1 – 244.1	−61.1±51.9a	−196.1 – 359.4	144.7±44.5a	−205.8
	Comprehensive	−520.1 – 255.3	−40.5±28.3	−196.1 – 359.4	119.8±24.5	−160.3

Note: The CS indicated the contribution of sunlight to tundra N_2O and CH_4 fluxes. The M_A and M_B indicated the mean CH_4 fluxes in the presence and absence of sunlight, respectively. Within the columns, the different suffix letters (a and b) indicate that the mean N_2O and CH_4 fluxes between years for a given measurement type (i.e. in presence of sunlight or in absence of sunlight) are not significantly different (ANOVA and LSD tests, P>0.05). CH_4 flux was not obtained from tundra sites in 2011/2012 summer.

3.4 Correlation of tundra N_2O and CH_4 fluxes with other environmental variables

The N_2O and CH_4 fluxes showed no significant correlations (P>0.05) with SM, TOC, TN, soil temperatures at the surface (0 cm; ST_0), 5 cm depth (ST_5), 10 cm (ST_{10}), and NH_4^+-N and NO_3^--N contents when the data from all sites were combined (Table 4). Therefore, the environmental variables investigated in this study appear to have no significant effect on N_2O and CH_4 fluxes.

4 Discussion

4.1 Effects of sunlight presence and absence on tundra N_2O fluxes

In this study, no significant correlations (P>0.05) were found between N_2O fluxes and other environmental factors (Table 4). However, N_2O emissions significantly increased in the presence of sunlight, which confirmed that sunlight might stimulate tundra N_2O production in maritime Antarctica. A previous study from the Arctic tundra found that sunlight could stimulate N_2O production (Li et al., 2016). The amount of N_2O efflux was enhanced with increased SM under sunlight in High-Arctic ecosystems with an increase in N_2O consumption in the dark (Stewart et al., 2012). Similarly, higher N_2O fluxes were observed under light conditions in the littoral zones of East Antarctica (Ding et al., 2013).

In general, anaerobic denitrification and aerobic nitrification are major sources of N_2O in soils (Figure 5), whereas the dominance of N_2O consumption over production occurs in tundra soils under constant, totally anoxic conditions (Chapuis-Lardy et al., 2007; Bourbonnais

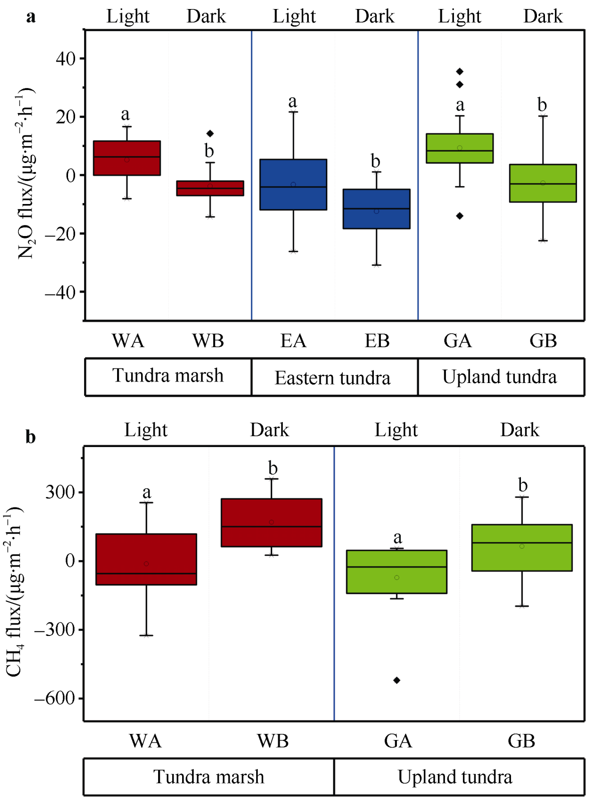

Figure 3 Comparisons of the mean N_2O fluxes (**a**) and CH_4 fluxes (**b**) in the presence and absence of sunlight. The red squares indicate fluxes from the western tundra marsh sites, blue squares indicate fluxes from the eastern tundra sites and green squares indicate fluxes from the upland tundra sites. The bars with different letters (a, b) indicate statistically significant differences (ANOVA and LSD tests, P<0.05) between the mean fluxes measured in the presence and absence of sunlight for each tundra area.

et al., 2017). Higher N_2O emissions in the presence of sunlight suggests that aerobic processes such as nitrification are the most significant contribution to soil N_2O production. Sunlight and associated photosynthetic activities might decrease the release of N_2O by constraining denitrification with increasing O_2 in soils (Moseman-Valtierra et al., 2011). Concentrations of O_2 in the plant root zone were positively correlated with incoming sunlight intensity (Jørgensen et al., 2012). All of the energy for biological metabolism is likely based on sunlight and captured by photosynthetic vegetation (La Rocca et al., 2015). Particularly in our study area, the long days and short nights in the summer and subsequent light conditions favor tundra vegetation photosynthesis. Therefore, increased N_2O production might occur in tundra soils in the presence of sunlight through enhanced nitrification from the generation of O_2 during plant photosynthesis (Zhu et al., 2014).

Additionally, a previous study found that plants are also GHG sources with high N_2O and low CH_4 emissions (Lenhart et al., 2015). Plants can produce N_2O via nitrification (Gogoi and Baruah, 2012; Abalos et al., 2018), and plant aerenchyma can control N_2O fluxes by serving as conduits for gas exchange (Chapuis-Lardy et al., 2007; Bao et al., 2020). Plants transpire significant quantities of N_2O during periods of high transpiration, when N_2O concentrations are high in the soil solution (Gogoi and Baruah, 2012). One possible explanation for higher N_2O emissions from plants under more light might result from enhanced nitrification in soils that supply O_2 to nitrifiers; however, the underlying mechanisms remain unclear. N_2O production in light-dependent vegetation (e.g., *Deschampsia antarctica*) during N assimilation has been observed in maritime Antarctica (Krywult et al., 2013). We found a positive average N_2O flux with sunlight, but not in darkness (Table 3), which might also indicate similarly complex interactions between sunlight and plants regulating N_2O emissions. Li et al. (2011) found that the response of plant N_2O emissions to several environmental parameters was different between dark and sunlight conditions, which suggests a special gas transport mechanism in light-dependent plants. The effect of sunlight on N_2O emissions might result from short-term influences on resource competition between soil microorganisms and plants

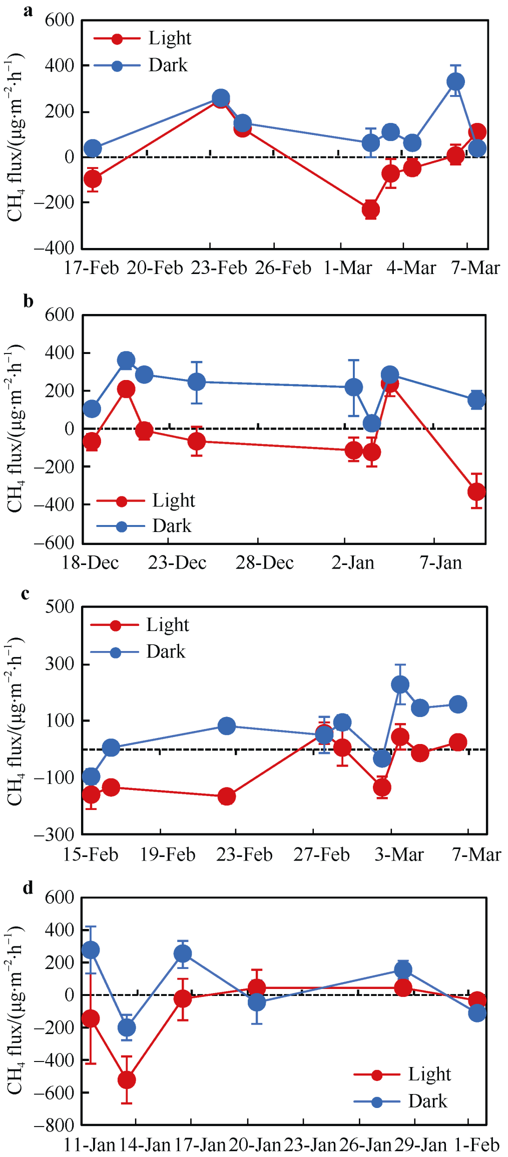

Figure 4 CH_4 flux from the western and upland tundra sites with sunlight presence and absence during the summers of 2013/2014 and 2014/2015. Western tundra CH_4 fluxes in 2013/2014 (**a**) and 2014/2015 (**b**). Upland tundra CH_4 fluxes in 2013/2014 (**c**) and 2014/2015 (**d**). The red lines indicate fluxes in the presence of sunlight, and blue lines indicate fluxes without sunlight.

Table 4 Pearson correlation coefficient between N_2O and CH_4 fluxes and soil physicochemical property during the observation period

Correlation	pH	SM/%	TOC /%	TN/%	NH_4^+-N /(μg·g^{-1})	NO_3^--N /(μg·g^{-1})	ST_0 /℃	ST_5 /℃	ST_{10} /℃	CT /℃
N_2O Flux	−0.33	0.21	−0.22	−0.27	0.04	−0.12	0.14	0.12	0.24	−0.36
CH_4 Flux	0.47	0.34	0.08	0.11	−0.59	−0.50	−0.17	−0.11	−0.33	0.09

Note: SM, TOC and TN indicate soil moisture, total organic carbon and total nitrogen, respectively. ST_0, ST_5, ST_{10} and CT indicate 0 cm soil temperature, 5 cm soil temperature, 10 cm soil temperature and chamber temperature, respectively.

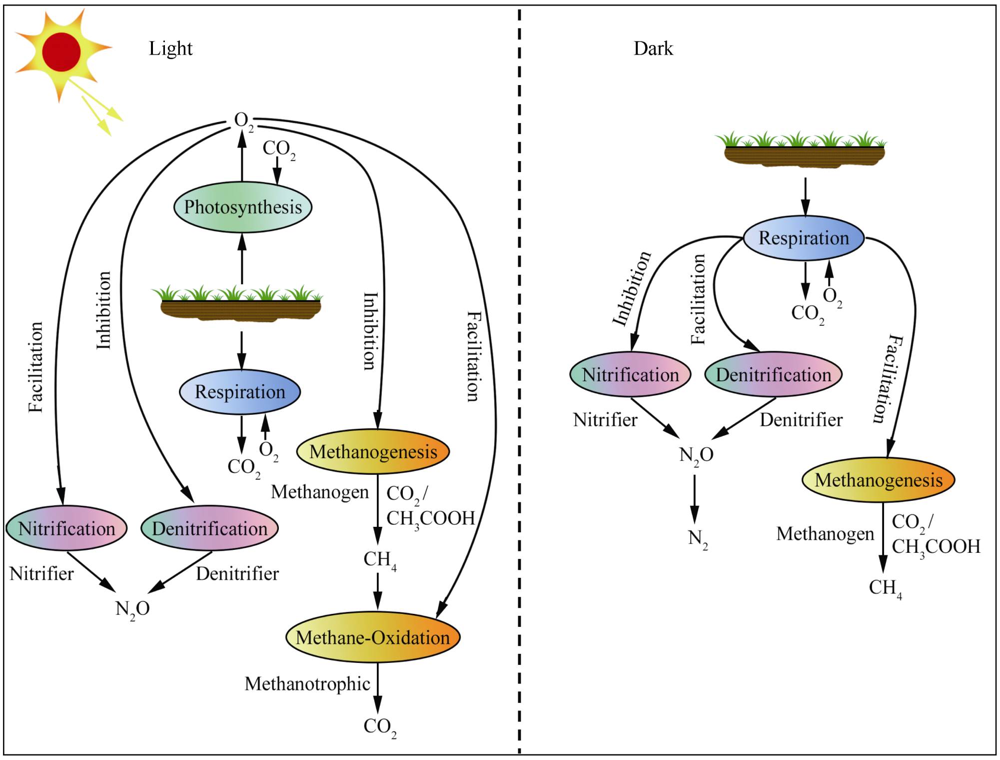

Figure 5 Schematic of possible biochemical reactions in the transparent and opaque chambers.

in response to light-driven changes in O_2 availability (Stewart et al., 2012). Accordingly, N_2O flux models would need to be established and calibrated to plant community composition (Jørgensen et al., 2012; Stewart et al., 2012). For future studies of tundra N_2O fluxes, researchers should consider the influence of soils and assess the individual contributions of plant species under different light conditions.

Negative N_2O fluxes occurred at all sites in the absence of sunlight (Figure 2). The negative fluxes from our measurements are similar to previous studies (−1.3 to −126.7 $\mu g \cdot m^{-2} \cdot h^{-1}$) conducted in diverse terrestrial ecosystems (Dalal and Allen, 2008; Holst et al., 2008). Aerobic denitrification acts as the pathway for a N_2O sink in low-O_2 soil (Chapuis-Lardy et al., 2007; Krywult et al., 2013; Zhu et al., 2014), which leads to the consumption of N_2O during denitrification because of the reduced NO_2^- supplied to denitrifiers by nitrification (Jungkunst and Fiedler, 2007). Therefore, most previous studies that showed negative fluxes in Antarctic tundra marshes only considered anaerobic denitrification in soil under waterlogged conditions (Gregorich et al., 2006; Vieira et al., 2013; Zhu et al., 2014). In this study, a N_2O sink was present in upland tundra soils with low SM (42.8%–45.7%) in the absence of sunlight. Plant photosynthesis might be constrained in light-limited conditions with the result of decreased O_2 production, especially in tundra with high moss and lichen cover (Li et al., 2016). Therefore, such anaerobic denitrification in the dark could lead to a lowering of N_2O efflux or the switch to acting as a N_2O sink in maritime Antarctica.

4.2 Effects of sunlight presence and absence on tundra CH_4 fluxes

Similar to N_2O, no significant correlations (P>0.05) were found between CH_4 fluxes and other environmental factors except for sunlight (Table 4). In this study, sunlight significantly increased tundra CH_4 uptake in maritime Antarctica, which is similar to tundra sites in the High Arctic (e.g., Ny-Ålesund; Li et al., 2016). In our study area, the tundra contains large areas colonized by mosses and lichens that account for ~90%–95% of vegetation coverage (Zhu et al., 2014; Bao et al., 2018), and their photosynthesis under sunlight can emit O_2 while inhibiting CH_4 release (Frenzel and Karofeld, 2000; von Fischer et al., 2010). Generally, both CH_4 production and oxidation are partially inhibited by O_2 availability (Bao et al., 2016; Michaud et al., 2017). Additionally, root oxidase activity is closely related to root respiration, and a small fraction of O_2 that is not consumed by respiration probably diffuses into the rhizosphere and is consumed by the oxidation of reduced substances, including CH_4 (Gilbert and Frenzel, 1998). Within the C balance, tundra CH_4 uptake and emissions might be influenced by O_2 concentration fluctuations under different light conditions (von Fischer et al., 2010; McEwing et al., 2015). We found negative CH_4 fluxes at all sites in the presence of sunlight (Figure 4), which confirms that sunlight can stimulate tundra CH_4 uptake in maritime Antarctica.

CH_4 cycling is accomplished by a variety of soil microorganisms (Whalen, 2005; Michaud et al., 2017) with CH_4 produced by methanogens under anaerobic conditions and consumed by methanotrophs in aerobic conditions (Figure 5). Broadly, the balance between microbial production and consumption is critical as it drives the soil–atmosphere CH_4 exchange (Frenzel and Karofeld, 2000; Whalen, 2005; von Fischer et al., 2010). O_2 diffusing into tundra soil can cause patterns of reduced and oxidized zones during plant growth and development, and this may greatly influence the microbial assemblage (e.g., methanogens and methanotrophs; Schmidt et al., 2011). High O_2 concentrations in the presence of sunlight could dramatically decrease soil CH_4 emissions by facilitating aerobic CH_4-oxidizing bacteria in surface or subsurface soil layers (Whalen, 2005; McEwing et al., 2015; McNicol and Silver, 2015). Over short timescales, soil CH_4 emissions have been showing to be strongly affected by aerobic microbial respiration rates (McNicol and Silver, 2015). Therefore, O_2 from tundra vegetation photosynthesis is one important component of the soil redox environment in the presence of sunlight (Conrad, 1996). Additionally, it is a highly favored oxidant with direct effects on the activity of methanotrophs and methanogens, could inhibit tundra CH_4 emissions and stimulate CH_4 oxidation in maritime Antarctica.

Furthermore, substrate quality is an important constraint on methanogenesis in tundra soil, with previous research suggesting that substrate supply is the major control on CH_4 production once anaerobic conditions are reached (Yavitt et al., 1997; Coles and Yavitt, 2002; Whalen, 2005). Sunlight can impact vegetation cover and high vegetation cover is conducive to producing autochthonous dissolved organic matter, which in turn could supply C substrates for methanogenic bacteria, especially in tundra wetland ecosystems (Li et al., 2016). Photosynthesized C could stimulate methanogenic activity, resulting in more soil CH_4 emissions under sunlight (Dacey et al., 1994; Li et al., 2016). In the presence of sunlight, net CH_4 fluxes might be closely related to CH_4 oxidation via direct microbial activity and photosynthesized C substrates could greatly enhance the production of CH_4 (von Fischer et al., 2010; Schmidt et al., 2011; McNicol and Silver, 2015). However, in the total absence of sunlight, respiration of tundra vegetation and soil microorganisms would decrease concentrations of O_2 (Li et al., 2016) and enhance the activity of methanogens through the formation of an anaerobic environment. Our results confirm that diverse concentrations of O_2 in the absence and presence of sunlight might be enough to drive changes in tundra CH_4 emissions in maritime Antarctica.

4.3 Implication of sunlight presence and absence in tundra N_2O and CH_4 balance

N_2O and CH_4 emissions in relation to environmental factors have been research foci over the past 3 decades. Several environmental variables involved in N transformations could influence soil N_2O exchange, such as ground temperature (Zhu et al., 2005; Carvalho et al., 2010; Zhu et al., 2014; Lenhart et al., 2015), soil humidity (Lohila et al., 2010), pH (Stevens et al., 1998), microtopography (Zhu et al., 2014), mineral N availability (Jørgensen et al., 2012) and permafrost thawing (Repo et al., 2009; Elberling et al., 2010). Soil temperature, moisture and vegetation cover were key factors affecting the processes of CH_4 exchange (Gregorich et al., 2006; Ullah and Moore, 2011; Zhu et al., 2013, 2014; Bao et al., 2016, 2018). Additionally, potential effects of ultraviolet radiation on N_2O and CH_4 emissions have been discussed in previous studies (Bao et al., 2018). However, it is difficult to assess the individual contributions of driving factors in a given area because of temporal and spatial variability in soil trace gas emissions (Mosier, 1998). The key parameters driving patterns in N_2O or CH_4 fluxes have yet to be consistently identified (Stewart et al., 2012). However, our results suggest that N_2O and CH_4 fluxes in the absence and presence of sunlight were considerably variable and confirmed that sunlight likely plays a key role in driving C–N cycles in maritime Antarctic tundra.

Our results indicate that, on average, the presence of sunlight increased tundra N_2O emissions by 10.3 $\mu g \cdot m^{-2} \cdot h^{-1}$ and CH_4 uptake by 160.3 $\mu g \cdot m^{-2} \cdot h^{-1}$ (Table 3). These results are comparable to those from High Arctic tundra (Li et al., 2016) and the littoral algal-rich zone of Lake Daming, East Antarctica (Ding et al., 2013; Figure 6). Therefore, sunlight might have a key effect on N_2O and CH_4 budgets in polar regions. Especially in Antarctica, the diurnal pattern with long ST and short nights in summer means that light conditions, as one key environmental factor, might be more important here than in other global areas. Excluding the effects of sunlight might lead to an underestimate of the N_2O budget, but an overestimate of the CH_4 budget in Antarctic tundra ecosystems.

5 Conclusions

Overall, the presence of sunlight significantly increased N_2O emissions and CH_4 uptake rates by 10.3 and 160.3 $\mu g \cdot m^{-2} \cdot h^{-1}$, respectively. Therefore, the presence of sunlight might have a key effect on N_2O and CH_4 budgets in maritime Antarctica. The exclusion of sunlight might underestimate the N_2O budget but overestimate the CH_4 budget in maritime Antarctic tundra ecosystems. Projecting future

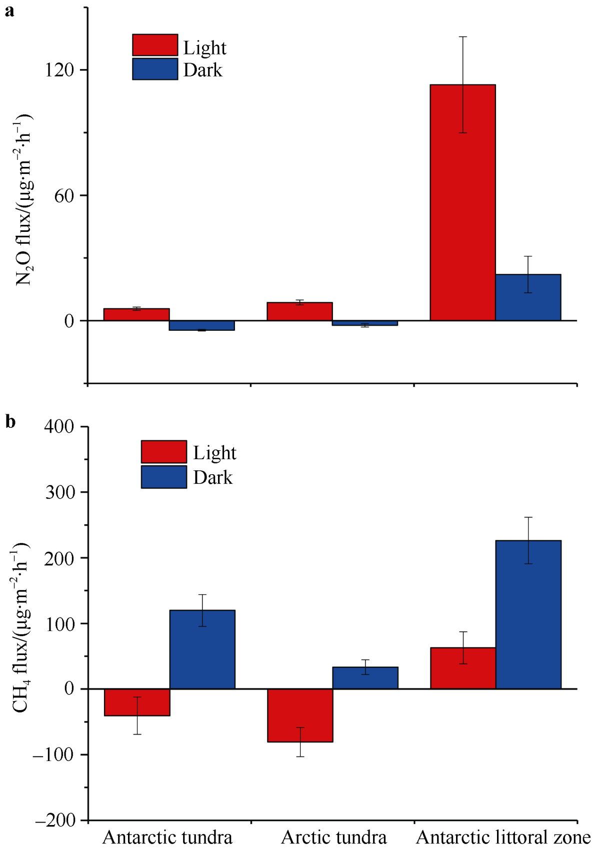

Figure 6 Comparisons of N_2O (**a**) and CH_4 (**b**) fluxes between maritime Antarctic tundra, Arctic tundra and Antarctic littoral zone in the presence and total absence of sunlight.

effects of climate change on N_2O and CH_4 fluxes in the presence/absence of sunlight will remain a considerable challenge and will require more high-frequency and long-term monitoring across polar regions.

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Appendices

1 Study area and investigation sites

One study area was located on Ardley Island (62°13′S, 58°56′W; 2.0 km length and 1.5 km width). This island was defined as an area of special scientific interest by the Scientific Committee of Antarctic Research (SCAR). The tundra ecosystem can be categorized into the following three types of tundra according to local topography and penguin activities: (i) The lowland tundra marsh (TM), which is located in the western coast of this island with the vegetation coverage of about 95%. Mosses and lichens dominate the vegetation in the poorly drained tundra areas. The area around TM was occupied by penguin population during the historical period dating to 3000 years ago although at present penguins have not colonized this area. (ii) The hilly and relatively dry upland tundra in the middle with the vegetation coverage of 90%–95%. Penguins lack in the middle upland tundra. (iii) The eastern tundra (ET) which concentrates in the east of this island. Every summer this area supports approximately 10200 individuals including Gentoo penguins (*Pygoscelis papua*), Adelie penguins (*Pygoscelis adeliae*) and Chinstrap penguins (*Pygoscelis antarctica*). The nesting sites in penguin colonies are highly enriched with penguin guano and devoid of vegetation due to toxic overmanuring and trampling. However, tundra patches, almost completely (90%–95%) covered by cushions of mosses and lichens, have formed in marginal zones of penguin nesting sites.

Another study area was on Fildes Peninsula (61°51′S–62°15′S, 57°30′W–59°00′W), which is situated in the southwestern part of King George Island with an area of about 30 km^2. The communities formed of lichens and mosses dominate over the vegetation in the peninsula. An upland tundra (UT) was in the northwest of Chinese Great Wall Station located on the peninsula, about 500 m apart from this scientific station. The upland tundra was almost dry with the elevation of about 40 m a.s.l. The sampling grounds were covered completely with mosses (*Bryum Pseudotriquetrum* and *Bryum muelenbeckii*) and lichens (*Usnea* sp.), and the depth of vegetation layer is about 5–10 cm. Under the vegetation cover is an organic clay layer of about 10–15 cm.

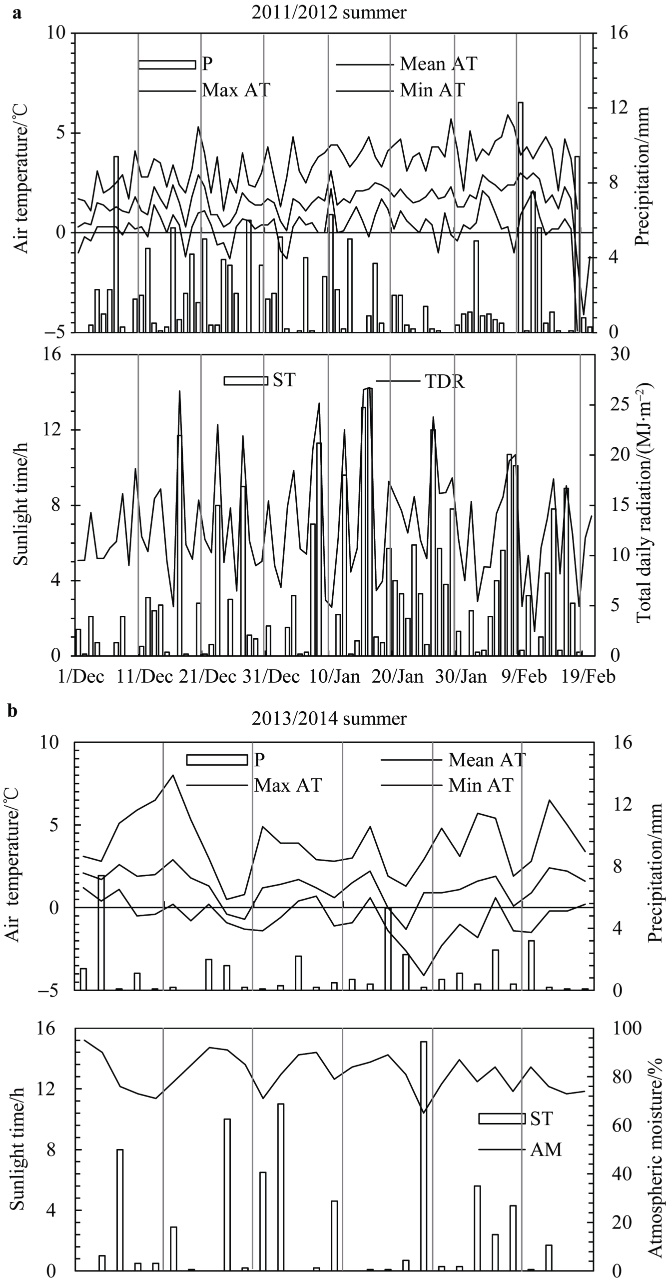
2 *In situ* N_2O and CH_4 flux measurement

The fluxes of N_2O and CH_4 from tundra sites were determined using a static chamber technique. Open-bottomed transparent or opaque plexiglass chambers (50×50×25 cm^3) were placed on the PVC collars installed at the measurement sites. These collars enclosed an area of about 0.25 m^2 and were inserted into the soils to a depth of about 5 cm at each site. The use of flux collars allows the same spot to be measured repetitively, minimizes the site disturbance, and ensures that flux chambers are well sealed since the chambers fit into a water-filled notch in the collars. The average height of the chamber was 20 cm above the ground, which met the minimum required without influencing gas diffusion patterns that would prevail under normal atmospheric pressure.

During N_2O and CH_4 flux measurements, the chambers were inserted into the water-filled notch of the collars. Upon enclosure of the collars with cover chambers, headspace gas samples were collected at 0-, 10- and 20-min intervals with a both ends needle connected to pre-evacuated glass vials (17.8 mL) stopped with butyl rubber septa. For each gas flux measurement, a total of three samples were withdrawn from each chamber after enclosure. Air temperature inside the chambers was simultaneously measured through the thermometer installed on the chambers. The chambers were removed from the collars immediately after the gas sampling to minimize potential microclimatic modification of the sampling area. In our study area, the cloudy, foggy, snowy, and sleety days dominate over the summer due to effects of polar cyclone. The changes in chamber temperature (generally 1–4 ℃) during translucent chamber enclosure have insignificant effects on local soil temperature, thus the potential effects of chamber heating on the fluxes can be neglected in our study area. N_2O and CH_4 fluxes were determined between 9:00–11:00 (local time) at all the sites, resulting in two replicate measurements per site, and measuring order was varied to ensure that the measuring time did not bias the results. Our observation period fell within polar day during the austral summer, and the measurements at 9:00–11:00 (local time) can approximately represent the actual N_2O and CH_4 fluxes in local tundra environment.

3 Climate conditions

During the three summer periods of 2011–2015, air and ground temperatures showed large fluctuations (Figure A1 and Table A1). The mean AT smoothly increased from December to January, and then declined until February. The mean air and ground temperatures in summer 2014/2015 (1.7 and 5.4 ℃) were significantly higher (P<0.01) than those in summer 2011/2012 (1.6 and 4.1 ℃) and in summer 2013/2014 (1.3 and 4.3 ℃). The daily minimum air and ground temperatures were often below 0 ℃, while the daily maximum air and ground temperatures were generally above 5 ℃. The total precipitation varied significantly (P<0.01) between the summers of 2011/2012 (166 mm) and 2014/2015 (124 mm), and total sunlight time (ST) was 220 h and 153 h, respectively (Table A1). Overall, more precipitation occurred in summer 2011/2012 and summer 2014/2015 was relatively warmer and drier than summer 2011/2012.



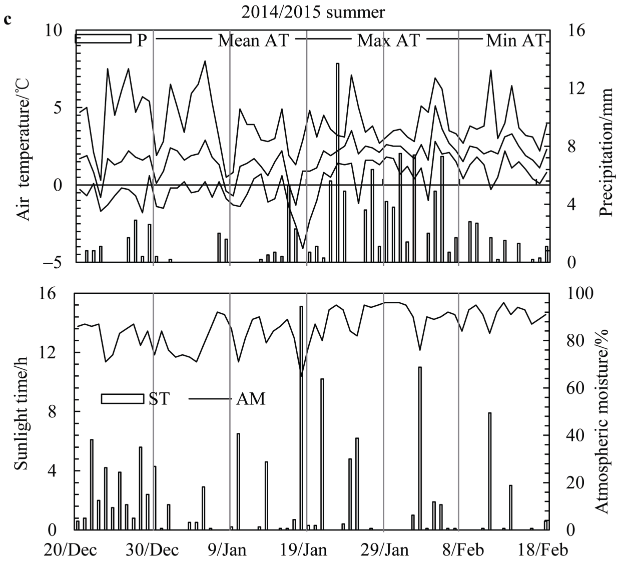


Figure A1 Meteorological characteristics during the summertime in the study area. 2011/2012 summer (**a**); 2013/2014 summer (**b**); 2014/2015 summer (**c**). Note: The data for total daily radiation (TDR) during 2013/2014 and 2014/2015 summer and the data for atmospheric moisture (AM) during 2011/2012 summer were not obtained from Chinese Great Wall Station. AT, P and ST indicated daily mean air temperature, precipitation, and sunlight time, respectively.

Table A1 Summary of climatic data set in the study area during N_2O and CH_4 flux observation period

Climatic factors	Summer 2011/2012	Summer 2013/2014	Summer 2014/2015
Daily mean AT (± SD)/℃	1.6±0.1	1.3±0.2	1.7±0.1
Maximum AT/℃	5.9	6.5	7.5
Minimum AT/℃	−4.9	−4.1	−4.1
Number of day at mean AT>0 ℃	80	26	78
Number of day at mean AT<0 ℃	3	3	5
Daily mean GT (± SD)/℃	4.1±0.2	4.3±0.5	5.4±0.6
Maximum GT/℃	13.0	16	17
Minimum GT/℃	−3.0	−2.8	−3
Number of day at mean GT>0 ℃	72	26	69
Number of day at mean GT<0 ℃	11	3	14
Total precipitation/mm	166.3	27.2	124
Total sunlight time/h	219.7	76.2	152.9

Note: AT and GT indicated daily air temperature and ground temperature, respectively.