

## Temporal and spatial variations of atmospheric methane concentration and $^{13}\text{C-CH}_4$ near the surface on the Millor Peninsula, East Antarctica

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**Abstract** During the 22nd Chinese Antarctic Research Expedition (CHNARE-22, 2005/06), the atmospheric gas samples near the surface were taken on the Millor Peninsula and adjacent areas, east Antarctica, using Tedlar gas bags. The methane ( $\text{CH}_4$ ) concentration and  $^{13}\text{C-CH}_4$  in those samples were analyzed in the laboratory. The average value of atmospheric  $\text{CH}_4$  concentration on this peninsula was  $(1.87 \pm 0.12) \times 10^{-6}$ , slightly higher than the global average  $\text{CH}_4$  concentration. The summertime variation of  $\text{CH}_4$  concentrations showed a large fluctuation, corresponding to the variation of air temperatures. The average  $^{13}\text{C-CH}_4$  was  $(-38.26 \pm 0.52)\text{‰}$ .  $\text{CH}_4$  concentrations and  $^{13}\text{C-CH}_4$  at different sites varied from  $1.74 \times 10^{-6}$  to  $2.56 \times 10^{-6}$  and from  $-39.31\text{‰}$  to  $-31.25\text{‰}$ , respectively. The factors affecting  $\text{CH}_4$  concentrations and  $^{13}\text{C-CH}_4$  values have also been discussed in this study.

**Key words** Antarctica, Millor Peninsula, atmosphere, methane, carbon isotope

### 1 Introduction

Methane ( $\text{CH}_4$ ) is an important, reactive greenhouse gas at trace level<sup>[1-3]</sup>.  $\text{CH}_4$  concentration has increased to twice since the industrial revolution. In recent 20—30 years, its increase rate obviously falls down. At present, the global atmospheric  $\text{CH}_4$  concentration is about  $1.8 \times 10^{-6}$ <sup>[4-5]</sup>. Methane sources and sinks have been extensively studied from all kinds of ecosystems on the globe, indicating that about 70% of  $\text{CH}_4$  is from anthropogenic sources and 30% of  $\text{CH}_4$  is from natural sources<sup>[6]</sup>. Anthropogenic sources include fossil fuel combustion, waste landfill, ruminants, paddy fields and biomass burning, etc. Natural sources include wetland, termites and ocean, etc.<sup>[7]</sup>. The important sink of atmospheric  $\text{CH}_4$  is the chemical reaction with OH in the troposphere<sup>[8]</sup>, and the minor sink is the consumption by the water-unsaturated soils and transportation into the stratosphere<sup>[9, 10]</sup>.

Recently, the isotopic technology is a rapidly developing method for the studies on

CH<sub>4</sub> sources and sinks<sup>[11-13]</sup>. The CH<sub>4</sub> from different sources has different isotopic characteristics due to the isotopic fractionation effect. The stable isotopic values of CH<sub>4</sub> depend on the methanogenic processes. The <sup>13</sup>C-CH<sub>4</sub> from heat effect sources (such as biomass burning and fossil fuel combustion) generally shows a high value, whereas <sup>13</sup>C-CH<sub>4</sub> from methanogenic bacteria shows a low value. The value of <sup>13</sup>C-CH<sub>4</sub> in atmospheric samples may be the mixture of multi-sources. Therefore, the information about atmospheric CH<sub>4</sub> sources can be obtained using the isotope-tracing technology.

Currently, the data about atmospheric CH<sub>4</sub> concentration and its carbon isotopic value near the land surface in Antarctica are still scarce. During the 22nd Chinese Antarctic Research Expedition (CHNARE-22) of the austral summer 2005/2006, air samples were collected on the Millor Peninsula and adjacent areas, east Antarctica. In this study, the CH<sub>4</sub> concentration and <sup>13</sup>C-CH<sub>4</sub> were measured, and temporal and spatial variations of CH<sub>4</sub> concentration and its <sup>13</sup>C were analyzed and discussed.

## 2 Study area and methods

### 2.1 Study area

The sampling areas are located on the Millor Peninsula and adjacent areas, around the Zhongshan Station, east Antarctica (Fig 1). This peninsula is one of the several main ice-free areas along the coast of Antarctica in summer. It has the cold and dry Antarctic climate due to the effects of circular cyclone and high pressure from the Antarctic continent<sup>[14, 15]</sup>. According to the meteorological records from the Zhongshan Station, mean annual air temperature is around -10 °C. Precipitation is about 250 mm. Mean annual relative humidity is about 60%. The vegetation is very sparse, the biological and chemical weathering processes are weak and no true soil develops in this area due to severe climatic environment and exposed bedrock<sup>[15]</sup>.

A normal observation site for atmospheric CH<sub>4</sub> was set up on the top of a hill (altitude of about 30 m) to the southwest of Zhongshan Station (Fig 1, Site 4). And the prevailing wind direction there is mostly southeast. Therefore the scientific station has an insignificant effect on such sampling site. In order to compare the temporal variations of atmospheric CH<sub>4</sub> concentration and its <sup>13</sup>C from different sources, three normal sites (named as TJ, ZW, GW) were set up in Wolong Marsh (Fig 1). The soil water contents increased in turn: site TJ with a thick layer of alga at the bottom; site ZW with much alga and continuously flooded; site GW with much moss and alga. During most of time every year, Wolong Marsh is covered with accumulated snow and the soils are frozen. Accumulated snow and frozen soils melt, and tundra wetland are exposed every summer (from December to February)<sup>[16]</sup>. In addition, gas samples were collected in other potential CH<sub>4</sub> source areas such as Emperor penguin colony, Nella Bay, Mochou Lake and Tuanjie Lake. The air samples at the hilltop (height about 50 m) behind Russian station and Luojiashan Glacier were also collected. Then, the temporal and spatial variations of atmospheric CH<sub>4</sub> concentration near the surface can be reflected on this peninsula in the summer. All the sampling sites were illustrated in Fig 1.

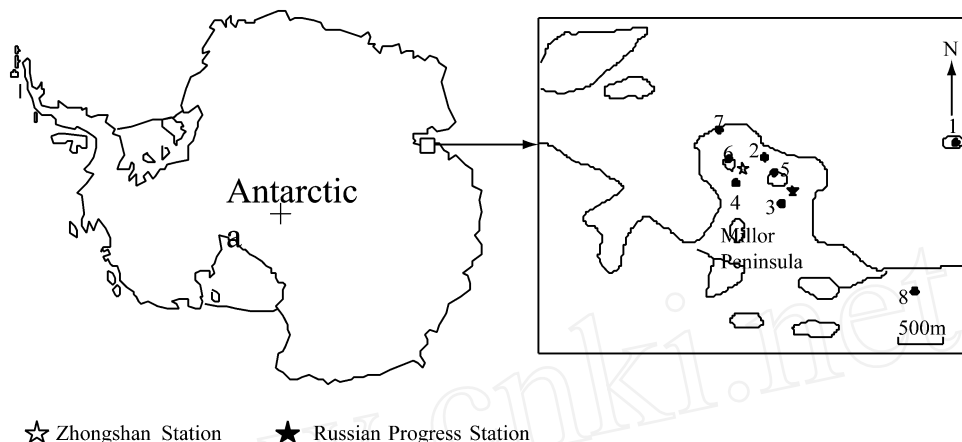


Fig 1 Study area and air sampling sites on the Millor Peninsula: 1. Emperor penguin colony; 2. Salt marsh of Wolong Beach; 3. Hilltop behind Russian Progress Station; 4. Hilltop behind Zhongshan Station; 5. Tuanjie Lake; 6. Mochou Lake; 7. Nella Bay; 8. Luojiashan Glacier

## 2.2 Gas sampling

Gas samples at three normal sites in Wolong Marsh were collected at 2 m above the land surface from December 23, 2005 to February 17, 2006, using vacuum vials (18 ml) made in Japan. High vacuum inside the vial can maintain for a year at least<sup>[1]</sup>. At other sites, 0.5 L Tedlar gas bags were used to collect gas samples. The bags were washed with the local air for five times before sampling. The air samples were sucked from the outside through silicic rubber tube installed to the tread pump and stored in Tedlar gas bags (with polypropylene valves). The sampling height was about 2 m. The sampling time was 10:00 and 22:00 (local time) every day to compare the night-day differences of CH<sub>4</sub> concentration and its <sup>13</sup>C. The air samples stored in Tedlar bags were almost stable due to the airtight and light-escaped properties of Tedlar bags<sup>[17,18]</sup>. In total 79 air samples near the surface on Millor Peninsula were collected during the summer. Some samples were eliminated due to human pollution, and the data for the rest 70 samples were analyzed.

## 2.3 Determination of CH<sub>4</sub> concentration

CH<sub>4</sub> concentrations in all 70 air samples were determined using GC (Shimazu GC-12A) with a flame ionization detector (FD). The chromatographic column was 2m stainless-steel column. Filling material was 5 A molecular sieve. The column and detector temperatures were 80 °C and 200 °C, respectively. The flow rates of N<sub>2</sub>, H<sub>2</sub> and air were 40 mL · min<sup>-1</sup>, 35 mL · min<sup>-1</sup> and 350 mL · min<sup>-1</sup>, respectively. CH<sub>4</sub> standard gas was produced in Nanjing Special Gas Plant. The variance coefficient for standard gas was within 0.1% ~ 0.6% in 24 h. The method of CH<sub>4</sub> measurement can be found in a literature<sup>[1]</sup>.

## 2.4 Determination of <sup>13</sup>C for CH<sub>4</sub>

The <sup>13</sup>C value for CH<sub>4</sub> was measured using Thermo Finnigan MAT-253 Isotopic Mass

Spectrometer in State Key Laboratory of Soil and Sustainable Agriculture, Nanjing Institute of Soil Science. This mass spectrometer has a fully automated interface for the pre-GC concentration (PreCon) of trace gases. The procedures are as follows<sup>[19]</sup>:

The glass bottles were vacuumized before the gas samples were analyzed, and then 100 ml gas samples were immediately injected into the bottles. If the volume of gas sample is lower than 100 ml, the inert gases without CH<sub>4</sub> must be added to make the bottle in normal pressure. The bottles with the gas samples were installed into PreCon. After their thresholds were blown by He, the valves at both ends of gas sampling bottles were opened, and then the gas samples were blown into the cold trap by He. The volatile components (N<sub>2</sub>, O<sub>2</sub>, Ar, CH<sub>4</sub>) enter into 1000 °C burning furnace via cold traps (-196 °C). There was an alumina oxidative pipe filled with three 0.13 mm nickel wires in the burning furnace and CH<sub>4</sub> was oxidized forming CO<sub>2</sub> and H<sub>2</sub>O. The CO<sub>2</sub> from CH<sub>4</sub> was collected by another cold trap and transported into the third cold trap. Then CO<sub>2</sub> went into the GC and was separated from other compositions. The calibrated standard CO<sub>2</sub> gas was injected into the ionic source three times continuously every 30 seconds. Three cups received the ionic flows of  $m/z 44 [^{12}\text{C}^{16}\text{O}^{16}\text{O}]^+$ ,  $m/z 45 [^{13}\text{C}^{16}\text{O}^{16}\text{O}]^+$  and  $m/z 46 [^{12}\text{C}^{16}\text{O}^{18}\text{O}]^+$ , respectively. The peak intensity of  $m/z 44$  was controlled within 2V-3V by adjusting the flow rate of reference gas. The No. 2 peak was set as the standard sample peak. The CH<sub>4</sub> peak occurred at about 870 s. The ratio line was a positive peak. Because CO<sub>2</sub> reference gas (code, Lab Gas) was calibrated, according to the ratios of the CO<sub>2</sub> peak for the working standard to the intensity for three ionic flows  $m/z 44$ ,  $m/z 45$  and  $m/z 46$ , the  $^{13}\text{C}_{\text{PDB}}$  for CO<sub>2</sub> from CH<sub>4</sub> was obtained relatively to PDB for the international standard. The standard deviations for the  $^{13}\text{C}$  of CH<sub>4</sub> in the compressed air were  $\pm 0.196\%$  through 9 repeated measurements.

### 3 Results and discussions

#### 3.1 Summer variations of atmospheric CH<sub>4</sub> concentration near the surface on Millor Peninsula

CH<sub>4</sub> concentrations and air temperatures at the observation site on the hilltop behind Zhongshan Station showed evident variations in the summer (Fig 2). Atmospheric CH<sub>4</sub> concentrations at 10:00 were low and fluctuated steadily in January, reached the maximum (about  $2.08 \times 10^{-6}$ ) at the start of February and then dropped quickly in the middle ten days of February. The concentrations at 22:00 were lower than the global average CH<sub>4</sub> concentration ( $1.8 \times 10^{-6}$ ) at the start of January, reached the maximum ( $2.05 \times 10^{-6}$ ) in the later half of January and slightly dropped in February. In addition, atmospheric CH<sub>4</sub> concentrations in daytime were lower than those in nighttime in January while the results were opposite in February. The average concentration of all samples was  $(1.87 \pm 0.12) \times 10^{-6}$ , which was slightly higher than the global average (about  $1.8 \times 10^{-6}$ ). Summertime air temperatures showed a large fluctuation with the date, whereas atmospheric CH<sub>4</sub> concentrations showed lag response to air temperatures (Fig 2).

During the summertime, atmospheric CH<sub>4</sub> concentrations in Wolong Marsh showed

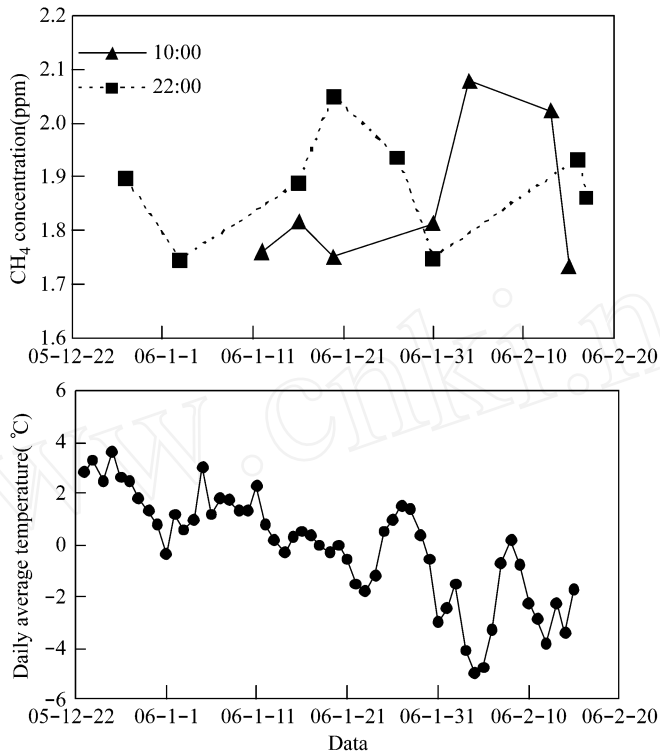


Fig 2 The variations of atmospheric CH<sub>4</sub> concentration and air temperature at the normal site on the hilltop behind Zhongshan Station on the Millor Peninsula Note: The data for air temperature were from weather station of Zhongshan Station The gas sampling was not conducted at 10: 00 before January 10, 2006 and the data were lost

great fluctuation (Fig 3). Similar changing trends in the three normal sampling sites at the marsh can be observed. On the whole, CH<sub>4</sub> concentrations at site GW were higher than those at other two sites. CH<sub>4</sub> concentrations at site ZW reached the maximum (about  $2.23 \times 10^{-6}$ ) during the first ten days of January, dropped to about  $1.92 \times 10^{-6}$ , fluctuated between  $1.9 \times 10^{-6}$  and  $2.0 \times 10^{-6}$  during the middle and last ten days of January and then rised in February. Three peaks of CH<sub>4</sub> concentration at site GW were observed in the first ten days of January, the middle ten days of January and the first ten days of February, respectively. The fluctuation of the concentrations at site TJ was small and two small peaks appeared in the first and the middle ten days of January. The average CH<sub>4</sub> concentration of all samples in Wolong Marsh was  $(2.05 \pm 0.10) \times 10^{-6}$ , evidently higher than the global average and that at the site of the hilltop behind Zhongshan Station. The air temperature showed the similar variations at three sites. The temperature dropped with the date and strongly fluctuated in the first ten days of February. T-test (ZW-GW:  $t = -2.207, p = 0.037$ ; GW-TJ:  $t = 2.596, p = 0.017$ ; ZW-TJ:  $t = 0.211, p = 0.835$ ) indicated that the relationship of CH<sub>4</sub> concentration between ZW-GW and GW-TJ was considered statistically significant. Air temperature and CH<sub>4</sub> emission intensity of different sites in Wolong Marsh may affect atmospheric CH<sub>4</sub> concentration near the surface.

Atmospheric average CH<sub>4</sub> concentrations at the sites on the hilltop behind Zhongshan

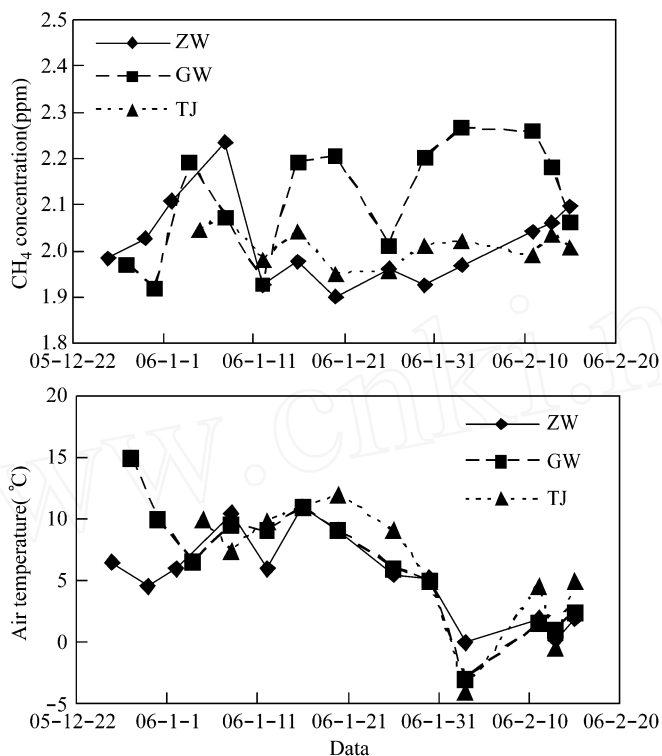


Fig 3 The summertime variations of atmospheric CH<sub>4</sub> concentrations and air temperature at three normal sites of Wolong Marsh on the Millor Peninsula. Note: The data for air temperature at the different sites were in situ obtained using the thermometers. The measurement time for air temperature was simultaneous to that of gas sampling.

Station and in Wolong Marsh were all higher than global average concentration (nearly  $1.8 \times 10^{-6}$ ), which may be due to CH<sub>4</sub> emission from lake and marsh, human activity and sea animal excreta in this area. Wolong Marsh is situated near the sewage of Zhongshan Station, and the algae bloomed in the marsh<sup>[20,21]</sup>. Algae and human excrements may be important sources of organic matter in the marsh, which produced and emitted CH<sub>4</sub> by the methanogenic bacteria into the local atmosphere. The in situ measurements of CH<sub>4</sub> flux indicated that the fluxes ranged from  $(170.4 \pm 68.6) \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  to  $(182.8 \pm 13.5) \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$  at sites ZW, GW, TJ<sup>[16]</sup>. Therefore atmospheric CH<sub>4</sub> concentrations in Wolong Marsh were higher than those on the hilltop behind Zhongshan Station due to high CH<sub>4</sub> emissions from the wetlands. Many lakes distributed on this peninsula and they may be another important sources of atmospheric CH<sub>4</sub> in this region.

In addition, the colonies of Emperor penguins and Adélie penguins are situated in the northeast of this peninsula. Results of measurement on the Fildes Peninsula, west Antarctica, showed high CH<sub>4</sub> fluxes ( $(227.9 \pm 212.9) \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ) from penguin colonies<sup>[22,23]</sup> due to the deposition of a large amount of penguin guano. In the austral summer, penguin guano could quickly decompose and emit CH<sub>4</sub> into atmosphere under the effects of microorganism and high temperature<sup>[24-26]</sup>. In addition, the rate of CH<sub>4</sub> production and emission could be accelerated by the soil freeze-thawing processes. The Millor Peninsula sit-

uated downwind from penguins colonies<sup>[18]</sup>, therefore high concentration atmospheric CH<sub>4</sub> there may be partly from the emissions of penguin colonies

### 3.2 Summer variations of atmospheric <sup>13</sup>C-CH<sub>4</sub> near the surface on the Millor Peninsula

Average <sup>13</sup>C-CH<sub>4</sub> on the Millor Peninsula in the summertime was - 38.26‰ ± 0.52‰, ranging from - 39‰ to - 38‰. Most of <sup>13</sup>C-CH<sub>4</sub> values at 10:00 were slightly lower than those at 22:00 (Fig 4). According to mass balance characteristic of isotope, carbon stable isotopes of atmospheric CH<sub>4</sub> were due to the mixture of enriched-<sup>13</sup>C-CH<sub>4</sub> and depleted-<sup>13</sup>C-CH<sub>4</sub> from different sources or the fractionation of CH<sub>4</sub> sinks<sup>[27]</sup>. Stevens<sup>[27]</sup> measured the global atmospheric methane concentration and its <sup>13</sup>C in 1982, indicating that the average concentration was 1.66 × 10<sup>-6</sup> and average <sup>13</sup>C was - 47.0 ± 0.3‰. Methane concentration (about 1.87 × 10<sup>-6</sup>) and its <sup>13</sup>C (about - 38.26‰) near the surface on the Millor Peninsula were evidently higher than those measured by Stevens in 1982<sup>[27]</sup>.

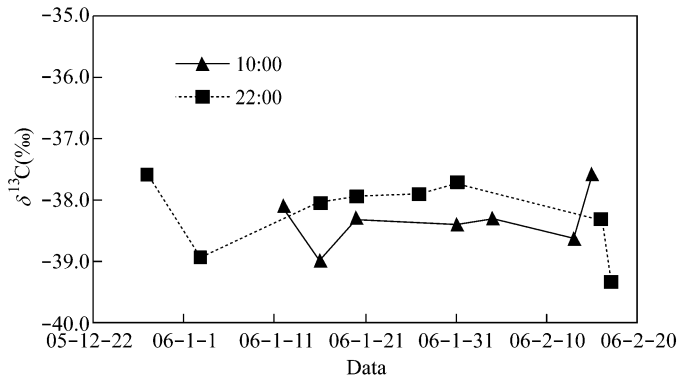


Fig 4 The variations of <sup>13</sup>C of atmospheric CH<sub>4</sub> on the Millor Peninsula

There are three kinds of important sources of atmospheric CH<sub>4</sub> including biogenic sources, fossil fuel burning and biomass burning. The <sup>13</sup>C-CH<sub>4</sub> ranges of those sources are - 65‰ - - 55‰, - 50‰ - - 30‰ and - 28‰ ~ - 12‰, respectively<sup>[28]</sup>. CH<sub>4</sub> from biogenic source is depleted in <sup>13</sup>C while CH<sub>4</sub> from fossil fuel burning and biomass burning is relatively enriched in <sup>13</sup>C. Besides the biogenic sources like wetland and penguin colony (depleted-<sup>13</sup>C-CH<sub>4</sub>), the anthropogenic sources (enriched-<sup>13</sup>C-CH<sub>4</sub>), such as fossil fuel burning in scientific station, may affect atmospheric CH<sub>4</sub> concentration and slightly enrich the <sup>13</sup>C of CH<sub>4</sub> on the Millor Peninsula. In recent 30 years from 1982, a large amount of fossil fuel was consumed in the world and much enriched-<sup>13</sup>C-CH<sub>4</sub> was emitted into the atmosphere. At the same time, seasonal biomass burning occurred frequently in tropic areas and also a large amount of CH<sub>4</sub> was emitted into the atmosphere. These CH<sub>4</sub> can be transported to the Antarctic atmosphere by atmospheric circulation. Therefore the enriched-<sup>13</sup>C-CH<sub>4</sub> could affect the isotopic values of CH<sub>4</sub> near the surface on Antarctica. In addition, our results may indicate the increase of average <sup>13</sup>C-CH<sub>4</sub> in global atmosphere is due to CH<sub>4</sub> e-

missions from anthropogenic sources

### 3.3 Comparison of atmospheric CH<sub>4</sub> concentrations and their <sup>13</sup>C values near surface at different sites

As listed in Table 1, the CH<sub>4</sub> concentrations are close to or slightly higher than the global average ( $1.8 \times 10^{-6}$ ). CH<sub>4</sub> concentrations in human activity areas and penguin colonies were higher than those at remote inland<sup>[11]</sup>. The concentrations at Tuanjie lakeside were notably higher and the average was  $(2.31 \pm 0.35) \times 10^{-6}$ . The averages of <sup>13</sup>C-CH<sub>4</sub> at each sampling site were higher than global average ( $(-47.0 \pm 0.3)\text{‰}$ )<sup>[27]</sup>, and <sup>13</sup>C value increased with the concentration.

Similarly to Mochou Lake, a large amount of skua and other seabird guano has deposited into the Tuanjie Lake, and the algae grow very well. Furthermore a thick layer of sediments has been formed at the lake bottom<sup>[15]</sup>. Recently, high CH<sub>4</sub> emissions have been observed from lakeshore wetlands<sup>[16]</sup>. Therefore CH<sub>4</sub> emission from Tuanjie Lake may be an important source for local atmospheric CH<sub>4</sub>. On the other hand, the sampling sites at Tuanjie Lake are situated near the Russian Progress Station. Therefore atmospheric CH<sub>4</sub> may be from the emissions of anthropogenic sources at this station (Fig 1). In contrast, the sampling site on the hilltop behind Zhongshan Station is very high at altitude and other sites are far away from scientific stations, indicating an insignificant effect of anthropogenic activities on the surface CH<sub>4</sub> concentration. Therefore CH<sub>4</sub> concentrations at Tuanjie Lake sites were much higher than those at other sites. Additionally, the average <sup>13</sup>C value of CH<sub>4</sub> at Tuanjie Lake sites was the highest of all sampling sites, indicating that considerably proportional CH<sub>4</sub> may be from the anthropogenic emissions at the scientific station. On the whole, the <sup>13</sup>C-CH<sub>4</sub> in the atmosphere of all the sites were enriched compared with global average ( $-47.0 \pm 0.3\text{‰}$ )<sup>[27]</sup>. The enriched-<sup>13</sup>C-CH<sub>4</sub> may be from anthropogenic emissions in local or global areas. Our results also suggested that the present global atmospheric <sup>13</sup>C-CH<sub>4</sub> might be higher than historical values. Temporal and spatial variations of atmospheric CH<sub>4</sub> concentration and its carbon isotope in global and Antarctic areas require further research in the future.

## 4 Conclusions

The atmospheric CH<sub>4</sub> concentration and its <sup>13</sup>C near the surface at different sites were measured on the Millor Peninsula and adjacent areas, east Antarctica in the summer. The following conclusions are drawn:

(1) The average of CH<sub>4</sub> concentrations on the Millor Peninsula was  $(1.87 \pm 0.12) \times 10^{-6}$ , slightly higher than the global average value (about  $1.8 \times 10^{-6}$ ).

(2) The CH<sub>4</sub> concentrations at each site were higher than those at sites of remote inland areas, indicating that human activities may affect atmospheric environment in Antarctic areas to some extent.

(3) The average <sup>13</sup>C-CH<sub>4</sub> was  $(-38.26 \pm 0.52)\text{‰}$  on this peninsula during the summertime of 2005/2006.



(4) CH<sub>4</sub> from anthropogenic sources in the scientific stations may affect the isotopic compositions of atmospheric CH<sub>4</sub> on this peninsula and the present background CH<sub>4</sub> concentration and <sup>13</sup>C-CH<sub>4</sub> in the global atmosphere may be higher than those during the historical period

Table 1. The average CH<sub>4</sub> concentrations and <sup>13</sup>C at the different sites

Site	The sample numbers	CH <sub>4</sub> concentration range ( ×10 <sup>-6</sup> )	Average CH <sub>4</sub> concentration ( ×10 <sup>-6</sup> )	<sup>13</sup> C range (‰)	Average <sup>13</sup> C (‰)
<i>Millor Peninsula in east Antarctica</i>					
The hilltop behind Zhongshan Station	15	1.74 - 2.08	1.87 ±0.12	-39.31 ~ -37.56	-38.26 ±0.52
Emperor penguin island	4	1.88 - 2.17	2.03 ±0.14	-39.20 ~ -31.25	-36.43 ±3.57
Mochou lakeside	5	1.79 - 2.13	1.95 ±0.15	-39.00 ~ -36.98	-38.28 ±0.95
Tuanjie lakeside	2	2.06 - 2.56	2.31 ±0.35	-35.59 ~ -32.30	-33.95 ±2.33
Zhongshan sewage outlet	3	1.75 - 2.08	1.92 ±0.17	-38.57 ~ -38.37	-38.45 ±0.11
WobngMarsh	41	1.90 - 2.26	2.05 ±0.10		
<i>Fildes Peninsula in west Antarctica*</i>					
Ebb algae zones	8	2.37 - 2.02	2.12 ±0.12		
Penguin activity zones	19	1.84 - 2.48	2.08 ±0.16		
Human activity zones	23	1.84 - 2.09	2.02 ±0.09		
Remote inland area	14	1.73 - 1.84	1.78 ±0.05		
Moss zones	54	1.55 - 1.84	1.72 ±0.03		
Lichen zones	10	1.65 - 1.77	1.72 ±0.04		

\* The data of atmospheric CH<sub>4</sub> concentrations on the Fildes Peninsula, west Antarctica was cited from literature<sup>[1]</sup>.

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