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# Preliminary studies on methane flux from the ornithogenic soils on Xi-sha atoll, South China Sea

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Abstract: Methane flux from the ornithogenic soils was preliminarily measured by closed chamber method on Xi-sha atoll, South China Sea during March 10 to April 11, 2003 for the first time. The CH<sub>4</sub> flux ranged from  $-226.7~\mu g/(m^2 \cdot h)$  to  $226.3~\mu g/(m^2 \cdot h)$  at the observation sites on Dong Island. High atmospheric CH<sub>4</sub> consumption was observed from the ornithogenic soils on sunny days. CH<sub>4</sub> uptake rates showed the highest value after the midday and they had a strong positive correlation with soil temperatures. Under the same weather conditions, the CH<sub>4</sub> fluxes were also observed from the intact and disturbed soils on Yongxing Island. Results showed that the intact soils with natural vegetation also showed high atmospheric CH<sub>4</sub> consumption and the average flux was  $-141.8~\mu g/(m^2 \cdot h)$ . However, disturbed soils via anthropogenic reclamation showed CH<sub>4</sub> emissions and the average flux was  $441.7~\mu g/(m^2 \cdot h)$ . Therefore land use changes may have an important effect on the CH<sub>4</sub> fluxes from the tropical ornithogenic soils. In addition, different observation sites show a high spatial variation in CH<sub>4</sub> fluxes. The wetland in salt marsh showed the CH<sub>4</sub> emission on Dong Island, and the dry soil sites all showed high atmospheric CH<sub>4</sub> consumption, suggesting that CH<sub>4</sub> fluxes were predominantly controlled by soil water regime. The effects of soil chemical properties on CH<sub>4</sub> fluxes were also analyzed and discussed in this paper.

Keywords: methane; flux; South China Sea; ornithogenic soil; Xi-sha atoll

### Introduction

Methane (CH<sub>4</sub>) is a radiatively active trace gas, contributing approximately 20% to global (Bouwman, 1990). An increasing concentration in the atmosphere, and ill-defined sink and source strengths have led to a proliferation of the studies of CH4 fluxes from a variety of land use types, soil types, and climatic areas during the last two decades (Steudler, 1989; Mosier, 1997; Cai, 1999; Lu, 2000; Huang, 2001; Sun, 2001; 2002; Ding, 2002; Qi, 2002). Many studies have demonstrated that dry soils in a wide variety of ecosystems consume atmospheric CH<sub>4</sub>, typically at rates ranging from < 1 to about 10 mgCH<sub>4</sub>/( $m^2 \cdot d$ ). CH<sub>4</sub> consumption is shown in forest soils (Steudler, 1989; Castro, 1995), agricultural soils (Hütsch, 1993; Cai, 1999; Li, 1999), tundra soils (Whalen, 1991) and desert soils (Striegl, 1992). As a result of these studies, there is now good consensus that the principal factor regulating the soil sink strength for CH4 is land use type, it is consistently true that undisturbed soils consume methane more strongly than disturbed soils, or soils that have been subjected to inorganic fertilizer application (Mosier, 1991; Hütsch, 1993; Ojima, 1993). However, the global estimate of the CH4 sink strength of aerobic soils is still unclear, in particular, the CH4 consumption of dry soils has not been studied exclusively in tropical areas. In this paper, we will describe a case study conducted with the ornithogenic soils, which were influenced by seabird guanos and formed, from tropical Xi-sha atoll, South China Sea. During March 10 to April 11, 2003, we carried out an integrated environmental investigation in the Xi-sha atoll. Atmospheric CH4 uptake rates by dry ornithogenic soils were observed on Dong Island and Yongxing Island, which are two important rookeries for the seabirds. The relationships between CH4 fluxes and environmental variables were also analyzed and discussed in this paper.

### 1 Materials and methods

#### 1.1 Study area

Xi-sha atoll  $(15^{\circ}47'-17^{\circ}08' \text{ N}, 111^{\circ}10'-112^{\circ}55' \text{ E})$ locates in the center of South China Sea and belongs to Hainan Province, China. It is about 300 km southeast of Sanya, Hainan Island. It extends from northeast to southwest with a length of 250 km and a width of 150 km, enclosing over 50000 km<sup>2</sup> sea area. This largely enclosed sea is probably one of the most biologically diverse bodies of water on the planet and has thousands of reefs, atolls, submerged reefs and banks like Dongsha area (Provided by Oceanic Office of Hainan Province, 1999). Many islands are covered with flourishing tropical thickets, which is very suitable for the propagation of all kinds of seabirds. The accumulation of seabird guano forms phosphorite and the ornithogenic soils, which provide the development of the vegetation with abundant nutrients (Gong, 1997). CH<sub>4</sub> flux observation sites were set in the areas with low thickets on Dong Island and Yongxing Island. Dong Island (16°39' N-16°41' N, 112°43' E-112°45'E) is located in the east of Xi-sha atoll, with the area of 1.55 km<sup>2</sup>. Annual average air temperature is 26-27℃, annual precipitation is about 1500 mm, and dry and wet seasons are very evident. Rainfall is predominantly concentrated during the period from June to November due to the effects of tropical cyclone, occupying 87% of all precipitation. Other months show dry seasons due to the effects of northeastern monsoon. The annual evaporation is about 2400 mm, well above annual precipitation and average relative humidity is 78%-84%. Shrub, such as Scaevola sericea, Guettarda speciosa, Aporosa villosa, distributes on the periphery and continuous Pisonia grandis grows in the middle part of this island. This island is also the rookery of thousands of the rare Sula sula. The CH4 flux observation sites D1 and D2 are located in the shrub areas on this island. The ground surface is 20-30 cm black organic layer, under which is about 30 cm brown soil layer amended by seabird guanos until gray coral floor. In addition, two observation

sites LT1 and LT2 were set in the wetland of salt marsh named Liu Tang, which is only fresh water reservoir with deep sediments and abundant organic matter, and they are 100 m far away from the coastline. The Sesuvium portulacastrum and some herbaceous vegetation flourished in the salt marsh. Two observation sites YX1 and YX2 were also set in Jiangjun forest on Yongxing Island. This island is the largest one on Xi-sha atoll with 1.85 km². Thousands of the trees Cocos nucifera grow in the middle part of this island and the shrubs are mainly Guettarda speciosa and Aporosa villosa. The soils at the observation sites YX1 and YX2 were intact with natural vegetation. To elucidate the effects of anthropogenic disturbance on CH4 fluxes, two sites YXD1 and YXD2 without the vegetation via the reclamation were also selected.

# 1.2 CH<sub>4</sub> flux measurements

The net CH<sub>4</sub> fluxes were determined by a closed chamber technique (Sun, 2001; 2002; Zhu, 2002). At the measurement sites, open-bottomed acrylic resin chambers  $(50 \text{ cm} \times 50 \text{ cm} \times 50 \text{ cm})$  were placed on plastic collars installed at the measurement sites for the entire study period. The collars enclosed an area of 0.25 m<sup>2</sup> and were inserted into the ground to a depth of about 10 cm in the soils. The use of flux collars allows the same spot to be measured repetitively, minimizes site disturbance, and ensures that flux chambers are well sealed in the uneven ground surface since the chambers fit into a water-filled notch in the collars. Head-space samples were removed from the chamber every 20 min(including zero time) and stored in vacuum vials (17.5 ml) made in the Institute of Japanese Agricultural Environment, which had been vacuumized to close to zero Pa in advance. The vials was sealed with a butyl rubber septum and then covered by a plastic cap. High vacuum inside the vial can maintain for a year at least (Sun, 2002; Zhu, 2003; 2004). In addition, gas standards for CH4 stored in the vials showed no significant changes in concentration during one month storage in the laboratory and during transport from the field site to the laboratory, suggesting that the quality of sample air in the vials did not change during the sampling and transporting period as well. Net CH4 fluxes from the ornithogenic soils on Dong Island were measured on 20 March, 22 March and 24 March. CH<sub>4</sub> fluxes from the salt marsh were measured on 29 March. The fluxes from the ornithogenic soils on Yongxing Island were measured on 8 April and 9 April. The CH<sub>4</sub> fluxes from all the sites were observed at four time intervals of 0:00-1:00, 6:00-7:00, 12:00-13:00 and 18:00-19:00 within one day. A total of four samples were taken during a flux measurement.

The collected gas samples were analyzed in the Laboratory of Material Cycling in Pedosphere, Nanjing Institute of Soil Science, Chinese Academy of Sciences, for the CH<sub>4</sub> concentrations. CH<sub>4</sub> concentrations in the samples were determined by GC using a flame ionization detector (FID). The temperature of detectors (FID) was  $200\,^{\circ}\mathrm{C}$ . The stainless column was 2 m long and its temperature was  $80\,^{\circ}\mathrm{C}$ . The flow rates of carrier gases were N<sub>2</sub> 40 ml/min, H<sub>2</sub> 35 ml/min and the air 350 ml/min, respectively. The standard gas for CH<sub>4</sub> was 8 ppmv demarcated by the National Institute of Japanese Agricultural Environment. The variance coefficient

for standard samples was within  $0.1\,\%$  —0.6% in 24 h. CH<sub>4</sub> fluxes were calculated by linear regression of the concentration changes in the four samples and the average chamber temperature .

#### 1.3 Environmental variables

The air temperatures in the chambers were simultaneously taken by the thermometer inserted into it. Ambient air temperatures, 0 cm ground temperatures and the precipitations were collected at the weather station on Yongxing Island. Determinations of pH in the soils were made on fresh soil mixed with distilled water(soil:water, 1: 2.5) and the pH measured in the supernatant. The analyses of chemical and physical properties for the ornithogenic soils at the observation sites were carried out in the laboratory of Metallurgical and Geological Center in East China.

#### 2 Results and discussion

# 2.1 CH<sub>4</sub> flux from the ornithogenic soil on Dong Island

the  $CH_{-}$ relationships between environmental variables were illustrated in Fig. 1. CH<sub>4</sub> flux from the ornithogenic soils on Dong Island ranged from  $-226.7 \mu g/(m^2 \cdot h)$  to  $226.3 \mu g/(m^2 \cdot h)$  during the observation period. High CH4 consumption was shown on the sunny days (March 20 and March 22), with the average uptake rate of 118.4  $\mu g/(m^2 \cdot h)$ . The diurnal variation cycle in the fluxes was also obtained at the observation sites. The CH4 uptake rates showed the highest values after midday, corresponding to the local air temperatures, with the highest uptake rate at about 32 °C. According to Yan and Cai(Yan, 1996), soil sample incubated at 30°C showed the maximum CH4 oxidation potential. However, no CH4 oxidation was observed at 5°C or 50°C and oxidation activity was very little at 12.5 °C. The results reported by Whalen et al. (Whalen, 1990) showed that a landfill covered soil showed a maximum CH₄ oxidation activity at 31 °C. Soils in different ecological environment show different response to temperature change. Therefore in our study highest CH₄ uptake rate at about 32 °C may be related with the strong oxidation activity in the dry ornithogenic soils. In addition, according to some reported references, at most sites CH<sub>4</sub> uptake rates show a negative relationship with soil temperature (Adamsen, 1993; Whalen, 1991). However, in pure cultures or soil slurries CH<sub>4</sub> uptake rate typically shows a strong positive response to temperature (Dunfield, 1993; King, 1992). The results show that CH<sub>4</sub> uptake rate shows a strong positive correlation with soil temperature, which is consistent with the latter (Fig. 2). Therefore soil temperature may be one of the main factors influencing the CH4 uptake rate in the ornithogenic soils. In the study area the daily average soil temperature is above 20℃, thus atmospheric CH<sub>4</sub> consumption can persistently conduct at high flux rate in the ornithogenic soils in the dry season.

However, on March 24 CH<sub>4</sub> consumption decreased dramatically when heavy precipitation occurred and the soils converted from the sinks for CH<sub>4</sub> into the sources, which may be related with the abrupt increase of soil moisture. Soil moisture influences atmospheric CH<sub>4</sub> consumption in two aspects in upland soils, supplies of CH<sub>4</sub> and oxygen and the

activities of methanotrophs in soil. With increase in soil moisture, pores pace in soil for gas diffusion decreases, leading to the decrease in CH<sub>4</sub> and oxygen supplies, as a result, CH<sub>4</sub> uptake rate decrease (Yan, 1996). Following wetting, CH<sub>4</sub> consumption is suppressed by restricted diffusion in wet soil. At most sites CH<sub>4</sub> uptake rates show a negative relationship with soil moisture (Adamsen, 1993;

Whalen, 1991). Our observation results are consistent with the reported references above. Atmospheric CH<sub>4</sub> uptake rate decreased abruptly and the emission increased to a maximum with 186.6  $\mu g/(m^2 \cdot h)$  due to the increase in soil moisture. Therefore the CH<sub>4</sub> flux from the ornithogenic soils is very sensitive to the change in soil moisture.

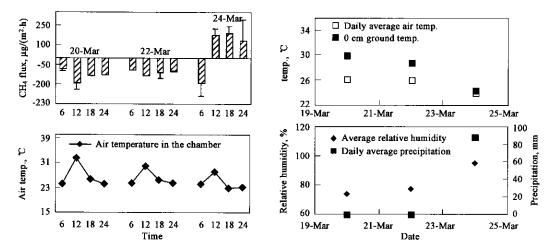


Fig. 1 The relationships between the average CH<sub>4</sub> flux and environmental variables at Dong Island observation sites (D1 and D2)

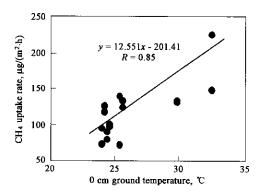


Fig. 2 The correlation between the CH<sub>4</sub> uptake rates from the ornithogenic soils and soil temperatures on Dong Island

# 2.2 Effects of land use change on CH<sub>4</sub> flux on Yongxing Island

Under the same weather conditions, the CH4 fluxes were also observed from the ornithogenic soils on Yongxing Island, with the natural vegetation and without the vegetation via anthropogenic reclamation (Fig. 3). The intact soils with natural vegetation showed high atmospheric CH<sub>4</sub> consumption and the average flux was  $-141.8 \mu g/(m^2 \cdot h)$  (Fig. 3a). However, the soils via anthropogenic disturbance showed CH<sub>4</sub> emissions and the average flux was  $441.7\mu g/(m^2 \cdot h)$  (Fig. 3b). Other studies showed that the conversion from native grasslands and forests to managed pastures and cultivated erops generally decreased the normal aerobic soil CH4 sink. The intensity of soil perturbation played an important part in the magnitude of this decrease. The studies in northeastern Colorado in the USA (Mosier, 1991; Bronson, 1993) compared CH<sub>4</sub> uptake rates in a native short grass steppe to an adjacent, annually fertilized pasture, a non-irrigated winter wheat field, an irrigated N-fertilized maize field, and results showed that CH<sub>4</sub> uptake rate from native grass steppe

was 6—8 times higher than disturbed soils. Keller *et al*. (Keller, 1990; 1993) quantified the effect of converting tropical forests in Panama and Costa Rica, respectively, to the pastures. In Panama they found that the pastures consumed much less CH<sub>4</sub> than the forest did. In Costa Rica, Keller *et al*. (Keller, 1993) found that conversion of forest to cattle pasture transformed a net sink of 330 mgCH<sub>4</sub>/(m<sup>2</sup>·a) to a net source of 180 mgCH<sub>4</sub>/(m<sup>2</sup>·a). CH<sub>4</sub> consumption has also proven to be very sensitive to cultivation. Cultivated soils generally show much lower CH<sub>4</sub> uptake rates than soils under native vegetation (Keller, 1990; Paustian, 1995; Mosier, 1997). The conclusions above are in accordance with this study, therefore it is further confirmed that land use changes have an important effect on the CH<sub>4</sub> fluxes from the tropical ornithogenic soils.

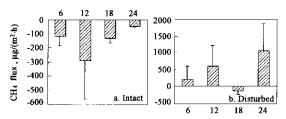


Fig. 3 The effects of land use changes on CH<sub>4</sub> flux from the ornithogenic soils on Yongxing Island

# 2.3 Comparisons between average CH<sub>4</sub> fluxes from different sites

The spatial variations of CH<sub>4</sub> fluxes from six sites were analyzed and compared in the same weather conditions (Fig. 4 and Table 1). The average CH<sub>4</sub> fluxes from two observation sites D1 and D2 were  $-146.3~\mu g/(m^2 \cdot h)$  and  $-137.5~\mu g/(m^2 \cdot h)$ , respectively, on Dong Island; the fluxes from observation sites LT1 and LT2 were  $1402.5~\mu g/(m^2 \cdot h)$  and

228.3  $\mu$ g/(m<sup>2</sup>·h), respectively, in salt marsh. The CH<sub>4</sub> fluxes from two observation sites YXS1 and YXS2 were  $-113.6 \mu g/(m^2 \cdot h)$  and  $-170.1 \mu g/(m^2 \cdot h)$ , respectively, on Yongxing Island. The wetland of salt marsh showed high CH4 emissions. However, all the dry soil sites showed atmospheric CH<sub>4</sub> consumption and the differences between their average fluxes are insignificant, suggesting that CH<sub>4</sub> fluxes were predominantly controlled by soil water regime on the tropical islands (Fig. 4 and Table 1). In addition, the chemical properties for the soils at different sites were also analyzed and compared as listed in Table 2. The chemical properties of ornithogenic soils on Dong Island were very close to those on Yongxing Island. However, the salt marsh on Dong Island showed higher salinity, conductivity, TOC, TN and NH<sub>4</sub> -N, therefore high CH<sub>4</sub> emission from salt marsh on Dong Island may be related with high TOC and salinity.

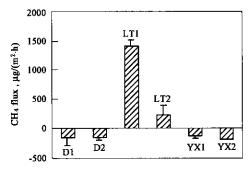


Fig. 4 The spatial variations of CH<sub>4</sub> fluxes from different observation sites

Table 1 The comparisons between average  $\mathrm{CH}_4$  fluxes from the different observation sites under the same weather conditions

Observa- tion duration	Wea- ther	Average air temp.,	Observa- tion sites	Flux range, μg/(m²·h)	Average flux, μg/ (m²·h)
March 20-22	Clear	29.0	Site D1	- 148.4	- 146.3
			Site D2	- 672.9— - 90.9	- 137.5
March 29	Clear	30.4	Site LT1	340.1—2910.3	1402.5
			Site LT2	109.5-442.1	228.3
April 8	Clear	29.5	Site XY1	- 46.7 <del></del> - 165.2	- 113.6
			Site XY2	- 36.2 482.9	- 170.1

# 2.4 Comparisons with other studies

In this study, CH4 uptake rates from ornithogenic soils ranged from 71.8 to 226.7  $\mu g CH_4/(m^2 \cdot h)$  and the average was 127.6 μgCH<sub>4</sub>/(m<sup>2</sup> · h) on the tropical Xi-sha atoll. These fluxes were comparable to some previous reports (Steudler, 1989; Adamsen, 1993; Castro, 1995) where relatively high values (11.3—266.7 μgCH<sub>4</sub>/(m<sup>2</sup>·h)) had been demonstrated. The dry ornithogenic soil CH4 flux was about eightfold larger than the uptake rates (17.5 μgCH<sub>4</sub>/(m<sup>2</sup> ·h)) of the medium soils estimated by Dörr et al. (Dörr, 1992). Our results suggest that Dörr et al. (Dörr, 1992) may have underestimated the global CH<sub>4</sub> uptake rate, and that more information is needed on the global scale variations of CH4 uptake. At the observation sites on Dong Island, the average flux was 126.0 µgCH<sub>4</sub>/(m<sup>2</sup>·h) and the highest uptake rate was 226.7 μgCH<sub>4</sub>/(m<sup>2</sup>·h) in March 2003. This may be one of the highest ever reported for the tropical soils. This soil

Table 2 The chemical and physical properties for the soils at different sites on Xi-sha Islands

Sampling sites	The shrubbery on Dong Island		Salt marsh on Dong Island		Jiangjun forest on YX Island	
	Site D1	Site D2	LTI	LT2	YXSI	YXS2
Salinity, 10 <sup>-3</sup>	0.1	0.1	7.0	6.3	0.1	0.1
Conductivity, ms/cm	0.24	0.25	12.3	11.1	0.20	0.18
TDS, mg/L	117.6	124.3	6.14	5.56	99.8	136.0
pН	8.14	8.25	7.65	7.68	8.46	8.47
Redox, mV	186.6	220.1	178.3	152.6	175.0	222.0
TOC, %	6.27	7.30	9.37	9.27	2.95	2.35
Total S, %	0.06	0.13	0.80	0.73	0.09	0.06
Total N, %	1.12	1.30	2.31	2.44	0.54	0.58
$NO_3^{-}$ , $10^{-6}$	402.0	198.0	-	-	185.5	148.5
$NH_4^+$ , $10^{-6}$	41.1	81.0	306.0	-	37.1	32.9
$PO_4^{3-}$ , %	19.2	15.6	1.44	-	5.26	4.65
$Fe$ , $10^{-6}$	347.5	232.5	295.0	_	552.5	662.5
Mn, 10 <sup>-6</sup>	55.0	32.5	10.0	-	27.5	35.0

had a high porosity due to the mixture of much corallites and the plot had good drainage properties because it was in the middle of a long slope (31°). These soil properties minimized diffusion limitation of CH4 from the air into the soil and maintained good aeration properties. In addition, other factors may have contributed to the unusually large flux, because the flux was much larger than that estimated for coarse-textured soils by Dörr et al. (Dörr, 1992). The factors affecting CH4 uptake rate in the field have been widely reported, including inorganic nitrogen (Steudler, 1989; Adamsen, 1993), soil temperature (Priemé, 1997), and water content (Singh, 1997). The population of methanotrophs is likely to be an important factor affecting CH4 uptake rate, but little information on this exists. Further research is needed to clarify the relationship between CH<sub>4</sub> flux and environmental factors in our studies.

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