大 气 科 学　1993
Chinese Journal of Atmospheric Sciences
Volume 17, No.1, pp. 49–62

Estimate on Methane Emission from China

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Chinese manuscript received March 7, 1992; revised June 20, 1992.

Methane flux from rice fields was measured in Hangzhou in 1987–1989 using an automatic sampling and analysis system, and at Leshan, Sichuan Province at 1988–1990 using periodically sampling technique. The results show that the methane flux from rice fields has significant diurnal, seasonal and interannual variations, which may be related to soil characters, rice growing activities and local meteorological conditions. Great differences in the rate and variation pattern of the flux were also found at different locations, which may be related to differences in soil type, rice variety and local climate. Based on the present observations, the total annual emission of CH_4 from Chinese rice fields is estimated at 17 × 10^{12} g. Three–year systematic observations on the CH_4 leakage from biogas pits show that the CH_4 leakage from biogas pits is very small on the whole, though large in variation range, and the 10 million biogas pits in China are not a significant source of atmospheric CH_4. Based on the measured data on biogas pit leakage, CH_4 emission from agricultural waste was estimated at 3.2×10^{12} g / yr, that from urban area was estimated based on the measurements of atmospheric concentration of CH_4 in urban, rice field and desert areas, that from ruminants was estimated based on their food comsumption, that from coal mines was estimated based on the gas exhaust data, and that from Chinese wetlands was estimated according to the published emission coefficients from wetland. Finally the total emission of CH_4 from various sources in China and its future trend were also estimated. In 1988, the total CH_4 emission from China was about 35×10^{12} g, of which half was from rice fields. In 2000 the total emission might reach 40×10^{12} g, and the major increase will be due to the increase of emissions from ruminants and coal mines.

Key words: methane; rice field; biogas pit; China.

1. INTRODUCTION

Methane (CH_4) is one of the important trace gases in the atmosphere. Like CO_2, CH_4 is a long–lived greenhouse gas, the increase of which will directly cause climatic change through radiative processes. Unlike CO_2, CH_4 is a chemically active component, the increase of which will cause changes in atmospheric chemical processes and affect the concentrations of other trace gases, and hence exert indirect effects on the climate.

Recent atmospheric monitorings and the analyses of air bubbles trapped in ice cores indicate that the concentration of atmospheric CH_4 has been increasing significantly during the past 100 years. Before the Industrial Revolution, the global mean concentration of atmospheric CH_4 had been about 0.6–0.8 ppmv, while it was 1.72 ppmv in 1990, increased by about

150%. In the last four decades after the Second World War the concentration of atmospheric CH_4 increased even faster. During 1945–1985 the mean annual increase rate was about 1%. The rate lowered down since 1986 with the present global mean increase rate of 0.9%. Causes for the increase of atmospheric CH_4 are not yet fully understood. One possible explanation is a continuous increase of the CH_4 sources, while a reduction of CH_4 sink strength due to air pollution cannot be excluded.

In order to understand the causes for the increase of atmospheric CH_4 and predict its future trend, it is necessary to investigate the CH_4 emission rates from various sources and their future trends quantitatively. On the global scale, major sources of atmospheric CH_4 are natural wetlands, rice fields, ruminants, fossil fuel production and transportation, garbage disposal, and shallow–water lakes. China is a large contributor of CH_4 emission, and the CH_4 emission from Chinese rice fields is of significant importance. In this paper the annual CH_4 emission from various sources is estimated based on in–situ flux measurements and atmospheric concentration data analyses. The total CH_4 emission from China and its future trend have been briefly discussed.

2. ESTIMATE ON CH_4 EMISSIONS FROM VARIOUS SOURCES

2.1 *CH_4 Emission from Rice Fields in China*

Rice field is one of the major sources of atmospheric methane. The increase of sown area of rice fields might partly account for the increase of atmospheric methane during the last 100 years or so. China is a large rice producing country. In 1988, China harvested 32 million ha rice, accounting for 22% of the world total, and next to India, is the second world largest rice–growing country by sown area. All the Chinese rice fields are irrigated and fertilized with organic and inorganic fertilizers. The unit area yield of the Chinese rice fields is much higher than that of Indian rice fields and close to that of Japanese rice fields. Thus in 1988 rice production of China was the first in the world, accounting for 38% of the world total. The Chinese rice field was expected to be the major source of methane in China and is important for the global atmospheric methane.

2.1.1 The distribution of rice fields in China

China is one of the pioneers in the development of rice growing in the world, with a 5000 year's rice growing experience. Over a long period of rice growing activities Chinese have cultivated various types of typical rice soil. Rice fields cover one fourth of the farm land and distribute all over the country, from the north, Mohe, Heilongjiang Province (53°36′N), to the south, Yaxian, Hainan Province (18°20′N), and from the east, Taiwan Province, to the west, Xinjiang Uygur Autonomous Region and Xizang (Tibet) Autonomous Region, with the density decreasing from the subtropics to the warm temperate and from the east coastal plain to the Yunnan–Guizhou Plateau. The rice fields are concentrated in the middle and lower reaches of the Changjiang River, Chengdu Plain, Zhujiang River delta, Yunnan–Guizhou–Sichuan Hills, eastern coastal areas and Taiwan Plain.

Chinese rice fields may be divided into the following five categories based on the climatic zone, geomorphologic features and farming practice[1].

(a) South China rice growing area. Located in the southern subtropics, this area may harvest 3 crops a year, and the rice field covers 40%–60% of the total farm land, with prevalent double cropping of rice. The rice fields are distributed in hilly tablelands, basins, valley plains, and coastal plains.

(b) Central China rice growing area. Since the topography of this area is hilly land, the rice fields are distributed in hills, basins, valley plains and coastal plains in Hunan, Hubei, Jiangxi, Fujian and Zhejiang provinces. The rice fields are located in the central subtropics, covering 40%-60% of the total farm lands. Except in some mountainous areas where single cropping of rice is planted, double cropping of rice is prevailing in that area.

(c) The middle and lower reaches of the Changjiang River rice growing area. This area includes the Taihu Plain, Boyanghu Plain, and Jianghan Plain, and is located in the subtropics. The rice fields cover 20%-40% of the total farm lands. Double cropping of rice or rice-winter wheat system is prevailing.

(d) Southwestern rice growing area. This area is located in the subtropics with an elevation of 1500-2000 m and above.

In this area hills and plateau basins crisscross, and single cropping of rice is prevailing. The rice fields cover about 20% of the total farm lands.

(e) Northern China rice growing area. The landform is a mixture of plains, plateau and basins. It is in the warm temperate and temperate climate zones. The rice fields cover 10% of the total farm lands, and single cropping of rice is prevailing.

Table 1 lists the fertility of soils and the flooding days of the above rice growing areas.

TABLE 1. Fertility and flooding periods of Chinese rice fields

Farming practice	Location	Nutrition content in soil (%)				flooding period (d)
		O.M	N.	P_2O_5	K_2O	
Single cropping of rice	Hills in southwestern China	1:4	0.05	0.1	1.5	120-150
	North China Plain	1.79	0.10	0.14	2.0	120-150
	Northeastern Plain	3.20	0.15	0.24	2.2	
Single late rice	Middle and lower reaches of the Changjiang River					120-150
Double Cropping of rice	Plains in the middle and lower reaches of the Changjiang River	2.20	0.13	0.11	1.2	90-100 (early rice)
	Hills in the above area	1.59	0.1	0.08	1.4	
	Triple cropping of rice at plain area	2.40	0.16	0.12	1.9	100-120 (late rice)
	Triple cropping of rice at hills area	2.20	0.14	0.09	2.3	

Chinese rice fields concentrate in the south. The rice cultivation includes processes of seed soaking, seedling raise, transplanting, weedling, and harvesting. In winter green manure, wheat, or rape is grown in the fields. In southern China seedling raise usually begins at the beginning of April, and transplanting at the end of April or early May. Organic fertilizers (ash, manure, or straw) are spread into the soil before flooding or transplanting, and chemical fertilizers are applied at the tillering stage. Harvesting is practised at the end of July or early August. Hence the whole process covers a total growing period of 90-100 days. After the harvesting of early rice, some organic fertilizers are applied and the fields are ploughed and flooded, and then late rice is transplanted immediately. The late rice is harvested at the beginning of November, and thus the whole process covers a growing period of 100-120 days. The single late rice (rice after winter wheat) has a growing period of 120-150 days. The single cropping of rice grows in North China and mountainous areas in South China and has a growing period of 120–150 days, which covers a small portion of rice fields. As China is a country with large population, short of farm land and abundant in labour force. Chinese rice fields are well managed with high yield.

2.1.2 Observational results of CH_4 flux from the rice fields in China

As Chinese rice–growing area covers one fourth of the sown areas in the world. the ovservational data are important for the source of global atmospheric CH_4. Early estimates on the total CH_4 emission from rice fields are questionable due to lack of the measured data from this area.

Since August 1987, ovservations of CH_4 flux from a rice field in Hangzhou were carried out by the Institute of Atmospheric Physics, Chinese Academy of Scicences and the Fraunhofer Institute for Atmospheric Environmental Research (FIAER), which was the first in Asian rice fields, using the automatic sampling and analysis system developed by FIAER in their field studies in Spain and Italy. Since May 1988 flux measurements using chamber technique were carried out in a single cropping of rice field at Leshan, Sichuan Province. supported by a US / DOE and PRC / CAS joint programme.

(a) Measurement results obtained in Hangzhou

From August 1987–October 1989 CH_4 flux measurements were carried out in an experimental rice field in Zhejiang Agricultural University, which might represent the rice soil type of the middle and lower reaches of the Changjiang River area. Detailed experiments and some results can be found in Ref. [3], and CH_4 flux from the rice fields for 5 growing seasons. (1987–1989), is summarized as follows.

For the early rice (observed in 1988–1989) and the late rice (observed in 1987–1989). the CH_4 emission fluxes showed significant diurnal variations throughout the entire growing seasons. However, the regularities of variation differ significantly for the early rice and late rice. as shown in Figures 1 (a) and (b), respectively. Moreover, the magnitudes of the fluctuations are also different for the early rice and late rice, and vary significantly during the entire growing season. For the early rice, the most maximum peak was generally found in the early afternoon, (13:00–16:00), with the maximum to minimum ratio ranging from 1.26 to 12. The second peak was often found at midnight, (0:00–3:00). For the late rice, however. the highest value was almost found at nights, while the lowest value appeared at midday. Bi–mode characteristics with the second peak in the afternoon were also found during the reproductive stage of rice plants for the late rice. These findings in a Chinese rice field differ significantly from diurnal patterns of the CH_4 emissions reported in Refs. [11,12]. These characteristics have revealed the complex nature of the processes governing the CH_4 emission flux. The CH_4 emission from planted paddy soil is mainly determined by three different processes, i.e.. CH_4 production, CH_4 reoxidation and gas transport [13]. Whenever the CH_4 production rate is low and / or the transport is poor, most of the produced CH_4 in the soil will be reoxidized on its way to the atmosphere, and hence the emission flux will be low. On the other hand. when the CH_4 production rate is high, and / or the gas transport is good, a substantial amount of the CH_4 produced in the soil will be able to reach the atmosphere, and hence the emission flux may be high. The complex combination of the above processes is responsible for the complex diurnal variation pattern of the CH_4 emission flux reported here. Generally, the higher temperature in the paddy soil in the afternoon is in favor of higher CH_4 production and may be responsible for the peak values found in the afternoon for both the early rice and the late rice. On the other hand, the gas transport efficiency, which is mainly determined by the vascular gas transport through the plant in the planted paddy soil and the changes in stomatal conductance, will determine the fate of produced CH_4, reoxidized or emitted to the atmosphere[13]. Therefore, it is the plant activity that may be responsible for higher emission fluxes found at midnight and lower values found at midday. We suppose here that the stomata of the rice plant may close during midday due to strong solar radiation. Thus the gas transport pathway is blocked, and the CH_4 emission flux from soil to atmosphere is significantly reduced although the CH_4 production rate in the soil will be high due to high temperatures. At the same time, the closure of plant stomata may also block the transport of O_2 from the atmosphere to the plant root system and cause a significant reduction in the reoxidation of the CH_4 produced in the anoxic part of the soil. Thus, the produced CH_4 may be accumulated in the deeper layer of the paddy soil during the day. After sunset the reopening of the plant stomata may enable transport the accumulated CH_4 to the atmosphere, thereby forming the peak of CH_4 emission observed at night. This mechanism is most pronounced in midsummer (June–August), when the solar radiation is stronger in the subtropical region; it further depends strongly on the variety of rice used. In addition to the diurnal fluctuations strong seasonal variations of the CH_4 emission fluxes have also been observed for the early rice of 1988 and the late rices of 1987 and 1988 (Figure 2). During the three growing seasons, the CH_4 emission fluxes showed three major maxima with minor short–term fluctuations. The first and largest maximum occurred about 10 days after transplanting at the beginning of the tillering stage of the rice plants. Two other maxima were found during the reproductive phase, shortly before and after the flowering stage of the rice plants. These characteristics of seasonal variations of the CH_4 emission rates are likely to be correlated with the availability of organic substrates in the paddy soil and the activity of rice plants, releasing organic substrates into the soil and exchanging gases between the soil and the atmosphere. The first maximum of CH_4 emission rate is apparently due to the decomposition of organic matter left in the soil before flooding and the good transport of the produced CH_4 by the rice plants growing most vigorously during the tillering stage. The second and third maxima are most probably due to the activities of the rice plants which have developed their root system during the tillering stage. The root system may provide the soil bacteria with organic substrates in the form of root exudates or root litter during the reproductive phase of the rice plants[14]. Root exudates of rice plants consist mainly of carbohydrates, organic acids and amino acids[15], which are readily decomposed by fermentative soil bacteria to CO_2, H_2, and acetate. These compounds are then the substrates used by methanogenic bacteria to produce CH_4.

The observed seasonal fluctuations may also be the consequence of changes in the activity of soil bacteria due to soil temperature fluctuations. Poor correlations were found between the in–situ measured soil temperatures and the CH_4 emission fluxes. However, if the

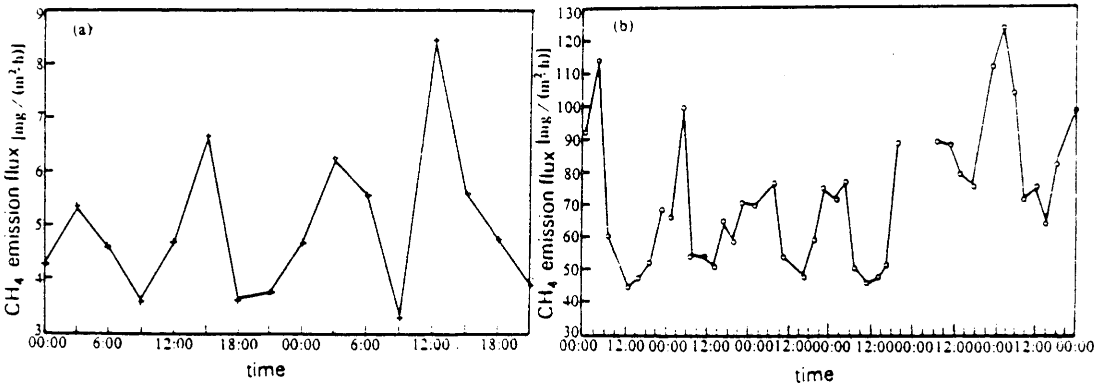

FIGURE 1. Diurnal variation of CH_4 emission flux from double cropping of rice fields. (a) Early rice, (b) late rice.

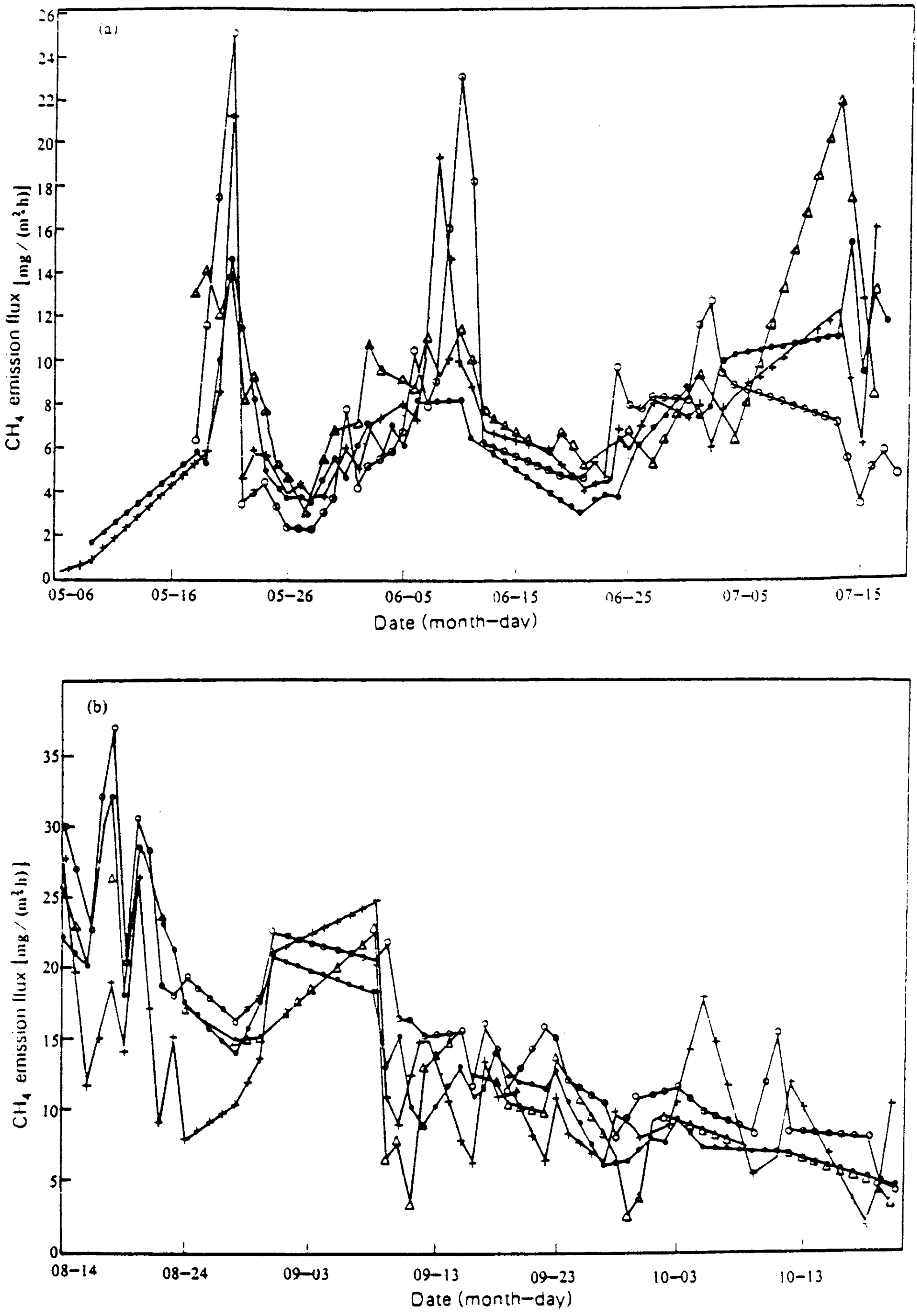

FIGURE 2. Seasonal variation of CH_4 emission flux from double cropping of rice fields. (a) Early rice, (b) late rice.

measurement of soil temperatures lagged two days behind the real measuring dates. much better correlations between the soil temperatures and the CH_4 emission rates were obtained. This two-day time lag of the CH_4 emission fluxes reflects the time needed for the development of the methanogenic bacteria plus the time needed for the transport of the produced CH_4 through rice plants.

The application of SO_4^{2-} containing fertilizer slightly reduced the CH_4 emission fluxes during the early period of the growing season, but enhanced the CH_4 emission during the late period of the growing seasons. However, no significant effect was found on the seasonal averages of the CH_4 emission rates.

The reduction of CH_4 emission rates due to the application of SO_4^{2-} containing fertilizer in the early period of the growing season may be caused by the scramble between sulfate reducers and methanogenic bacteria. The application of sulfate fertilizer may spur the growth of sulfate reducers; the acetate-utilizing sulfate reducers are able to outcompete methanogenic bacteria for their common substrate and acetate, thereby reducing CH_4 production in the soil[13]. On the other hand, fertilization caused the enhancement of plant growth and provided additional substrate for the methanogenic bacteria. As a consequence, CH_4 production during the late period of the growing season may be enhanced.

(b) CH_4 emission measurement in southwestern China

Since May 1988 CH_4 emission rates from 4 rice fields at Tuzhu, Leshan, Sichuan Province, which might represent the soil types of hilly areas in southwestern China (29°40′N, 103°50′E), have been jointly measured by the Institute of Atmospheric Physics, Chinese Academy of Sciences and the Department of Energy, USA. The experimental field was close to a 30 m high hill where a meteorological station was located. The soil belongs to purple soil type, acidic purple soil subtype and red-purple clay species. The texture of the soil is in-between the sandy loam and medium loam with a sand content of 59.7%-63.3%. The thickness of the cultivated layer is 13-31 cm, the contents of organic material and total N are 1.4% and 0.034%, respectively, and the PH of the soil varies in the range of 5.5-7 during the rice growing season. In comparison with the fields in Hangzhou, the organic content is lower and the acidity is higher, while the annual precipitation and relative humidity are similar. In this region single cropping rice is common. The field is ploughed in mid-April, transplanting begins at the end of April, and harvesting begins at the end of August, thus hvaing a growing period of 120-140 days. Our emission measurement usually began on May the first (several days after transplanting). Four fields were measured at the same time. Four times of sampling were made each week, in the mornings of Monday and Thursday and the afternoons of Tuesday and Friday, during the whole growing season. Before and after each CH_4 emission measurement CH_4 concentrations in the ambient air by the rice field and at the top of the hill were also determined. At the same time, soil and air temperatures were also measured. Samples were analysed in the laboratory within one or two days.

The technique used in Sichuan is similar to that employed in Hangzhou, but with a much lower frequency, which cannot give the detailed diurnal variation. There is a general tendency that the emission rate in the afternoon is higher than that in the morning, and there is also a positive correlation between the emission rate and soil temperature (Figure 3). During the whole growing season the daily mean emission rates fluctuate but no significant peak period was found in Hangzhou. Generally, emission rate is lower at the beginning of the season, reaches average value in mid-May and gets the highest value at the end of July, then it decreases gradually and reaches the lowest value in the harvesting time. This pattern of seasonal variation differs greatly with that found in Hangzhou, which again indicates the complex nature of the factors governing the CH_4 emission from rice fields and the importance of in–situ measurements over each of the major rice growing areas.

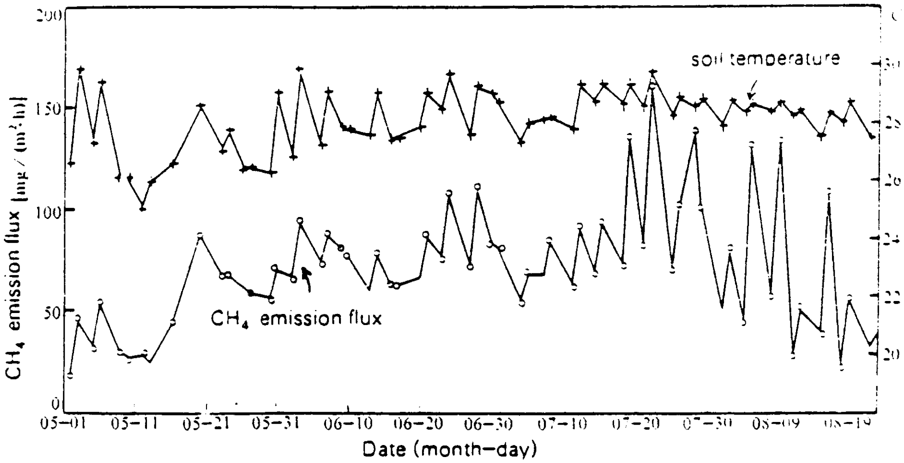

FIGURE 3. Seasonal variation of CH_4 emission flux from single cropping of rice fields.

A significant year–to–year variation has also been found in the CH_4 emission rate from the rice fields at Leshan. The mean emission rate in 1989 was lower than that in 1988 (Figure 4). This could be related to climatic changes, as in 1989 the area experienced a summer with lower temperature. At the same location the CH_4 emission rates from rice fields might differ for different rice varieties. Generally, emission rate from a field with hybrid rice is higher than that from a field with common rice.

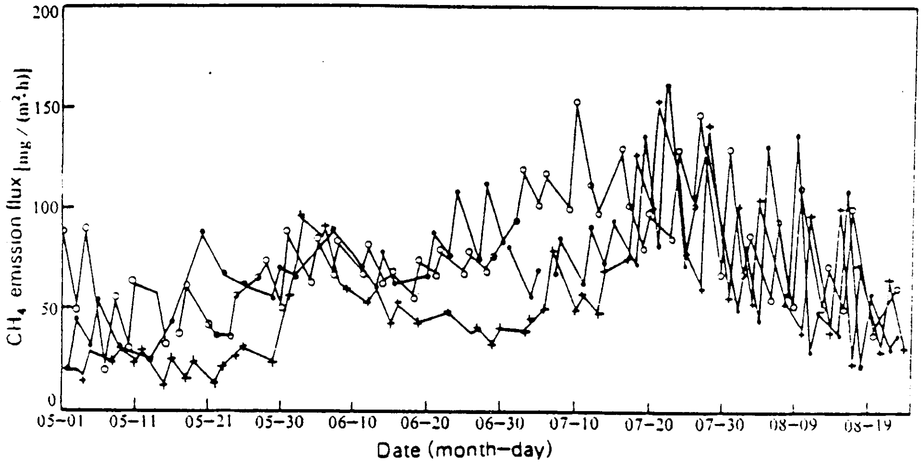

FIGURE 4. Year–to–year difference of CH_4 emission fluxes from single cropping of rice fields.

Therefore, to obtain a reliable total emission of the Chinese rice fields continuous measurements over the five major rice growing areas in China must be carried out for at least 3 years.

Our results for the rice fields in Hangzhou and at Leshan differ greatly from the published data obtained from the rice fields in USA and Europe. In addition to the different regularities of diurnal and seasonal variations, the overall emission rate of Chinese rice fields is comparatively higher, with the highest value found at Leshan. However, our measured emission rate of the Chinese rice field is lower than that obtained by an extrapolation of the measured results for Europe using temperature dependence. Our measurements made in Hangzhou in 1987–1989 have obtained the seasonal average CH_4 emission rates of 7.8 mg / (m^2 • h) for the early rice and 28.6 mg / (m^2 • h) for the late rice, while those made at Leshan in 1988–1990 have got the seasonal average CH_4 emission rate of 60 mg / (m^2 • h) for the single cropping of rice. The corresponding total seasonal emission rates are 16.2 g / (m^2 • yr) for the early rice, 75.9 g / (m^2 • yr) for the late rice, and 216 g / (m^2 • yr) for the single cropping of rice. However, it should be pointed out that the CH_4 emission rates from rice fields have a very large diurnal and seasonal variation, which is related to soil types, rice growing activities and local climate. One must be very cautious when calculating the total seasonal emission from the measured emission rates.

Based on the available data, we estimate that the total CH_4 emission from Chinese rice fields is about $(17 \pm 2) \times 10^{12})$ g / yr.

In the period of 1949–1988 the annual rice production in China increased by 3 times, while the sown area only increased by 30%. The sown area has remained at about 32 million ha., and will not change significantly in the next few decades. Thus the CH_4 emission from Chinese rice fields will not increase significantly in the future.

2.2 *Estimate on the CH_4 Emission from Domestic Ruminants*

In the animal intestines and rumens of ruminants there live various kinds of microorganism that ferment the food in the rumens to obtain their food and energy under the unaerobic environment.

During the ferment process in the alimentary canal of animals many trace gases may be produced. For the monostomach animal, e.g., pig and chicken, the energy loss due to trace gas formation and the production of trace gases are small and can be neglected. For the ruminants, e.g. cow, sheep and camel, the rumen is like a steady continuous fermentation tun that continuously ferments the intake food. After food intake the gas contents in the rumens of cow and sheep are 40% CO_2, 30%–40% CH_4, 5% H_2, and small amounts of O_2 and N_2. The CH_4 produced in the rumen accounts for 87% of the total produced in the whole alimentary canal, most of which is emitted during ruminating.

CH_4 production rate is highest immediately after food intake, with a value of 30 L / h for cow and 6 L / h for sheep, and then decreases gradually. On an average, a cow may produce 154 L CH_4 per day, and that value for a sheep is 30 L / d. In the exhaust of respiration the concentrations of CO_2 and CH_4 are 0.5%–3% and 0.03%–0.3% respectively. In 1988, there were 97.02525 million heads of cow, 0.5 million heads of camel, and 201.3362 million heads of sheep in China, which produced 7.6865×10^{12} L CH_4. The specific gravity of the CH_4 produced by animals was 0.71682 g / L, so that CH_4 emission from the animals in China was 5.5×10^{12} g in 1988.

It has been estimated that the domestic animals might increase to 147.05 million heads of cow, 327.3 million heads of sheep, and 0.5 million heads of camel by the end of this century when the CH_4 emission from the animals in China might reach 8.5×10^{12} g / yr, increase by 54%.

2.3 *Estimate on the CH_4 Emission from Industry*

CH_4 emissions from industry in China mainly come from the gas leakages of coal, petroleum and natural gas mines. There are no data on the gas leakage from petroleum and natural gas mines, so the CH_4 emission from these sources cannot be estimated. The

CH_4 emission from coal mines was estimated based on the limited data on gas exhaust in the large-scale coal mines, so the data are not accurate.

Coal mines in China are classified into 3 categories, namely state, local and private. No data are available on the gas emission from local and private coal mines, therefore the present estimate on the CH_4 emission from coal mines was made using the data on the absolute gas exhaust and relative gas exhaust from state coal mines. The CH_4 emission to the atmosphere was calculated by gas exhausts plus the unused portion in gas recycling. The CH_4 concentration in the exhausted gas from coal mines ranges from 30% to 90%. In the large-scale state coal mines the exhausted gases with a CH_4 content higher than 30% are usually recovered for use, while those with CH_4 content lower than 30% are emitted to the atmosphere directly. In the venting system of coal mines the exhausted gas normally contains little CH_4, and the CH_4 emission to the atmosphere can be neglected. Based on the above consideration CH_4 emission from coal mines in China is estimated at about 6.08×10^{12} g in 1989.

If the CH_4 emission rate for a unit coal production remains unchanged, the CH_4 emission from coal mines in 2000, when coal production in China reaches 1.4×10^9 T, will probably reach 8×10^{12} g / yr.

2.4 *Leakage from Biogas Generators and Agricultural Waste Treatment*

In the countryside in southwestern China biogas generators are commonly used for cooking and heating.

A typical biogas generator consists of 3 parts, a large central ferment chamber, a side chamber, and an entrance canal to toilet and pig house. At the top of the central chamber there is a hole covered with a concrete plug and sealed with clay and water. Human wastes, pig manures, rice straws, and other organic farmyard wastes are put into the bottom of the chamber and the residues are cleared away once or twice a year through the hole. Water is added through the side chamber to a certain level, thus, the organic material forms a sludge under water. The anaerobic processes in the sludge and the liquid above produce biogas, which is mostly CH_4, CO_2 and small quantities of other gases. These gases bubble up to the empty region at the top of the central chamber. The biogas in the upper part of the chamber is under pressure (10-40 cm H_2O), so that it is carried to the kitchen and the house through plastic tubing without the use of pump.

We identified three areas where methane could leak out. The removable concrete plug in the top hole is a potential source of leaks (6 experiments). The second place where methane and other gases may leak out is the top of the side chamber, which is covered with a concrete board (3 experiments). The water level is about 0.6 m below the top, and it is not sealed and gas is freely exchanged with the atmosphere. Methane released from this area is irrecoverable. Since most of the biogas is produced in the sludge at the bottom of the central chamber and bubbles rise straight to the top into the effectively sealed region at the top of the chamber, very little methane makes its way out to the side chamber. Finally, we also considered the losses of methane from the unburned biogas in the kitchens (1 experiment).

In these experiments, the chamber was a clear plastic bag that was placed on the top of the side chamber cover or the plug. At the beginning of the experiment a measured amount of a tracer (CF_3Br) was injected into the bag (typically 30-100 mL of 0.1 ppmv tracer). The bag was shaken gently to mix the tracer. Samples were taken with a pump into the 0.8 L stainless steel containers. Each experiment consisted of a background sample and 4 samples drawn about 5 minutes apart. The samples were analysed by GC for concentrations of CH_4 and CF_3Br.

The effective volume of the chamber is determined by the mass balance of the tracer. The time-dependence of the tracer concentration in the chamber is given by:

$$N_0 C_T(t) V = s \cdot e^{-1/\tau}, \tag{1}$$

where $C_T(t)$ is the tracer concentration in the sample taken at time t in the unit of volume mixing ratio; s is the amount of the tracer injected into the chamber at the beginning of the experiment; V is the effective volume of the chamber; τ is the residence time of gas in the chamber, which is used to correct the error due to incomplete seal; N_0 is the Avogadro's number. A simple logarithm operation on Eq. (1) gives:

$$\ln C_T(t) = \ln[S / (N_0 V)] - t / \tau. \tag{2}$$

V and τ are determined by using the measured $C_T(t)$ at different times and Eq. (2) with the least squares method.

Once V and τ are known, the flux of CH_4 leakage can be determined by using the measured CH_4 concentrations in the samples taken at different times. The variation of CH_4 concentration in the chamber is expressed as

$$\frac{dC_g}{dt} = F_{\text{in}} - F_{\text{out}}, \tag{3}$$

where F_{in} is the flux of CH_4 leakage to be calculated, F_{out} is the out flux of CH_4 due to incomplete seal and sampling losses, C_g is the molecular density of CH_4 in the chamber in the unit of CH_4 molecular number per unit volume,

$$C_g = C(t) V N_0, \tag{4}$$

where $C(t)$ is the mixing ratio by volume of CH_4 in the samples with a unit of pptv,

$$F_{\text{out}} = (1 / \tau)\, C_g. \tag{5}$$

Thus we have

$$C(t) V N_0 = F_{\text{in}} \tau (1 - e^{-t/\tau}) + C(0) \cdot e^{-t/\tau} V N_0, \tag{6}$$

where $C(0)$ is CH_4 volume mixing ratio in the ambient air sample taken at the beginning of the experiment. The flux of CH_4 leakage F_{in} can be determined by using the CH_4 volume mixing ratios measured at different times and Eq. (6) with the least squares method.

The two-year experiments on different biogas generators show that most of the leakage is from the top of the side chamber, the leakage from the top of the ferment chamber is very small, and no leakage during the usage of the gas (Table 2).

TABLE 2. Results of experiments on the CH_4 leakage from biogas generators.

Leakage location	Flux (mg / h) per pit			number of experiments
	minimum	maximum	average	
top of ferment chamber	1.5	170	11	50
top of side chamber	56	146	87	50
user	0	0	0	5
Total	60	320	98	

In summary, although the CH_4 leakage from biogas generators has a large range of variation, the leakage is very small on the whole. With the maximum flux we measured, the 10 million biogas generators used in China only leak 0.03×10^{12} g / yr. With the averaged flux we measured the total CH_4 leakage is only 0.01×10^{12} g / yr, which may be neglected for global CH_4 sources.

However, the biogas generator has indicated another important source of methane, i.e. manure treatment in the countryside. In the countryside of China organic manures, e.g. agricultural waste and human and animal wastes, are widely used as fertilizers. These manures are usually fermented in cesspools before their application to the fields to enhance the fertilization efficiency and to reduce the plant diseases and insect pests.

The environment in these cesspools is similar to that in the ferment chamber of the biogas generator. Therefore, CH_4 is generated in these cesspools, but no CH_4 is recovered, all of which emits to the atmosphere directly. There is no measurement on this kind of sources. The CH_4 emission from this kind of source was estimated based on the data of total farmyard waste in China and gas production rate of farmyard waste in biogas generators provided by Sichuan Biogas Institute. Assuming that the CH_4 production rate in cesspools for manure treatment is 10% of that in biogas generators, the total CH_4 emission from these cesspools is given by

$$F = 0.1GP\rho\eta = 0.1 \times 300 \times 1.9 \times 10^8 \times 0.71 \times 10^3 \times 0.8 = 3.2 \times 10^{12} \quad (\mathrm{g/yr}), \tag{7}$$

where $G = 300\ \mathrm{m}^3/\mathrm{yr}$ is the averaged gas production per household per year, $P = 1.9 \times 10^8$ is the total households in 1988, $\rho = 0.71\ \mathrm{kg/m}^3$ is the averaged density of menthane, $\eta = 80\%$ is the CH_4 content in the biogas.

It should be pointed out that this estimate is uncertain due to the lack of accurate data on the gas production per household and the efficiency factor of CH_4 generation in the cesspools and lack of detailed data on the environment of the cesspools and the residence time of manures in the cesspools. Nevertheless, the treatment of organic manure in the countryside is certainly an important source of methane in China and is worth to be further investigated.

2.5 *CH_4 Emission from Urban Areas*

Carbage and sewage treatments are major CH_4 sources of urban areas. In many cities in China part of the living waste is treated in septic tanks which are similar to the cesspools for fermenting organic manure in the countryside and may be the most important sources in the cities in China. This kind of sources has a large area, small emission rate and a wide range of conditions, so it is difficult to make in-situ flux measurement. We estimated the CH_4 emission from urban areas by using CH_4 flux measured in the rice fields through a comparison of CH_4 concentrations in ambient atmospheres in the urban areas, near the rice field and in the remote background regions.

CH_4 concentration in ambient atmosphere was measured in a desert area in northwestern China in 1985–1988, which is considered as the CH_4 background concentration in China. At the same time CH_4 concentrations in ambient air were measured in Beijing, the excess of which over the background level is considered as due to the CH_4 emission from Beijing. When CH_4 flux from the rice fields at Leshan, Sichuan Province was measured, CH_4 concentrations in the ambient air were also measured near the rice field, through which the CH_4 flux surface source was related to the CH_4 concentration in the ambient air (Table 3). It is assumed that the ratio of the annual average flux to annual average ambient concentration in excess of background levels is the same as that of the rice growing areas in Beijing. Thus we have

$$\frac{C_r - C_0}{F_r} = \frac{C_B - C_0}{F_B}, \tag{8}$$

where C_r is the CH_4 concentration in ambient air near rice fields, C_B is the CH_4 concentration in ambient air in Beijing, C_0 is the background concentration, F_r is the CH_4 flux from rice fields, F_B is the CH_4 flux in Beijing. By using the CH_4 concentration in the atmosphere

TABLE 3. The measured CH_4 concentrations in the ambient atmosphere at different locations (pptv).

Location	Beijing	Tuzhu Sichuan	Minqin Gansu	Chengdu	St.Louis
Mean maximum	1833	2864	1739	2009	1812
Mean minimum	1807	2593	1731	1739	1806
Average	1820	2725	1735	1870	1809

listed in Table 3 and the CH_4 flux measured over the rice fields at Leshan, the CH_4 flux in Beijing we obtained is 5.2 mg / (m^2 • h), which is extrapolated to the whole country by the following equation:

$$F_s = F_B A_B P_s / P_B, \tag{9}$$

where F_s is the total CH_4 emission from urban areas of the whole country, A_B is the area of Beijing, P_s is the whole urban population in China, P_B is the population of Beijing. Using the related data in the China's Agricultural Yearbook, we estimated that the total CH_4 emission from urban areas of the whole country is 0.6×10^{12} g / yr.

It should be pointed out that this estimate may have an error of an order of magnitude. Eq.8 is not strictly valid due to the differences in the structure and diffusion capacity of the atmosphere in Beijing and over the rice fields at Leshan. On the other hand, Eq. (9) has errors due to the differences in ratio of urban area to its population, climatic condition and atmospheric transport in Beijing and other cities.

3. TOTAL CH_4 EMISSION FROM CHINA AND ITS FUTURE TREND

The total CH_4 emissions from various sources and its future trend are summarized in Table 4.

TABLE 4. Total CH_4 emission from major sources in China and their future trend.

Source	Total emission 10^{12} g / yr	
	1988	2000
Rice fields	17 ± 2	17 ± 2
Domestic animals	5.5	8.5
Coal mine	6.1	8.0
Natural wetland	2.2	2.2
Manure treatment	3.2	3.2
Urban areas	0.6	0.6
Total	35 ± 10	40 ± 10

As shown in Table 4, the most important source of methane in China is the rice field, which accounts about half of the total emission from all sources in China. Due to the limited land resources, the total rice area in China will not increase significantly in the coming decades. The increasing food requirement due to increasing population will have to rely on increasing the unit area yield. The increase of CH_4 emission from China in the coming decades will mainly be due to the increase of fossil fuel production and domestic animals. Based on the present plan of economic development, the total CH_4 emission from China will probably