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METHANE EMISSION FROM AGRICULTURAL AREAS

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งานวิจัยนี้มีจุดมุ่งหมายในการศึกษาการปลดปล่อยก๊าซมีเทนจากพื้นที่เกษตรกรรม 2 ประเภท คือ พื้นที่ที่มีน้ำท่วมขัง และไม่มีน้ำท่วมขัง โดยใช้นาข้าวเป็นตัวแทนพื้นที่ที่มีน้ำท่วมขัง และไร่ข้าวสาลีและไร่ข้าวโพดเป็นตัวแทนของพื้นที่ที่ไม่มีน้ำท่วมขัง ผลการศึกษาแสดงให้เห็นว่า พื้นที่ที่มีน้ำท่วมขังปลดปล่อยก๊าซมีเทนออกมา 4.51 กรัมต่อตารางเมตร ในขณะที่ไร่ข้าวสาลีและไร่ข้าวโพดดูดซับก๊าซมีเทนเข้าไป 59 และ 40 มิลลิกรัมต่อตารางเมตร ตามลำดับ การบำรุงรักษาดินก็มีผลต่อการดูดซับก๊าซมีเทนด้วยเช่นกัน โดยที่พื้นที่ที่มีการพรวนดินลึกกว่าจะส่งเสริมให้มีการดูดซับก๊าซมีเทนมากกว่า และพบว่าการใส่ปุ๋ยหมักมีส่วนช่วยเพิ่มการปลดปล่อยก๊าซมีเทนด้วยเช่นกัน นอกจากนี้ยังพบว่า อุณหภูมิและความชื้นของดินเป็นปัจจัยสำคัญที่มีผลการการปลดปล่อยและการดูดซับก๊าซมีเทน โดยที่ค่าฟลักซ์ของก๊าซมีเทน จะแปรผันตามอุณหภูมิ และความชื้นของดิน

ในปีหนึ่ง พื้นที่นาข้าวน้ำท่วมขังทั้งหมดในประเทศไทย (21,850 ตารางกิโลเมตร) ปลดปล่อยก๊าซมีเทนออกมาในปริมาณเทียบเท่ากับก๊าซคาร์บอนไดออกไซด์ $3,750\times10^{9}$ กรัม ซึ่งคิดเป็นประมาณ 40% ของปริมาณก๊าซคาร์บอนไดออกไซด์ที่ปลดปล่อยออกมาจากโรงไฟฟ้าเนื่องจากการใช้ไฟของอุตสาหกรรมในประเทศไทย นอกจากนี้ยังพบว่าค่าฟลักซ์สุทธิของก๊าซเรือนกระจกในนาข้าวมีค่าติดลบ นั่นคือนาข้าวเป็นพื้นที่ที่ดูดซับก๊าซเรือนกระจกเหล่านี้เอาไว้

ภาควิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต..
สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่ออาจารย์ที่ปรึกษา..................................
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The aim of this work was to measure the emission fluxes of methane from 2 types of agricultural areas: (i) irrigated area represented by a rice paddy field and (ii) upland area represented by wheat and maize fields. The results showed that irrigated area emitted methane at about 4.51 gm^{-2}, while wheat and maize fields absorbed methane at approx. 59 and 40 mgm^{-2}, respectively. Soil treatment in the upland field also had slight effect on methane absorption. The deep-tilled area enhanced more methane absorbed than in shallow-tilled area. Moreover, the addition of manure fertilizer affected the emission of methane by increasing the production and emission rate of methane from upland area. Soil temperature and soil moisture were significant factors for methane emission and absorption. The results indicated that methane flux was directly proportional to soil temperature and soil moisture.

Annually, the whole irrigated areas in Thailand (21850 km^2) emitted methane in the quantity that was equivalent to 3750 Gg of carbon dioxide. This amount of carbon dioxide was approximately 40% of that released from the power plants for industrial sector in Thailand. However, the net greenhouse gas emission including carbon dioxide, nitrous oxide, and methane fluxes in irrigated area was negative which meant that irrigated area acted as a sink for greenhouse gases.

Department	Chemical Engineering	Student’s signature…………………………..
Field of study	Chemical Engineering	Advisor’s signature…………………………..
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CHAPTER 1
INTRODUCTION

1.1 Rationale

Natural mechanisms such as plant growth, wildfire, wetland, etc. have affected the earth average temperature. Statistically, it was found that the earth temperature in the past two centuries tended to increase continually (Figure 1-1). One of the significant factors influencing the earth temperature is the amount of greenhouse gases in the atmosphere. It was believed that the emission rate of greenhouse gases into the atmosphere at the time where this report was written is by far more than the rate at which the nature can accommodate. This resulted in the accumulation of greenhouse gases in the earth's atmosphere which led to the global warming problem.

Carbon dioxide is perhaps the most significant greenhouse gas in terms of its stability and the amount that has been released from industrial sources. The quantity of carbon dioxide in the atmosphere is controlled naturally by the Carbon cycle [Wuebbles, 1997]. In fact, this natural mechanism was observed to result in a slow accumulation of carbon dioxide as the changes in the earth average temperature tended to increase with time as shown in Figure 1-1. After the industrial revolution in the nineteenth century, many complex human activities particularly the combustion of large amount of fossil fuel had led to such a high emission rate of carbon dioxide that the nature could not cope with. This resulted in a much faster rate of carbon dioxide accumulation (Figure 1-2) and the problem of global warming became more apparent. Examples of disasters caused by this global warming problem include the melting ice at the earth's poles, changes in seasonal periods [Lyman, 1990], unusual animals' migrations, etc.

Several organizations have expressed their ultimate concerns for this problem, and many actions have been proposed or conducted in order to lessen its effect. The solution aims not only at the decrease of the heat and chemicals emitted form the activities but also at the elimination of the potential sources. For instance, the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) have launched the Intergovernmental Panel on Climate Change (IPCC) to investigate the effects of human activities on the climate. The IPCC has completed three assessment reports on climate changes in 1990, 1995, 2001, and also has issued methodology guidelines for national greenhouse gas inventories and other special reports and technical papers on this topic. Needless to say, the recent Kyoto protocol is about to launch with the aim of cutting carbon dioxide emission down about 5.2% below 1990 levels by 2012 and a final reduction of 60-80% of 1990 levels being the ultimate goal. Moreover, as a non-profit organization with members from 40 countries, Greenpeace focuses on the most crucial worldwide threats to our planet's biodiversity and environment with the aims to protect our surroundings such as stopping climate change, protecting ancient forests, stopping the nuclear threat, eliminating toxic chemicals, etc. For instance, Greenpeace has conducted an environmental protection campaign against one of the biggest oil companies and solicited that company to halt the climate change by researching and promoting clean energy solutions.

Although most attentions on the greenhouse problem have been located at the emission of greenhouse gases from industry, a past research indicated the importance of the greenhouse gases emitted from agricultural area [Boonyanopakun and Pavasant, 2002]. It is true that the flux at which greenhouse gases emitted from agricultural area is relatively low compared to the industrial. It should not be misjudged; however, as the agricultural activities cover a much larger area and the total quantity of gases being produced is therefore large. Methane is one of the main greenhouse gases of concern as it can be produced in large quantity provided proper conditions for microbial activities. Rice paddies are among the most abundant methane production areas. As the main food source and also a raw material for other kinds of food, rice is spaciously cultured. Thus, a large quantity of methane can be emitted from these areas. Interestingly or more anxiously rather, about 90% of the global rice field are located in Asia [Schütz *et al.,* 1991; Augenbraun *et al.,* 1999a], of which 60% falls in India and China [Parashar *et al.*, 1996].

Agricultural based countries such as Thailand and many countries in Asia also cultivate other types of vegetation e.g. corn, wheat, bean, etc. These vegetation areas can cover a large fraction of the overall agricultural area in the country. However, data on methane emission from these areas are sparse, or to be more precise, scarcely available. It is the aim of this work, therefore, to investigate the rate of methane emission from other vegetation areas and to compare with the emission rate from rice field in experiment and literature. In addition, the effect of soil parameters and others will be concerned. This information will facilitate the determination of the extent of global warming problem to which agricultural activities contribute. Comparison between greenhouse effect of agriculture with that of industry will also be introduced as a case study in this work.

1.2 Objectives

- to investigate the effect of types of vegetation on methane emission
- to investigate the effect of other parameters such as soil properties on methane emission
- to determine the contribution of agriculture activities on the global warming problem in comparison with that of industrial ones.

1.3 Scopes of this work

- All experiments were conducted at the experiment farm of Tokyo University of Agriculture and Technology in Japan.
- The type of vegetation considered in this study included rice, wheat, and maize. These were selected from the types of vegetation in the study area.
- The effects of agricultural treatments such as tillage, additive and soil properties such as temperature, pH, soil moisture, etc. on methane emission from each vegetation area were investigated.
- Combustion of fuels were used as a model study in the comparison between greenhouse gas emissions by agriculture and industry.

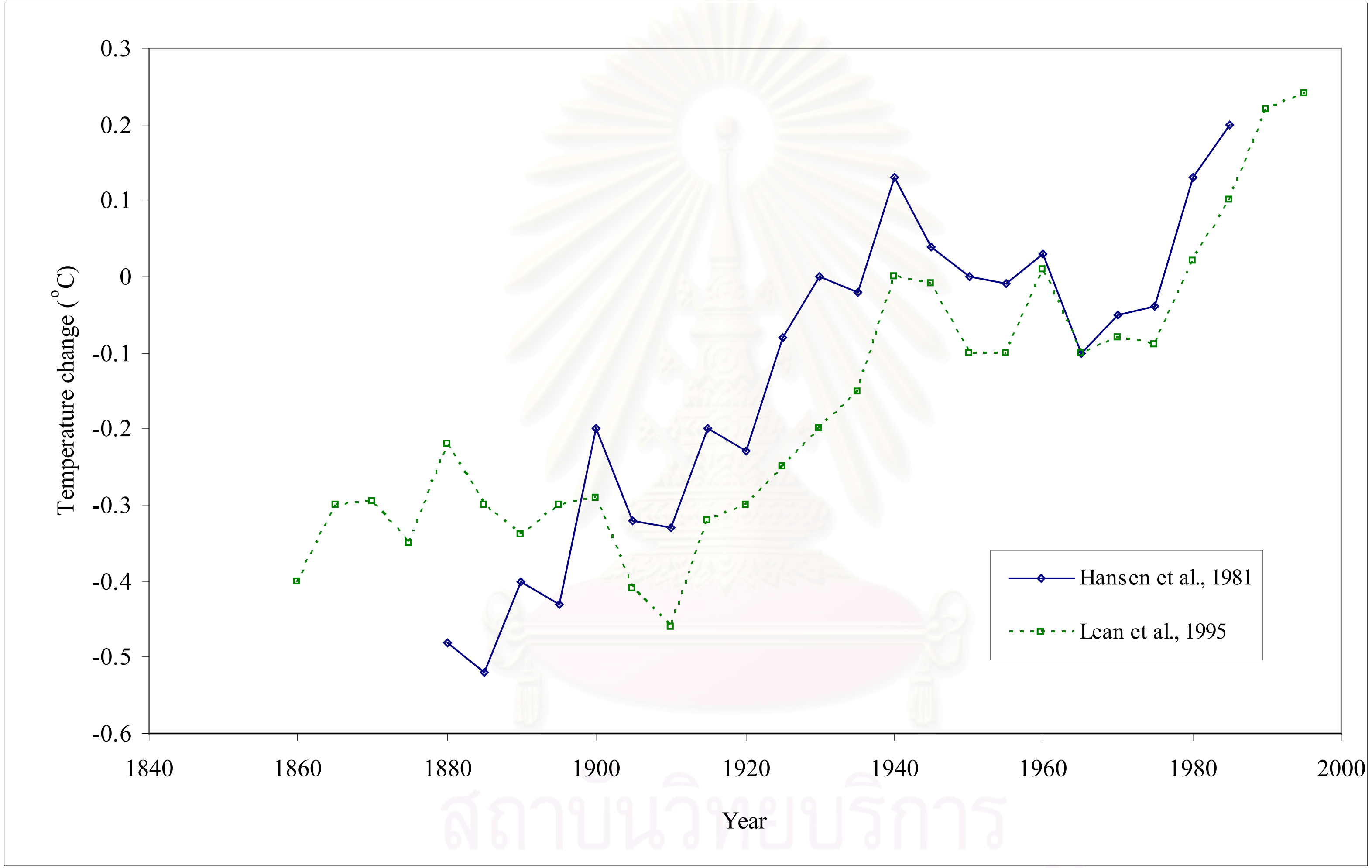


Figure 1-1 Global surface air temperature calculated from land stations over the past century [Hansen *et al.,* 1981; Lean *et al.,* 1995]

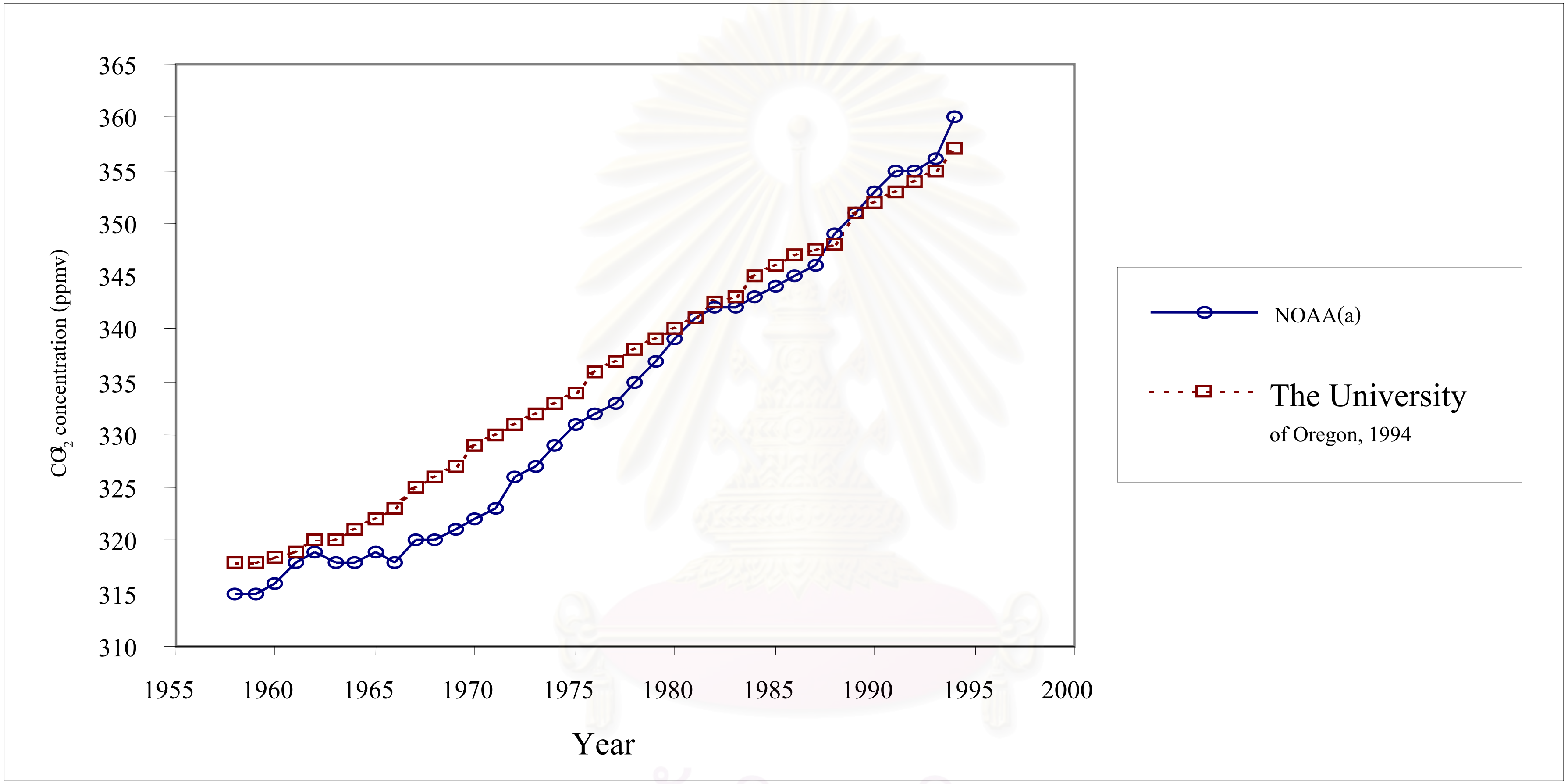


Figure 1-2 Atmospheric carbon dioxide in parts per million, Mauna Loa, Hawaii [NOAA(a); The University of Oregon, 1994]

CHAPTER 2
THEORY AND LITERATURE

2.1 Greenhouse effect and greenhouse gases

The main cause of the increasing average temperature of the earth is commonly known as “Greenhouse Effect”. This is a phenomenon where some “greenhouse” gases such as carbon dioxide, methane, etc. float up through the atmosphere and cover the earth like a sheet of glass. This prevents the heat from transferring out of the earth's atmosphere and results in the accumulation of heat. Hence, higher global temperature is evidenced.

2.1.1 Greenhouse Effect

The sun emits electromagnatic energy, which is a short wavelength radiation (0.2-0.4 microns), in every direction [Watts, 1997]. This high energy radiation is able to pass through the earth's atmosphere, with almost one third reflected back into the space by some gases and clouds at the top of the earth's atmosphere and by the surface of the earth. Another 20 to 25 percent of the incoming solar radiation directly warms the atmosphere and clouds. The remaining 40-45 percent are the radiation that can reach the earth's surface not only directly but also indirectly from the scatter of light by atmosphere or clouds [Lyman, 1990]. This mechanism is illustrated in Figure 2-1.

Figure 2-1 reveals that the short wavelength radiation from the Sun (or called “solar radiation”) reaches the top of the atmosphere, where air molecules, clouds, and the earth’s surface reflect about 31% of this incoming solar radiation back to the space. This type of reflection is called “Total Reflectivity”, or technically known as “Albedo”. Dusts, ozone and water vapor in the upper atmosphere (or commonly known as stratospheric layer) absorb 19% of the incoming radiation. Stratosphere is heated up by this absorbed radiation. In the lower atmosphere or troposphere, clouds absorb 4% of the radiation. The remaining 46% of the solar radiation reaches the earth’s surface [The University of Oregon, 1994] and are absorbed by ground surface and the ocean.

To maintain the thermal equilibrium of the earth, all surfaces that absorb the heat from the radiation must transfer the absorbed energy into the surrounding and finally to the space. Figure 2-1 also shows various mechanisms that control this equilibrium. There are 2 parts of the outgoing radiations, short and long wavelengths. The short-wave radiation is total reflectivity, which is approximately 31% of the incoming radiation as stated earlier. The rest (about 69%) is long-wave which is re-emitted by surface, gases, and clouds. There are several patterns of re-emission of the absorbed energy from the earth. 15% of the total incoming radiation is directly radiated back by the earth's surface in a form of low energy radiation with a wavelength band between 4 - 100 microns, or namely "Infrared Radiation" [Watts, 1997]. But only 9% can reach the space, the remaining 6% is absorbed by the atmosphere. Water vapor, ozone, and some gases emit as much as 40% of the outgoing long wavelength radiation into the space whilst clouds emit about 20% [The University of Oregon, 1994].

However, not all of the infrared radiation from the earth can be transferred through the earth's atmosphere to the space, which means that the thermal equilibrium does not exist. One of the causes for this inequilibrium is the existence of some gases. Short-wave radiation with high energy from the sun can permeate through these gases, but on the other hand, the long-wave with low energy from the earth cannot. Therefore the incoming energy is more than the outgoing resulting an accumulation of heat within the earth. Consequently, the average temperature of the earth increases gradually. This phenomenon is called "Greenhouse Effect". The gases that act as a sheet of glass covering the earth are known as "Greenhouse Gases". There are many types of greenhouse gases in the atmosphere such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), etc. Although nitrogen and oxygen is two main components of the atmosphere, they do not absorb any radiation [Stark, 1995].

In fact, the greenhouse effect is a natural phenomenon because greenhouse gases are naturally produced in several natural cycles. For instance, carbon dioxide is produced within the natural Carbon cycle. If no greenhouse gases were present in the atmosphere, calculations showed that the average earth's temperature would be much lower than what it is now [Stark, 1995; NOAA(b)]. Since the beginning of the 20th century, Figure 2-2 illustrates that the earth's average temperature kept on increasing, which was thought to be attributed to the increasing level of greenhouse gases in the atmosphere [Lean, 1995]. This increase in the greenhouse gases was a result of various human activities such as industries, agriculture, etc. If the rate of greenhouse gases production continues to increase at this rate, by 2050, the average temperature could be 4.5-5 ^{o}C more than now. On the contrary, if this rate stops, there will still be an increase in the temperature due to the existing quantity of greenhouse gases in the atmosphere, but the average temperature in 2050 could only be just 0.5-2 ^{o}C higher than now [Lyman, 1990].

2.1.2 Greenhouse gases

Most greenhouse gases, e.g. carbon dioxide (CO_2), methane (CH_4), ozone (O_3), water vapor (H_2O), etc. are present naturally in the atmosphere, although there are some such as chlorofluorocarbons (CFCs) that are produced by human activities. These gases are responsible for the greenhouse effect and global climate changes. Table 2-1 shows how each greenhouse gas affects the climate. This section gives brief details of some of the most important greenhouse gases.

2.1.2.1 Carbon dioxide (CO_2)

The natural carbon dioxide concentration changes with season depending on the plant growth as shown in Figure 2-3. In the growth seasons, i.e. spring and summer, plants absorb carbon dioxide for their photosynthesis whereas for the rest of year, plants hardly grow and they emit carbon dioxide out from their respiration activity. Hence, the concentration of carbon dioxide increases during fall and winter and declines during spring and summer [Wuebbles, 1997].

Human activities significantly influence the quantity of carbon dioxide in the atmosphere. The most important source of carbon dioxide is the burning of fossil fuel, like petroleum, natural gases, and coal, which accounts for as much as 80% of the annual emission from the earth to the atmosphere [Augenbraun *et al.,* 1999c]. The other 20% are mostly accounted for by deforestation and land use [Wuebbles, 1997].

As carbon dioxide is not chemically active, it is generally not consumed by any reactions, and instead, it is accumulated in the atmosphere, or taken up by the oceans, soil, and plants [Augenbraun *et al.,* 1999c]. Statistics show that, during the last 200 years, atmospheric concentration of carbon dioxide has increased about 25% [Stark, 1995]. Particularly, it was reported that atmospheric carbon dioxide concentration increased steadily at the rate of about 1 ppm annually for the last 50 years [The University of Oregon, 1994] as shown in Figure 2-4. Compared with other greenhouse gases, the content of carbon dioxide in the atmosphere is the largest [Wuebbles, 1997] and its lifetime is quite long [IPCC, 1992]. Thus, it might be concluded that carbon dioxide is one of the most important greenhouse gases.

2.1.2.2 Methane (CH_4)

The natural sources of methane are wetlands in which some reactions without oxygen leads to the formation of large amount of methane. Besides, wildfire and some mechanisms in wild animal's body also emit methane. Some anthropogenic activities e.g. rice cultivation, agricultural animals such as cattle, animal waste, and landfills also emit methane. Like carbon dioxide, the emission of methane varies seasonally [Augenbraun *et al.,* 1999c]. Moreover, the increase in the global temperature results in the melting ice at the earth's pole, which might lead to the release of frozen methane in the Arctic ice caps [The University of Oregon, 1994]. This can potentially lead to a rise in the atmospheric methane concentration.

Methane is chemically active. It can be broken down in the troposphere, the lower atmospheric layer close to the earth's surface and if it reacts with hydroxyl radical (OH•), carbon monoxide which is another source of carbon dioxide is produced according to the following stoichiometry [Wuebbles, 1997].

$$2CH_4 + 2OH\bullet \rightarrow 2CO + 5H_2$$

Although the content of methane in atmosphere is small with respect to carbon dioxide, methane contributes approximately 20% to the global warming [Schütz *et al.,* 1991]. This is because one molecule of methane is approximately equal to 24 molecules of CO_2 in terms of global warming potential [IPCC, 1992]. As shown in Figure 2-5, the concentration of methane increases at the rate of about 10 ppb per year [The University of Oregon, 1994] which is equivalent to an annual increase of approximately 0.24 ppm of carbon dioxide.

2.1.2.3 Nitrous oxide (N_2O)

A natural source of nitrous oxide is a microbial action in soils especially in tropical regions. This process is controlled by the status of oxygen, water, and nutrients in the soils [Augenbraun *et al.,* 1999c]. Furthermore, human activities, such as land cleaning, biomass burning, fossil fuel combustion, nitrogen fertilization, are also sources of nitrous oxide emission. Nitrous oxide emitted from the earth is accumulated in the atmosphere for tens of years and then it floats to the stratosphere, the upper atmospheric layer. Due to in active nature, nitrous oxide reacted, under sunlight, with ozone in this atmospheric layer resulting in the depletion of ozone. This decomposition of nitrous oxide with ozone is called "Photolysis".

The present concentration of nitrous oxide in the atmosphere is about 10% more than that of 200 years ago [Augenbraun *et al.,* 1999c] and continues to increase at the rate of about 0.2 - 0.3% per year (Figure 2-6) [Khalil and Rasmussen, 1992]. Although nitrous oxide exists in the atmosphere in a small amount and increases at the quite low rate, one molecule of nitrous oxide is able to absorb about 290 times infrared radiation more than one molecule of carbon dioxide [IPCC, 1992].

2.1.2.4 Chlorofluorocarbons (CFCs)

CFCs are chemical substances used as a cooling medium in refrigeration and air-conditioning, as blowing agents in packing materials and other plastic foams, and as solvents for cleaning electronic parts. Some CFCs are used in fire extinguishers [Lyman, 1990]. CFCs have a long term effect on the global climate because they have very long atmospheric lifetimes which can last even longer than 100 years [Wuebbles, 1997]. Besides, in the stratosphere, CFCs are destroyed by photolysis resulting in a release of an ozone depletion reagent, chlorine.

CFCs have abilities to absorb infrared radiation at about 20,000 times that of carbon dioxide. Moreover, CFCs are very strong ozone depletion agents where more than 10,000 molecules of ozone are destroyed by only one molecule of CFCs. This significantly increased the intensity of the UV light that reaches the earth's surface. In the past, atmospheric concentration of CFCs increased at the rate of about 5 - 7% annually [Lyman, 1990]. It was not until 1992 that the United Nations Environment Programme launched the Montreal Protocol which aimed at the elimination of the production of CFCs by 1996 [Wuebbles, 1997].

2.1.2.5 Ozone (O_3)

The effects of ozone on the global climate depend on the distribution of ozone in the atmosphere. In troposphere (approx. 30 km above ground level), ozone acts as a greenhouse gas which traps outgoing radiation with a wavelength of 9.6 microns (9600 nanometer). An increase of ozone in this atmosphere tends to raise the surface temperature of the earth. On the other hand, in the upper, stratosphere (above the troposphere), ozone acts as a shield against ultraviolet radiation form the sun by absorbing this radiation. This lessens the intensity of the ultraviolet radiation when it reaches the earth's surface [Wuebbles, 1997; NOAA(b)].

2.1.2.6 Water vapor (H_2O)

Water vapor in the troposphere exists due to evaporation, condensation, and other transport mechanisms. A higher global temperature results in a more water vapor produced, and vice versa is also correct. This is because water vapor is one of greenhouse gases, and an increase in water vapor can potentially lead to the global warming problem.

In stratosphere, concentration of water vapor increases with altitude. Water vapor is produced by the oxidation of methane where one molecule of methane yields 2 molecules of water. Hence, should the concentration of methane increase, the water vapor will also increase. Furthermore, water vapor in the atmosphere may have been resulted from a release of flying aircrafts at the lower stratosphere [Wuebbles, 1997].

There are other greenhouse gases such as VOCs. These gases have diverse properties and are not included here for brevity proposes. For more information, readers are advised to consult the reference [Wuebbles, 1997]

2.2 Methane

2.2.1 Methane as a global warming agent

As one of the natural atmospheric gases, methane is able to absorb infrared, long wavelength radiation, especially at wavelength between 6.52 and 7.66 microns. The absorption of infrared radiation by methane in the atmosphere varies with square root of methane concentration [Badr *et al.,* 1991]. Methane can heat up the global temperature by its absorption of infrared. As methane is chemically more active than carbon dioxide, its lifetime in the atmosphere is relatively short. Table 2-2 indicates that the lifetime of methane is only 10 years whereas carbon dioxide's is about 120 years [IPCC, 1990; IPCC, 1992]. However, its effect on the global climate is, by far, more than that exerted by carbon dioxide. Each kilogram of methane emitted to the atmosphere is about 60 times more effective in absorbing infrared radiation compared with each kilogram of carbon dioxide [Lindau and Bollich, 1993]. In terms of the global warming potential (GWP), methane is reported to be about 24 which means that methane can absorb the long wavelength radiation 24 times more effective than carbon dioxide [IPCC, 1992].

Apart from carbon dioxide, methane is another most abundant atmospheric carbon species [Schütz *et al.,* 1991]. In 1988, the concentration of methane in the troposphere was reported at about 1.7-1.8 ppmv [Blake and Rowland, 1988]. This figure was considerably higher than the pre-industrial concentration of 0.6-0.7 ppmv (which was believed to come from the release of gas enclosure in the ice cores) [Craig *et al.*, 1988]. This indicated clearly that the additional quantity of methane has mostly been derived from human activities.

2.2.2 Sources and sinks of methane

2.2.2.1 Sources of methane

Methane is almost exclusively produced by anaerobic methanogenic bacteria [Schütz *et al.*, 1991; Sass *et al.,* 1992; Yagi, 1996]. Acetic acid or methanol are reactants in this transmethylation activity [Houghton *et al.*, 1991; Rath *et al.,* 2000]. Moreover, hydrogen, fatty acids, or alcohols can be microbial-oxidized by carbon dioxide to methane [Rath *et al.,* 2000]. Table 2-3 shows the quantity of annual methane emissions form different sources, the description of each is detailed as follows.

a) Natural sources: This includes wetlands, termites, methane hydrate, oceans, etc.

Wetlands

Wetlands are the largest natural sources of methane [Augenbraun *et al.*, 1999a]. The overall average methane emission from wetlands is approximately 110 Tg annually [Schü tz *et al.*, 1991]. Methanogenesis by methanogenic bacteria in the sediments is an anaerobic microbial decomposition process of organic material which is responsible for the production of metane [Lindau *et al.,* 1993]. However, it is noted that when methane produced in water-logged soil moves upward through a dried surface soil, sometimes it might be oxidized resulting in zero methane emission [Augenbraun *et al.*, 1999a].

Termites

0-200 Tg of methane is annually produced by the activity of methane producing bacteria (methanogens) on the organic material consumed by the termites [Augenbraun *et al.*, 1999a].

Methane hydrate

Methane hydrate, methane molecules surrounded by rigid water cages, is stable at high pressure and low temperatures. Methane hydrate is normally captured in the regions which do not influence climate changes such as underneath the ocean [Augenbraun *et al.*, 1999a]. However, when the climate becomes warmer, methane hydrate can be released. It is estimated that methane hydrate released annually is about 5 Tg [IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993].

b) Anthropogenic sources: Human activities can lead to methane production. Examples of these activities are the fugitive losses through the natural gas exploration process, coal mining, landfills, animal waste, sewage treatment, etc. Some are involved in agriculture such as enteric fermentation of domesticated animals, rice paddies, biomass burning, etc.

[IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993]. This kind of methane sources contributes significantly to the overall methane production, and Figure 2-8 indicates that as much as 65% of the total methane sources are anthropogenic.

Domestic animals

Fermentation of carbohydrates by bacteria in the four-chamber stomach, called rumen, could lead to methane production [CIESIN, 2000]. The production varied among animal species, quantity and quantity of feed, body weight, age, and activity level. These animals are cattles, sheep, goats, camels, and horses [Augenbraun *et al.*, 1999a].

Rice cultivation

Methanogenic bacteria in water-logged soil produce methane by anaerobic decomposition of organic materials [Augenbraun *et al.*, 1999a]. Methane produced may enter the atmosphere by three different pathways [Nouchi, 1994; Schütz *et al.*, 1999; Augenbraun *et al.*, 1999a]: -

1) Through the water column (diffusion)
2) Through the gas bubble (ebullition)
3) Through the plants themselves

In 1993, Khalil and Shearer stated that methane emission from rice paddies is about 40 Tg per year.

Fossil fuel

Methane is the major component of coal gas and natural gas. Fossil sources of methane including coal mining and processing, and natural gas exploration, production, transmission, and distribution contribute about 14-24% to the total methane production [Wuebbles, 1997; Augenbraun *et al.*, 1999a].

Biomass burning

Figure 2-8 illustrates that about 8% of the total methane emission are derived from biomass burning. Because vegetation consists of carbon compounds, when it is incompletely burned, it releases some substances such as methane and carbon dioxide.

Landfills

Decomposition of biodegradable organic materials in landfills produces both carbon dioxide and methane [Augenbraun *et al.*, 1999a]. The same figure reveals that methane emitted from landfills contributes about 8% of the total emission.

2.2.2.2 Sinks of methane

When methane is released from the sources, it spreads into the atmosphere, both troposphere and stratosphere. Methane, in troposphere can reacts with hydroxyl radicals and result in the production of carbon monoxide as mentioned earlier.

In addition, at high NO_x concentrations (>10 ppt), the oxidation of methane by hydroxyl reactions leads to the formation of ozone [Schütz *et al.,* 1991] which also acts as a greenhouse gas. Furthermore, at low NO_x concentrations (<10 ppt), the reaction of methane with hydroxyl radicals leads to the formation of water vapor [Schütz *et al.,* 1991]. Hydroxyl radicals can be called a chemical sink of methane. Also, it acts as a chemical sink for other trace gases. For this reason, hydroxyl radicals are known as "the detergent of the atmosphere" [Augenbraun *et al.*, 1999b].

Methane is also oxidized by hydroxyl radicals in stratosphere [Schütz *et al.,* 1991], and when methane is broken down, hydrogen atom from methane molecule reacts with oxygen atom in the atmosphere resulting in water vapor or, in another sense, another greenhouse gas [Houghton *et al.,* 1991]. Although methane does not last long in the atmosphere, it can be decomposed into carbon monoxide, ozone, and water vapor. Therefore it is reasonable to say that methane has indirect effect on the climate as these gaseous products also contribute greatly to the global warming problem.

Another sink of methane is soil containing methane-oxidizing bacteria (methanotrophic bacteria or methanotrophs) [Neue, 1993; van Amstel, 1994]. Methane is oxidized and accumulated in the form of carbon dioxide [Neue, 1993].

2.3 Methane emission from rice cultivation

The IPCC has estimated global methane emission of 375 Tg annually from anthropogenic sources compared with natural emission of 160 Tg per year [Riemer and Freund, 1999]. This means that almost 70% of total methane emission are from anthropogenic sources. Table 2-4 indicates how much methane emission is from several areas in the world. Due to the possibility in controlling the emissions from anthropogenic sources, most research has been conducted in order to investigate the mechanism from which methane is generated and this will help decrease the emission rate. As shown in Figure 2-9, the two largest sources are enteric fermentation of domesticated animals and rice cultivation. The enteric fermentation of domesticated animals is perhaps out of our control and will be left out of the discussion for brevity purpose. In contrast, methane production from rice paddies has been reported to be controllable by adapting management of rice cultivation.

Several researchers have measured methane emission quantities from rice paddies. In 1980, Cicerone and Shetter measured emission of methane in California and estimated the global methane emission to be about 59 Tg per year. Annually 35-59 Tg of methane was emitted from rice paddies in Spain [Seiler *et al.*, 1984]. Estimation of annual methane emission to the atmosphere from rice field ranges from 50-170 Tg [Holzapfel-Pschorn and Seiler, 1986]. Khalil and his colleagues estimated in 1991 that average emission rate during the growing season was about 60 $mg \cdot m^{-2} \cdot h^{-1}$ from rice fields at TuZu in China. Moreover, Anastasi and his colleagues estimated in 1992 that methane emission from rice paddies could increase at an average rate of 1.1% per year over the next 30 years.

2.3.1 Methane production in rice paddies

In cultivation season, the flooded paddy soils acts as a barrier of oxygen transportation from the atmosphere into soils, and therefore oxygen and other oxidized organic compounds in the soil are absent [Yagi *et al.,* 1996]. This condition is proper for activities of methanogens, such as neutrophilic [Conrad, 1989], which is bacterial strain that can decompose some organic substance and release methane [Lindau *et al.,* 1993; Neue, 1993; Yagi *et al.,* 1996].

Degraded by hydrolytic bacteria, large organic polymers in soils are decomposed and converted into smaller molecular weight alcohols (e.g. methanol) and organic acids (e.g. acetic acid) by fermentative and acetogenic bacteria [Schütz *et al.,* 1989]. The cleavage of methanol and acetic acid by methanogens (or called transmethylation) results in methane production [Rath *et al.,* 2000]. This methanogenesis is most efficient in a narrow range of pH, 6-8 [Conrad, 1989]. These cleavages have been estimated to account for 50-90% of the methane produced in rice paddies [Schütz *et al.,* 1989]. Moreover, the reduction of carbon dioxide with acohols and fatty acids as hydrogen donor also produces methane [Rath *et al.,* 2000].

When the soils are flooded, methane is not produced immediately. The delay of methane production depends on many factors such as pH, temperature of soils, substrate availability, etc. The methane production starts in alkaline and calcareous soils at 25-30^{o}C after flooding for hours. In neutral soils, the production is delayed two to three weeks after flooding whilst in acid soils, the delay could be as long as five or more weeks [Neue, 1993]. However, methanogenesis is inhibited by the addition of seawater, sodium chloride, chloroform, acetylene, DDT, etc [Neue, 1993]. Besides, unbalance nutrient supply can decrease the decomposition of organic matter by methanogens [Neue, 1993].

Methane produced by methanogens in soil sometimes moves upward through the upper soils that contain methane-oxidizing bacteria (or namely methanotrophs whose growth deals with oxygen [Neue, 1993]) [Angenbraun *et al.*, 1999a]. These methanotrophs, existing in the floodwater-soil surface and in the rice rhizophere, oxidize methane to carbon dioxide where methanol, formaldehyde, and formate are produced as intermediates. [Neue, 1993]. Sass and his colleagues reported in 1990 that up to 60% of the methane produced during a rice growing season may be oxidized before it reaches the atmosphere [Sass *et al.,* 1990]. This methane oxidation greatly limits emission of methane to the atmosphere.

2.3.2 Transportation of methane to the atmosphere

Methane may enter the atmosphere by three different pathways as shown in Figure 2-10.

1) Diffusion through the water column (diffusion)
2) Ebullition through the gas bubble (ebullition)
3) Transport through the plants themselves due to difference in pressure and concentration.

During diffusion pathway, Schütz and his colleagues (1991) stated that the diffusion of dissolved methane across the air-water interface might occur due to the concentration gradients through the sediment-water and air-water interfaces. Fick's first law of diffusion can explain this diffusion. Diffusion coefficient (diffusivity) depends on wind speed and temperature differences between air and water. The wind speed above the water surface can decrease the thickness of boundary resulting in a higher mass transfer rate. Another factor affecting diffusivity is water temperature. The solubility of methane in the water depends on water temperature; the solubility increases with water temperature. Higher solubility means that more methane can dissolve in the water, and similarly, more methane diffuses through the water to the atmosphere. However, methane transportation by diffusion is generally limited by the low methane solubility in the water (12-40 mg/l) [Yamamoto *et al.,* 1976].

In the ebullition mechanism, Schütz and his associates also said in 1991 that when methane had a supersaturated condition in the water and the partial pressure of methane exceeded the hydrostatic pressure, gas bubble formation and ebullition could occur. The buoyancy force sent these bubbles to the water surface where they bursted and methane was released to the atmosphere. As these bubbles moved up to the surface, their volume became larger because of a decrease in the hydrostatic pressure.

Nouchi and his colleagues (1990) described the transport through the plant as illustrated in Figure 2-11. Dissolved methane in the soil surrounding the roots diffuses into the surface of the roots, into the cell wall of root epidermis cells, and then through the cell wall of the root cortex. These diffusions depend on the methane concentration gradient between the soil surrounding the roots and the lysigenous intercellular spaces in the roots. When methane enters the root cortex, it is gasified and transported to the shoots via lysigenous intercellular spaces and aerenchyma. Eventually, methane is released primarily through the micropores in the leaf sheath of the lower leaf position and secondarily through the stomata in the leaf blade.

In 1989, Schütz and his colleagues collected data about methane emission from rice fields and reported that in the first month after flooding, ebullition was a major factor in methane emission which contribute about 25-100% to the total methane flux. After flooding for 2-3 months (during the reproductive phase of rice plants), methane emission rate increased and approximately 90% of total flux are contributed by transportation through plant's aerenchyma, whereas diffusion of dissolved methane is about 1-5% of the total methane flux.

There are many studies involving methane release from other areas such as Florida wetland, Amazon floodplain, tidal freshwater estuary, etc. The main pathways of methane release of these areas are molecular diffusion and gas bubble ebullition [Schütz *et al.,* 1991]. Each area has a different main pathway of methane emission because of the differences in the environmental conditions. However, for rice fields, methane transportation by plants is a main pathway of methane emission.

2.4 Factors influencing methane emission from rice paddies

2.4.1 Vegetation period

Rice can excrete some substances from its root called "root exudates", and it also discards their dead tissue and cast-off skin from its root to the surrounding soils. These matters consist of carbohydrate, organic acid, amino acid, and phenol compound which are carbon/energy sources of methanogenic bacteria. In addition, the respiration of root rice also releases carbon dioxide, which is an electron receptor in methane production bacteria [Tiawyuenyong, 1994]. Chanton and his colleague reported in 1997 that the quantity of below-ground methane was greater in vegetated areas when compared to areas maintained free of vegetation. Sass and his associates (1990) concluded that release of methane from vegetated areas is larger than from unvegetated areas. This is attributed to the ability of the plants in facilitating the transport of methane from the soil to the atmosphere. Table 2-5 summarizes examples of the comparison between the rate of methane productions from the area with and without rice vegetation.

The cultivation of rice can be separated into many stages, i.e. transplanting, booting, grain-developing, grain-ripening, and harvesting. Methane emission rate depends not only on the rice cultivar but also on the cultivation stage. Literature indicates that booting and grain-developing were the two most significant stages in terms of methane production rate (Table 2-6).

2.4.2 Vegetation methods

There are many methods of rice cultivation depending on characteristics of each area. For example, rice cultivars that need a suitable level of flood throughout the vegetation period are grown in irrigated or lowland fields. Some rice can be cultivated in a rainfed rice field whose level of flood controlled solely by quantity of rainfall. A deepwater rice field is a rice field that has a flooding level of about 50 to 100 cm. Both rainfed and deepwater rice fields can be called floating rice fields. The other method of rice cultivation is called upland rice field where there is no flood throughout the growth period [Kanchanasuntorn, 1994; Tiawyuenyong, 1994]. Each method of rice cultivation generates different methane emission rates. Pasashar and his colleagues said in 1996 that methane flux from deepwater rice field was larger than from irrigated and rainfed types, respectively. Kanchanasuntorn (1994) reported that both methane production and emission from lowland rice fields were much larger than that from upland type. In addition, Table 2-7 shows that methane emission under rainfed condition was higher than under irregated condition. This was because rainfed condition had a longer submergence period and a deeper water level than the irregated [Rath *et al.,* 1999]. In contrast, Tiawyuenyong said in 1994 that methane emissions from lowland, irregated rice fields were larger than those from floating rice fields. Reasons for this result were however not mentioned.

In some areas, it is possible that rice is cultivated twice a year where the rice straw from the first cultivation is used as a fertilizer for the second cultivation. The first crop is called main crop and the second is known as ratoon crop [Lindau and Bollich, 1993]. Table 2-7 indicates that there was a large deviation of the methane emission data from these areas. Methods of fertilizing also play a significant role in mandating the rate of methane emission and this will be discussed later on.

2.4.3 Rice cultivars

Because transport through plants is the most important pathway of methane emission from rice fields to the atmosphere, rice cultivars can be one of the most important factors in determining the rate of methane release. Each rice cultivar has its own characteristics of growth, e.g. quantity of root exudates excreted, quantity of carbon dioxide released by their root respiration, dimension of methane pathways both through lysigenous intercellular spaces and aerenchyma, their heights and biomass yields, etc. Examples of the rate of methane productions from various rice cultivars are given in Table 2-8.

2.4.4 Soil properties

Soils from different sources usually have different properties, *i.e.* temperature, moisture, mineral composition, nutrient, organic material, type of bacteria, etc. and this could significantly affect the rate of methane production. Sass and his associates (1990) investigated the methane emission rate from the area with different types of soils, for example, Beaumont and Lake Charles soil which were in the same climatic environment, and found that the emission rates of methane were not equal. And in their subsequent work, Sass *et al.* (1994) concluded that the methane emission rate tended to vary linearly with the amount of sand in the soil (see Table 2-9).

2.4.5 Cultivation management

2.4.5.1 Fertilizers and chemicals

Plants such as rice need some fertilizers and chemicals to increase their productivity. These matters may be organic substances such as rice straw [Cicerone *et al.,* 1992; Lindau and Bollich, 1993; Nouchi *et al.,* 1994], or inorganic substances such as urea, nitrogen fertilizers, nitrification inhibitor [Rath *et al.,* 1999], calcium carbide [Lindau *et al.*, 1993], sulfate [Lindau *et al.*, 1993], etc. The addition of these materials could increase or decrease methane emission rate from rice fields depending on their effects on rice, soils properties, bacterial activities, etc (Table 2-10).

Rice straw is an effective substance in increasing methane production and emission [Cicerone *et al.,* 1992; Lindau and Bollich, 1993; Nouchi *et al.,* 1994]. In contrast, Lindau *et al.* (1993) stated that encapsulated calcium carbide, dicyandiamide, ammonium sulfate had a mitigating effect on methane emissions from rice fields where the encapsulated calcium carbide was the most effective compared to the urea treatment. Furthermore, adding gypsum which is a sulfate compound ($CaSO_4$) to a flooded rice field can reduce methane emission by approximately 55-70% (Table 2-10) due to the inhibition of methanogenesis by sulfate-reducing bacteria [van der Gon and Neue, 1994].

2.4.5.2 Field drainage

Field drainage is conventionally applied for the aeration soil in the rice cultivation during midseason and also during the end of the growing season, [Sass *et al.,* 1992]. By this method, the quantity of oxygen in soil is larger than that obtained from the field flooded throughout the growing season. This soil aeration inhibits methane production by methanogens while, at the same time, depletes existing methane through aerobic oxidation by methanotrophs [Sass *et al.,* 1992]. Sigren and his associates (1997) found that field drainage was an effective method of mitigating methane emissions from rice fields, with a 64% reduction in emission rate after a single midseason drainage at the Richmond, Texas, site. Table 2-11 gives some examples on the effect of field drainage on methane emission rate. Note that in the work of Yagi *et al.* (1996), the drainage in 1991 was performed with a few long drainage periods during the cultivation, while the drainage in 1993 was accomplished with a more frequent, short intermittent of drainage periods. The percentage reductions in methane emission rate from both cases were approximately equal to each other.

Table 2-1 Greenhouse gases and other important climate affecting gases [Watts, 1997b]

Trace constituent	Common name	Importance for climate
CO_2	Carbon dioxide	Absorbs IR radiation; affects stratospheric O_3
CH_4	Methane	Absorbs IR radiation; affects stratospheric O_3 and H_2O; produces CO_2
N_2O	Nitrous oxide	Absorbs IR radiation; affects stratospheric O_3
$CFCl_3$	CFC-11	Absorbs IR radiation; affects stratospheric O_3
CF_2Cl_2	CFC-12	Absorbs IR radiation; affects stratospheric O_3
C_2H_4, etc.	NMHC	Absorbs IR radiation; affects stratospheric O_3 and OH
O_3	Ozone	Absorbs UV, visible, and IR radiations
H_2O	Water vapor	Absorbs near-IR and IR radiations
CO	Carbon monoxide	Affects tropospheric O_3 and OH cycles; produces CO_2
NO_x	Nitrogen oxides ($NO+NO_2$)	Affects O_3 and OH cycles; precursor of acidic nitrates
$(CH_3)_2S$	Dimethyl sulfide (DMS)	Produces cloud condensation nuclei; affects cloudiness and albedo
OH	Hydroxyl	Scavenger for many atmospheric pollutants, including CH_4, CO

Table 2-2 Global warming potentials [IPCC, 1990, 1992; Lyman, 1990]

Trace gas	Estimated lifetime (years)[a]	Global warming potential[a]	Percentage contribution to global warming problem[b]
Carbon dioxide	120	1	49%
Methane (including indirect effects)	10	24	18%
Nitrous oxide	150	290	6%
$CFCl_3$ (CFC-11)	60	3500	15%
CF_2Cl_2 (CFC-12)	130	7300	
Other	-	-	12%

a - IPCC, 1990; 1992
b - Lyman, 1990

Table 2-3 Estimated sources and sinks of methane [IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993]

Source	Estimate of CH_4 production (Tg/y)
Natural	
- Enteric fermentation (wild)	4
- Wetlands (swamps, etc.)	115
- Lakes	5
- Tundra	4
- Oceans	10
- Termites and other insects	20
- Methane hydrates	5
- Other	40
Total *"Natural"*	203
Anthropogenic	
Energy related	
- Natural gas losses	40
- Coal mining	30
- Petroleum industry	15
- Biomass burning (e.g., fuel wood)	15
- Landfills	40
- Animal waste	25
- Sewage treatment	25
Total *"Energy related"*	190
Agriculture/non-energy related	
- Enteric fermentation (domesticated)	81
- Rice paddies	60
- Biomass burning	40
Total *"Agriculture/non-energy related"*	181
Total *"Anthropogenic"*	371
TOTAL *"SOURCE"*	574
Sink	Estimate of CH_4 production (Tg/y)
- Reaction with tropospheric OH	445
- Removal in stratosphere	40
- Microorganisms uptake by soils	30
- Accumulation	30
TOTAL *"SINK"*	545

Table 2-4 National net anthropogenic methane emission from various sources [van Amstel and Swart, 1994]

Country	Year	CH$_4$ emission (Tg/y)
Australia	1988	5.426
Belgium	1990	0.362
Canada	1990	2.942
Denmark	1989	0.645
Finland	1988	0.250
Germany	1989	3.100
Italy	1989	2.500
Japan*	1988	0.540
Netherlands	1988-1990	0.831
New Zealand	1988	1.700
Norway	1989	0.322
Poland	1988	1.543
Sweden	1990	0.460
Switzerland	1988	0.240
Thailand	1988	0.616
United Kingdom	1988	3.433
United States	1988	33.000
Former USSR*	1988	43.000

* Result of independent research, not official.

Table 2-5 Methane emission rate from vegetated and unvegetated areas

Condition	CH$_4$ emission rate (mg·m^{-2}·d^{-1})		Source
	Vegetated	Unvegetated	
Area: Crowley, Louisiana Cultivar: Texmont Soil: Crowley silt loam soil Fertilizer: Urea	441.56	64.94	Lindau and Bollich (1993)
Area: California Cultivar: Not specified Soil: Capay silty clay			Cicerone *et al.* (1992)
- Fertilizer: None	12.28	10.44	
- Fertilizer: 250 g/m^2 Straw	145.79	54.91	
- Fertilizer: 500 g/m^2 Straw	510.35	264.04	
- Fertilizer: Urea	25.26	10.35	
- Fertilizer: Urea + 250 g·m^{-2} Straw	79.82	243.86	
- Fertilizer: Urea + 500 g·m^{-2} Straw	375.44	182.46	
Area: Tsukuba, Japan Cultivar: Noppon-bare Soil: Gray Lowland soil Fertilizer: Straw 700 g·m^{-2}	103.56	96.71	Nouchi *et al.* (1994)

Table 2-6 Methane emission rate from rice field at various stages of cultivation

Condition	CH_4 emission rate ($mg \cdot m^{-2} \cdot d^{-1}$)	Source
Area: Ayutthaya, Thailand Method: Lowland Cultivar: RD 23		Tiawyuenyong (1994)
- Transplanting stage	67.24	
- Booting stage	831.22	
- Grain-developing stage	877.28	
- Grain-ripening stage	472.63	
Method: Lowland Cultivar: Suphanburi 90		
- Transplanting stage	101.11	
- Booting stage	977.35	
- Grain-developing stage	704.38	
- Grain-ripening stage	580.46	
Method: Floating Cultivar: Huntra 60		
- Transplanting stage	34.20	
- Booting stage	113.71	
- Grain-developing stage	134.59	
- Grain-ripening stage	37.34	
Method: Floating Cultivar: Leb Mue Nahng 111		
- Transplanting stage	42.50	
- Booting stage	177.12	
- Grain-developing stage	409.27	
- Grain-ripening stage	63.79	
Area: Chiang mai, Thailand Method: Lowland Cultivar: RD 23		Kanchanasuntorn (1994)
- Transplanting stage	69.75	
- Booting stage	178.00	
- Grain-developing stage	561.50	
- Grain-ripening stage	55.00	
Method: Lowland Cultivar: RD 6		
- Transplanting stage	83.33	
- Booting stage	191.00	
- Grain-developing stage	600.50	
- Grain-ripening stage	40.0	

Table 2-6 (continued)

Condition	CH_4 emission rate ($mg \cdot m^{-2} \cdot d^{-1}$)	Source
Method: Upland		Kanchanasuntorn (1994)
Cultivar: R 258		
- Transplanting stage	45.50	
- Booting stage	58.00	
- Grain-developing stage	45.33	
- Grain-ripening stage	35.00	
Method: Upland		
Cultivar: Sil Mae Chan		
- Transplanting stage	46.22	
- Booting stage	58.40	
- Grain-developing stage	48.33	
- Grain-ripening stage	32.00	

Table 2-7 Methane emission rate from different methods of rice cultivation

Condition	CH_4 emission rate ($mg \cdot m^{-2} \cdot d^{-1}$) Main crop	Ratoon crop	Source
Area: Crowley, Louisiana			Lindau and Bollich (1993)
Cultivar: Texmont			
Soil: Crowley silt loam soil			
- Fertilizer: Urea	411.56	712.33	
- Feritlizer: Urea + Straw (from the main crop)	-	2041.10	
	Rainfed	Irrigated	
Area: Cuttack, India Cultivar: Gayatri Fertilizer: Prilled urea	2196.43	615.00	Rath *et al.* (1999)
	Lowland	Upland	
Area: Chiang mai, Thailand			Kanchanasuntorn (1994)
- Cultivar: RD 23	199.10	-	
- Cultivar: RD 6	208.48	-	
- Cultivar: R 258	-	47.91	
- Cultivar: Sil Mae Chan	-	48.27	
	Lowland	Floating	
Area: Ayutthaya, Thailand			Tiawyuenyong (1994)
- Cultivar: RD 23	454.08	-	
- Cultivar: Suphanburi 90	493.68	-	
- Cultivar: Huntra 60	-	79.97	
- Cultivar: Leb Mue Nahng 111	-	173.18	

Table 2-8 Methane emission rate from areas with different rice cultivars

Condition	CH_4 emission rate ($mg{\cdot}m^{-2}{\cdot}d^{-1}$)	Source
Area: New Delhi, India		Mitra *et al.* (1999)
Soil: Silty clay loam		
pH: 8.20		
- Cultivar: Pusa 169	13.03	
- Cultivar: Pusa Basmati	19.49	
- Cultivar: Pusa 834	30.03	
- Cultivar: Pusa 1019	21.58	
- Cultivar: Pusa 677	21.14	
- Cultivar: Pusa 933	21.79	
Area: Chiang mai, Thailand		Kanchanasuntorn (1994)
Method: Lowland		
- Cultivar: RD 23	199.1	
- Cultivar: RD 6	208.48	
Method: Upland		
- Cultivar: R 258	47.91	
- Cultivar: Sil Mae Chan	48.27	
Area: Ayutthaya, Thailand		Tiawyuenyong (1994)
Method: Lowland		
- Cultivar: RD 23	454.08	
- Cultivar: Suphanburi 90	493.68	
Method: Floating		
- Cultivar: Huntra 60	79.97	
- Cultivar: Leb Mue Nahng 111	173.18	

Table 2-9 Methane emission rate from areas with different soils

Condition	%Sand	%Clay	%Silt	CH_4 emission rate ($mg{\cdot}m^{-2}{\cdot}d^{-1}$)	Source
Area: Texas					Sass *et al.* (1990)
Cultivar: Jasmine 85					
Fertilizer: Urea					
- Soil: Beaumont	-	-	-	60.00	
- Soil: Lake Charles	-	-	-	212.00	
Area: Texas					Sass *et al.* (1994)
Cultivar: Jasmine 85					
Fertilizer: Urea					
- Soil: Beaumont	4.3	65.2	30.5	12.42	
- Soil: Lake Charles	21.8	35.0	43.2	23.47	
- Soil: Bernard Morey	29.0	24.5	46.6	28.77	

Table 2-10 Methane emission rate from areas with different additional substances

Condition	CH_4 emission rate ($mg\cdot m^{-2}\cdot d^{-1}$)	Source
Area: California		Cicerone *et al.* (1992)
Soil: Capay silty clay		
- Add.: None	12.28	
- Add.: Rice straw 250 $g\cdot m^{-2}$	145.79	
- Add.: Rice straw 500 $g\cdot m^{-2}$	510.35	
Area: Crowley, Louisiana		Lindau and Bollich (1993)
Cultivar: Texmont		
Soil: Crowley silt loam soil		
- Add.: Urea	712.33	
- Add.: Urea + Rice straw	2041.10	
Area: Tsukuba, Japan		Nouchi *et al.* (1994)
Cultivar: Noppon-bare		
Soil: Gray Lowland soil		
- Add.: None	8.77	
- Add.: Rice straw 700 $g\cdot m^{-2}$	103.56	
Area: California		Cicerone *et al.* (1992)
Soil: Capay silty clay		
- Add.: None	12.28	
- Add.: Rice straw 250 $g\cdot m^{-2}$	145.79	
- Add.: Rice straw 500 $g\cdot m^{-2}$	510.35	
Area: Ratchaburi, Thailand		Jermsawatdipong *et al.* (1994)
Cultivar: SPR 90		
Soil: Fulvic Tropaquept		
Method: Irrigated		
- Add.: None	57.14	
- Add.: Chemical fertilizer	129.87	
- Add.: Organic material	764.94	
Area: Pathumthani, Thailand		
Cultivar: SPR 90		
Soil: Thionic Tropaquept		
Method: Irrigated		
- Add.: None	17.33	
- Add.: Chemical fertilizer	8.00	
- Add.: Organic material	222.67	
Area: Surin, Thailand		
Cultivar: KDML 105		
Soil: Anthraquic Paleaquult		
Method: Rainfed		
- Add.: None	394.94	
- Add.: Chemical fertilizer	441.77	
- Add.: Organic material	207.89	

Table 2-10 (continued)

Condition	CH_4 emission rate ($mg \cdot m^{-2} \cdot d^{-1}$)	Source
Area: Crowley, Louisiana		
Cultivar: Texmont		
Soil: Crowley silt loam		
- Add.: Urea	467.53	Lindau *et al.* (1993)
- Add.: Urea + Dicyandiamine (DCD)	402.60	
- Add.: $(NH_4)_2SO_4$	376.62	
- Add.: Urea + Na_2SO_4 (510 $kg \cdot ha^{-1}$)	337.66	
- Add.: Urea + Na_2SO_4 (1020 $kg \cdot ha^{-1}$)	311.69	
- Add.: Urea + Encapsulated CaC_2 (ECC)	298.70	
Area: Los Banos, Philippines		
Cultivar: IR 72		
Soil: Andaqueptic Haplaquoll		van der Gon and Neue (1994)
- Add.: Urea	40.2	
- Add.: Urea + Gypsum	18.6	
- Add.: Green manure	443.00	
- Add.: Green manure + Gypsum	128.00	

Add. = Additive

Table 2-11 Methane emission rate from areas with field drainage

Condition	CH_4 emission rate ($mg \cdot m^{-2} \cdot d^{-1}$)	Source
Area: Kanto, Japan		
Soil: Glay soil		
Year: 1991		
- Flooded	116.54	Yagi *et al.* (1996)
- Drained	67.95	
Year: 1993		
- Flooded	63.27	
- Drained	34.53	
Area: Texas		
Cultivar: Jasmine 85		
Soil: Bernard-Morey		
- Normal flood	106.54	Sass *et al.* (1992)
- Midseason drain	55.89	
- Multiple drain	13.21	
- Late flood	151.29	

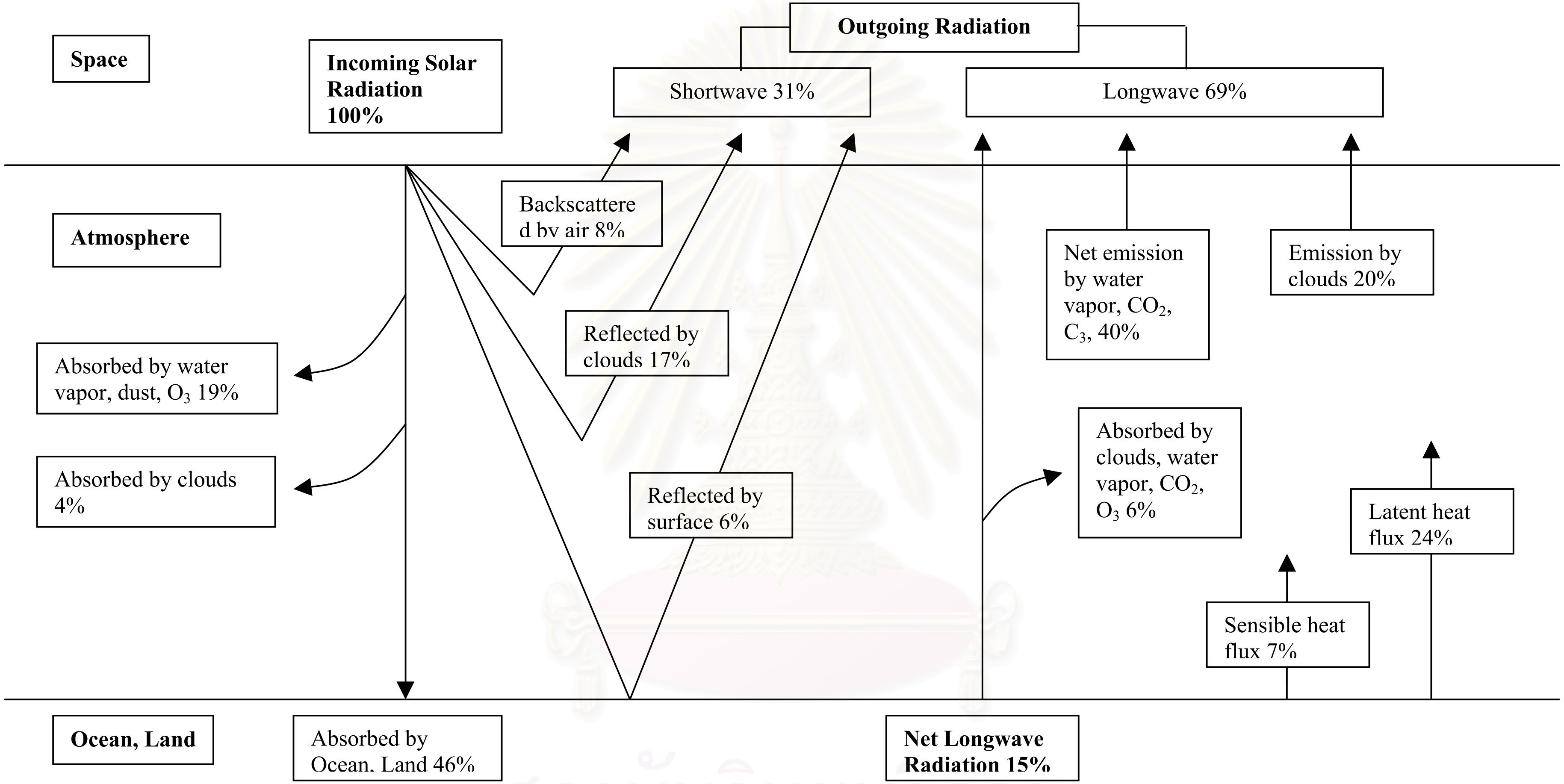


Figure 2-1 The mechanism of incoming radiation from the sun and outgoing radiation from the earth [The University of Oregon, 1994]

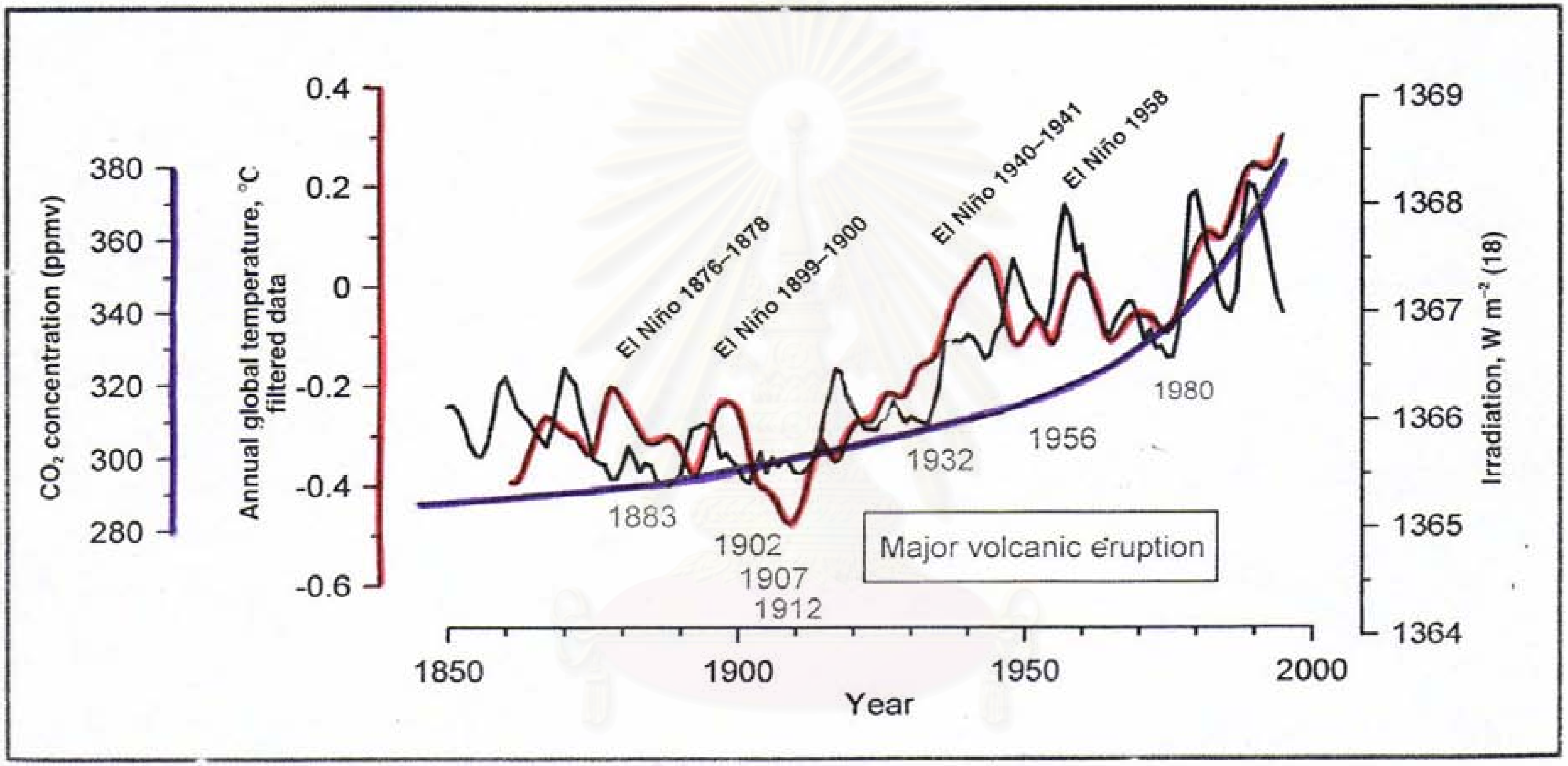


Figure 2-2 Time profiles of global temperature, both solar irradiation, and the atmospheric concentration of greenhouse gas [Lean *et al.,* 1995]

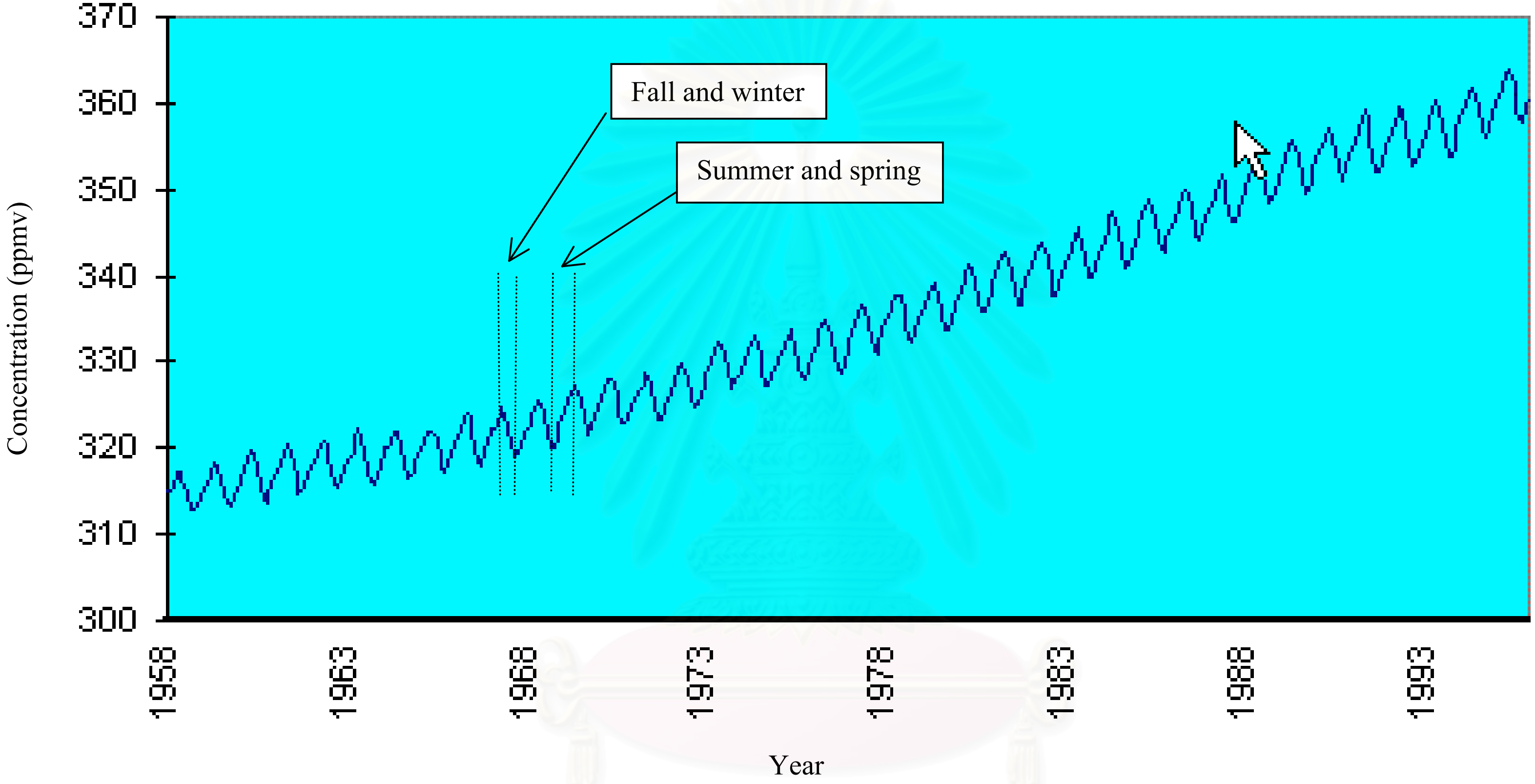


Figure 2-3 Seasonal variation of CO_2 concentration [NOAA(a)]

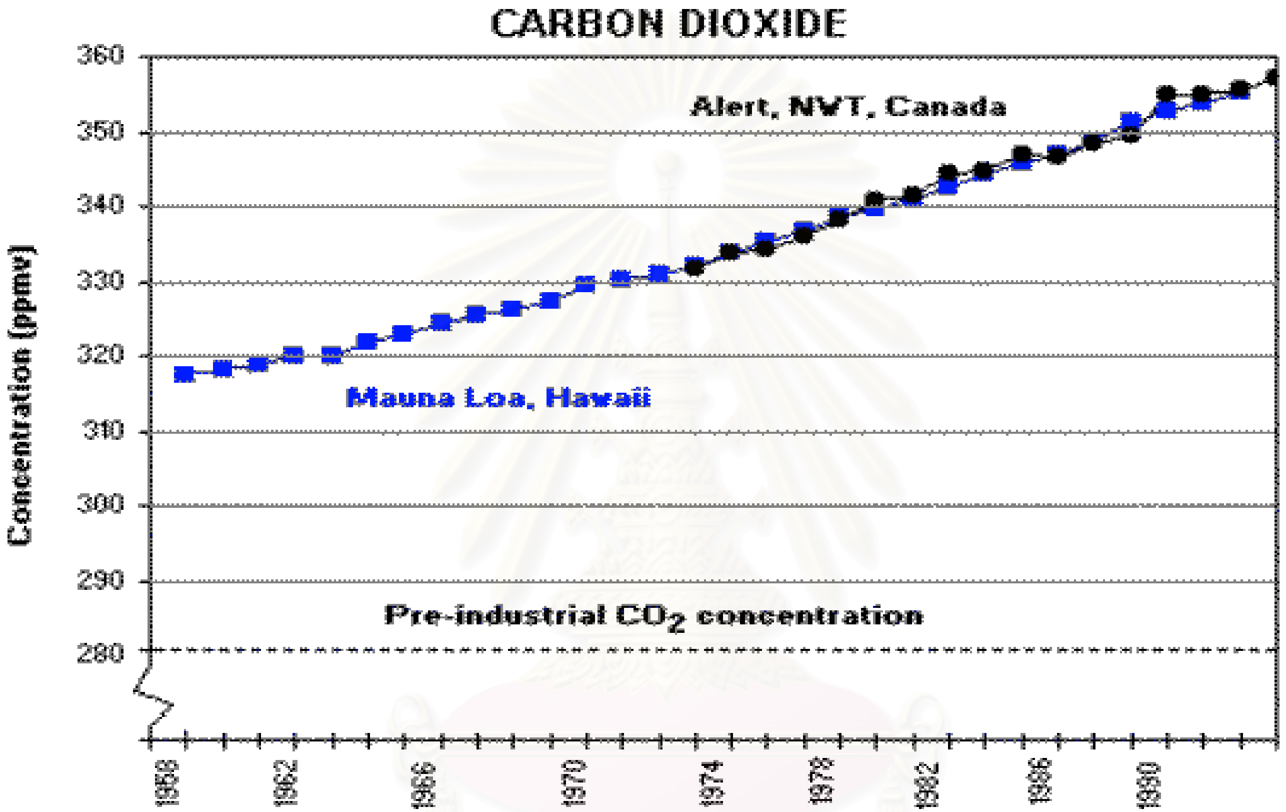


Figure 2-4 Trend of the global concentration of carbon dioxide [The University of Oregon, 1994]

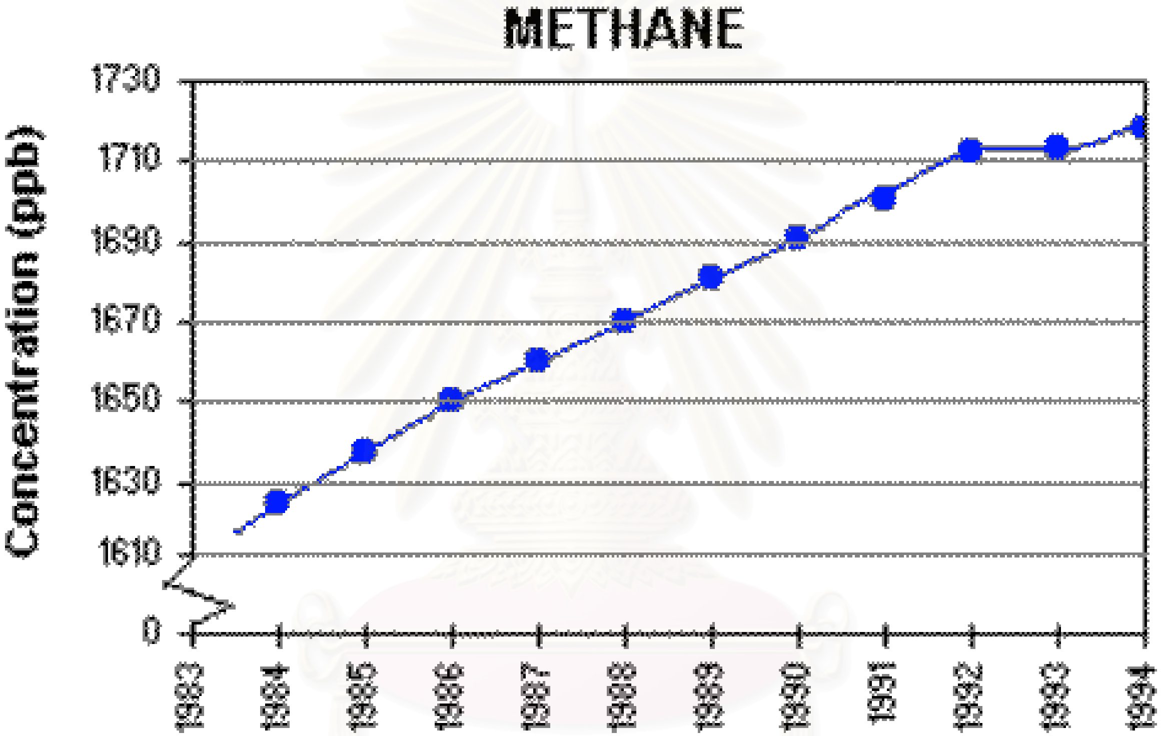


Figure 2-5 Trend of the methane concentration [The University of Oregon, 1994]

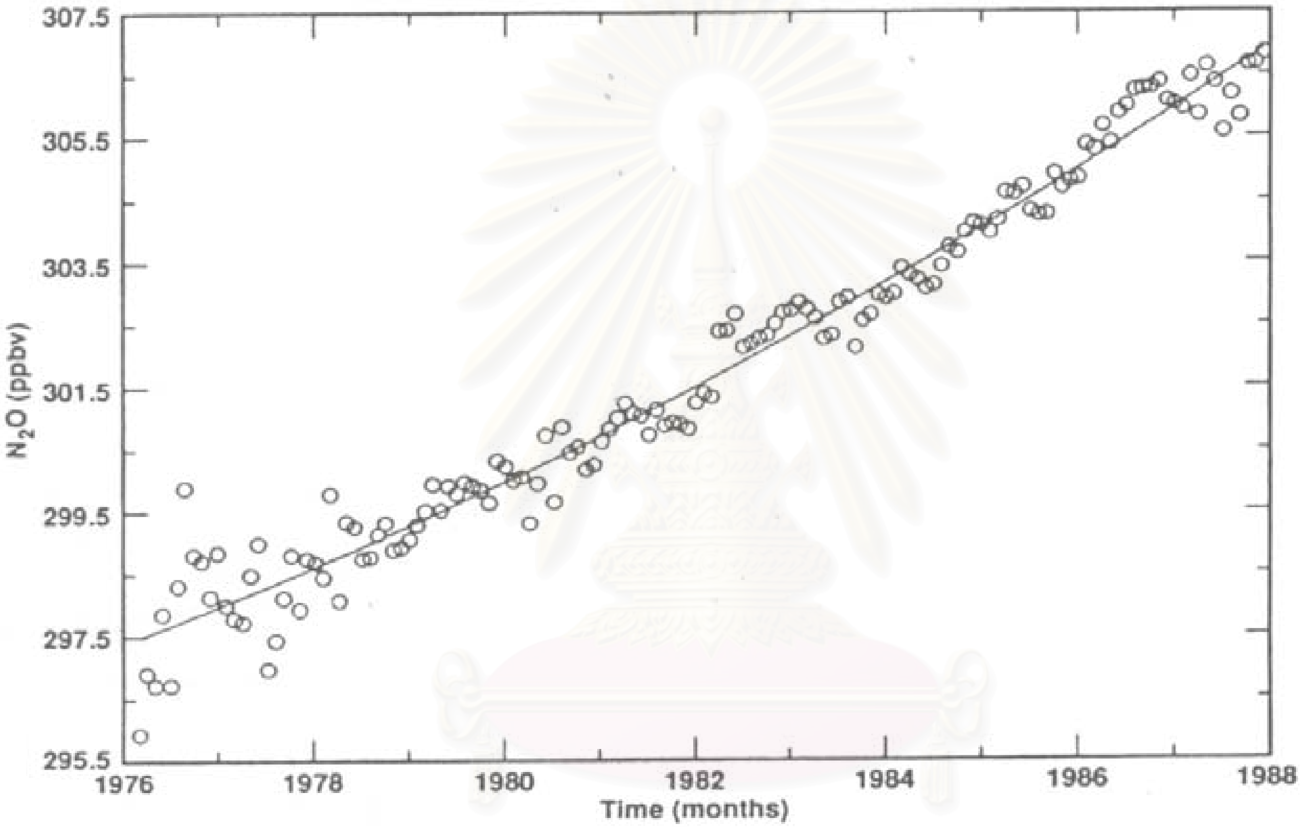


Figure 2-6 Time profile of nitrous oxide concentration [Wuebbles, 1997]

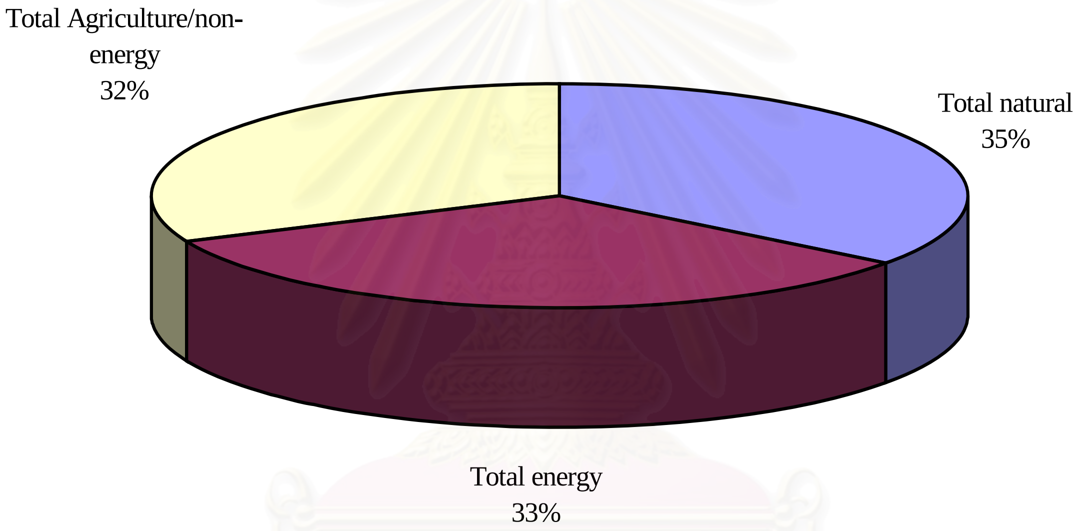


Figure 2-7 Main sources of methane

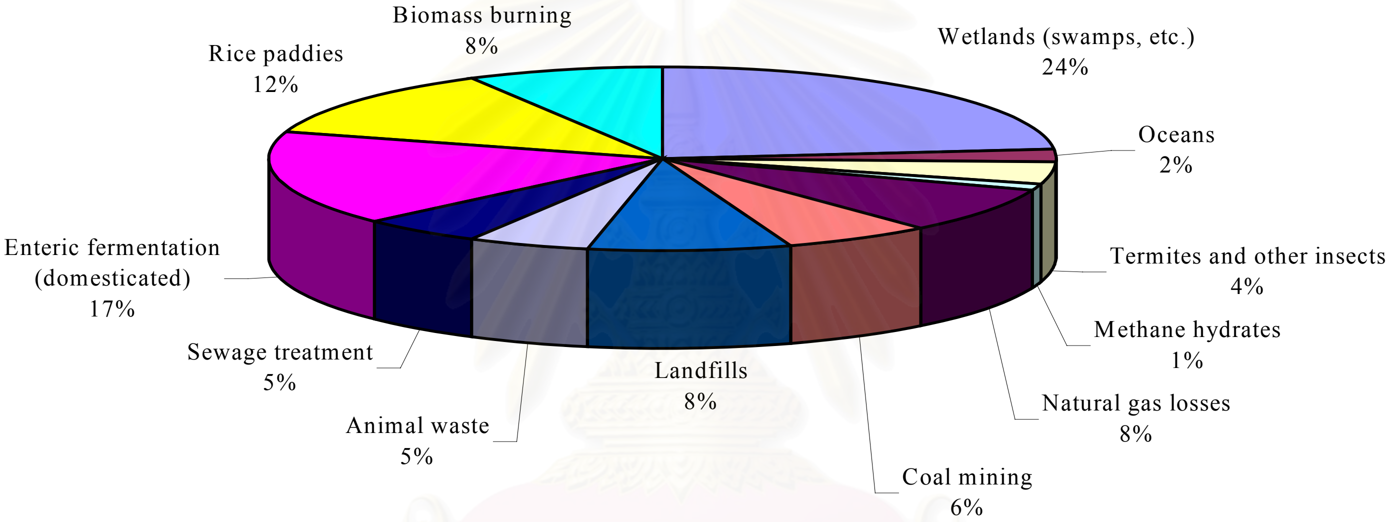


Figure 2-8 Anthropogenic and natural sources of methane [IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993]

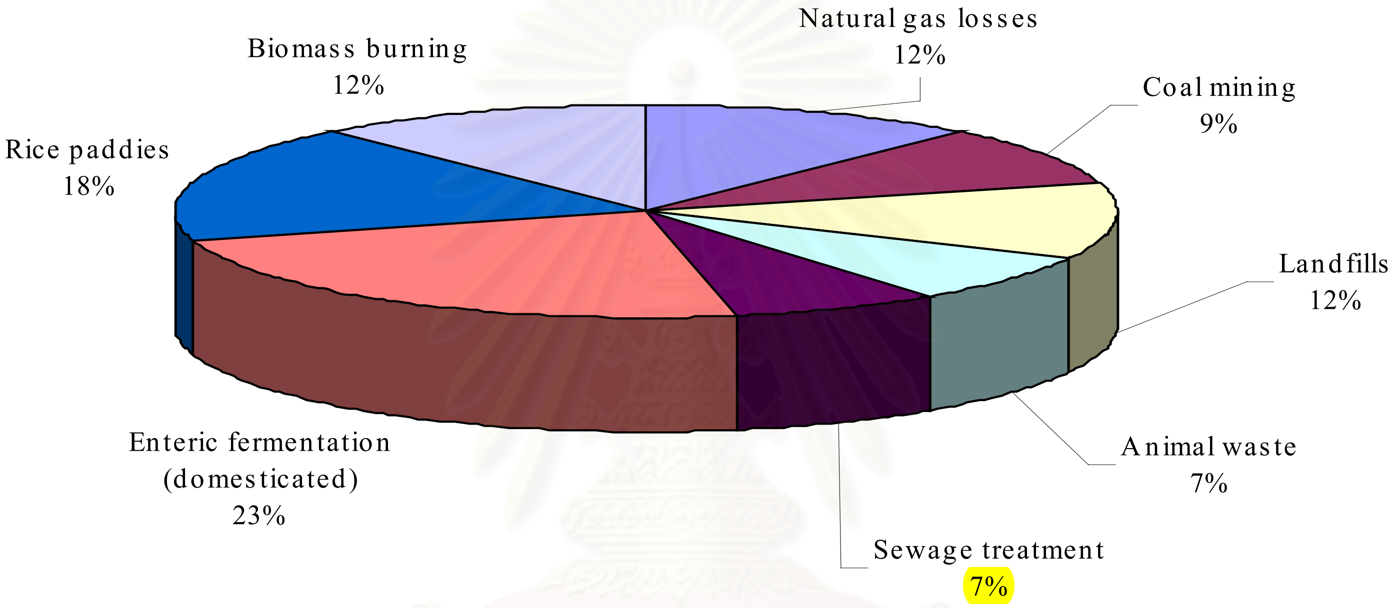


Figure 2-9 Anthropogenic source of methane [IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993]

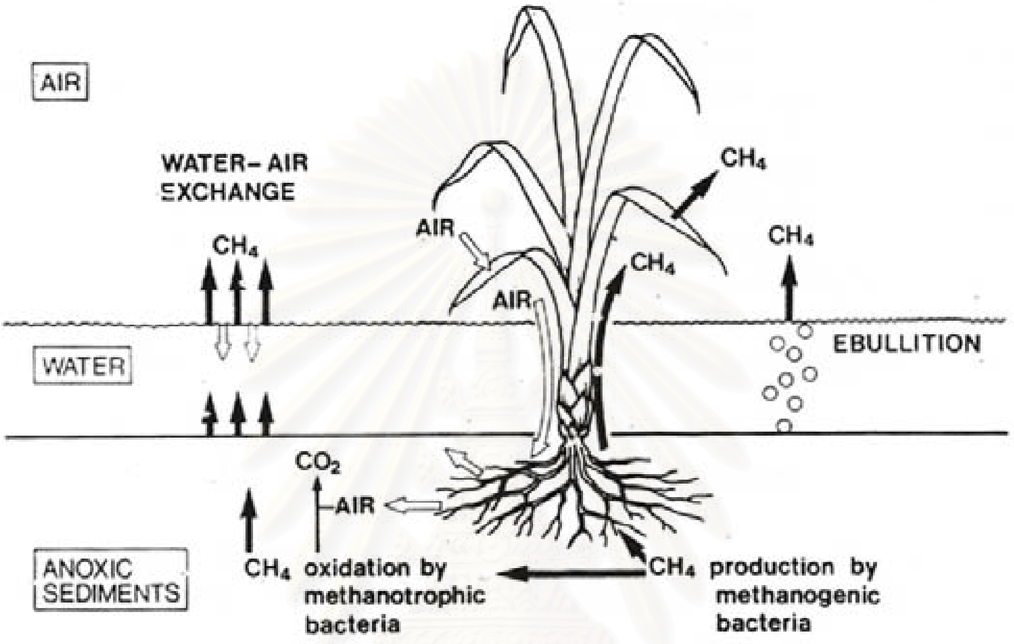


Figure 2-10 Scheme of the gas exchange between waterlogged sediments and the atmosphere. [Schütz *et al.*, 1991]

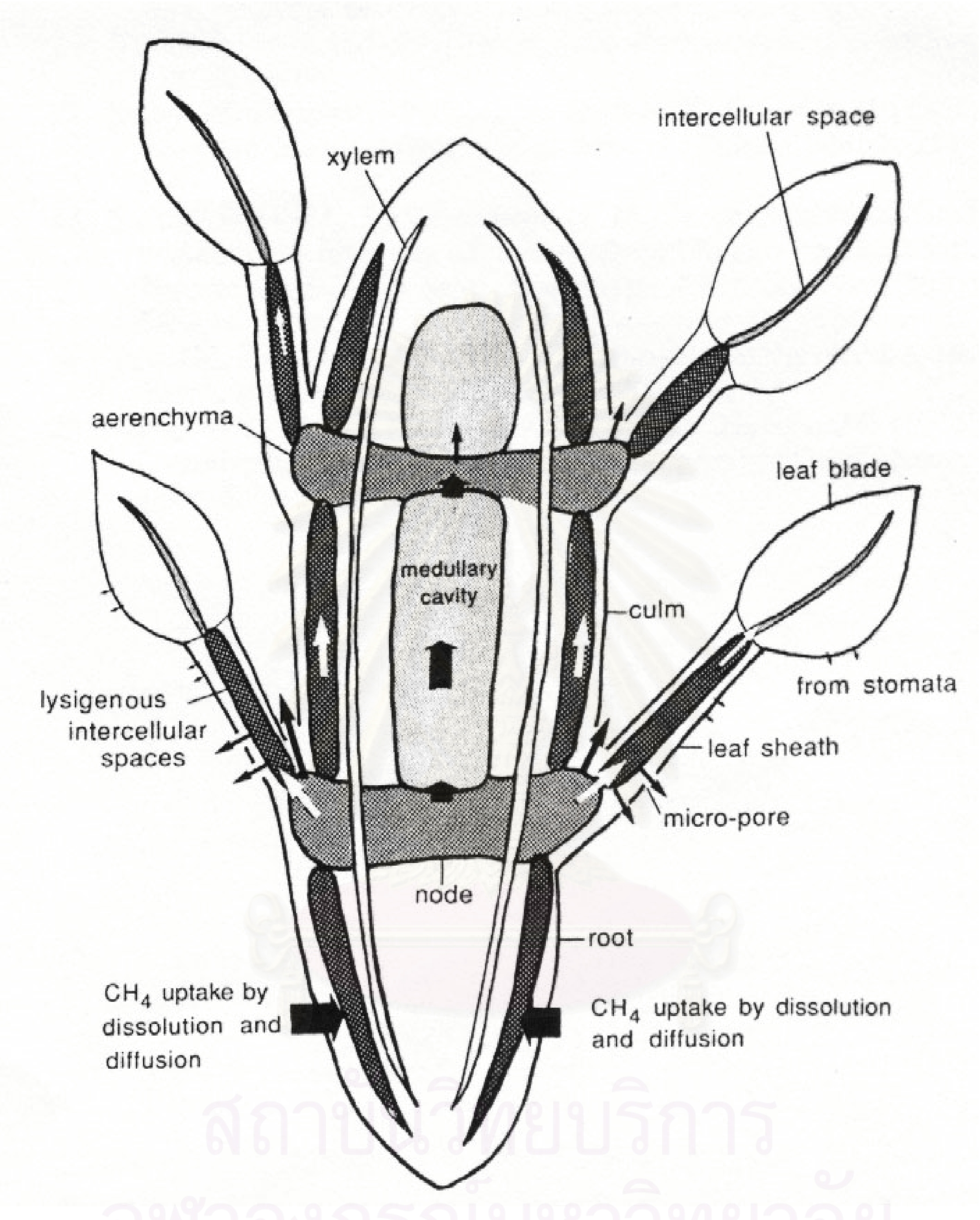


Figure 2-11 A hypothetical pathway of methane transport from the rhizosphere to the atmosphere. Both black and white arrows represent methane flow. [Nouchi *et al.,* 1990]

CHAPTER 3

METHODOLOGY

3.1 Experimental areas

3.1.1 Rice paddy field

An irrigated rice paddy field of 400 m^2 in Fuchu Honmachi was selected from an experimental farm at Tokyo University of Agriculture and Technology, Japan. Rice with cultivar "Tsuki no hikari" was planted from May till October 2003. When the field was tilled, chemical fertilizer (nitrogen 2.4 kg, phosphorus 2.4 kg, and potassium 2.4 kg) was also applied at the same time. The schedule for activities on this rice field is shown in Table 3-1.

3.1.2 Wheat and maize field

Four plots with different treatments of upland plant fields were selected from an experimental farm in Tokyo University of Agriculture and Technology, Japan. Wheat and maize were cropped in this area with the cropping schedule as shown in Table 3-2.

All plot areas covered 805 m^2 and could be divided by tillage depth into 2 groups, i.e. T (tillage depth at about 15-20 cm) and NT (tillage depth at about 5-10 cm). Each group was further separated by the types of additive. M (manure) and F (chemical and manure) are detailed in Table 3-3. Besides, Tables 3-4 and 3-5 indicate the amount of mineral contents in each fertilizer applied in each plot.

3.2 The Chamber technique

For measuring the emission rate of methane from soil in this study, the chamber technique was employed.

3.2.1 The chamber for rice paddy field

As illustrated in Figure 3-1 and a schematic diagram as in Figure 3-2, the gas collector chamber in rice paddy field was made from transparent polyvinylchloride (PVC) material covering the area of 0.16 m^2, which enclosed two bunches of rice. At the cover of the chamber, a Tedlar® bag was provided for pressure adjustment, a fan for mixing, and a septum for sample collection. The Tedlar® bag is a special bag where the air can be inflated and when the gas sample is taken out of the chamber, this bag can be inflated to compensate for the volume of the gas sample. This is to ensure that the pressure inside the chamber is kept as constant as possible. The fan at the chamber's cover was connected with direct current 12-volt battery through each experiment period to provide mixing in the chamber. To take a sample from each chamber in rice paddy field, a syringe was injected into a septum at that chamber's cover. This septum was made of silicone and fitted with a hole at the cover to prevent air leakage from the chamber. A water-tight channel was located at the bottom of each vertical section to provide a seal between paddy soil and the chamber. The chamber was installed on four polyvinylchloride pipes settled in the soil to prevent it from sinking into the soil.

3.2.2 The chamber for wheat and maize fields

With a direct current 12-volt fan and a septum at the cover, a chamber made from transparent polycarbonate with diameter of 17.3 cm was installed above the soil. The samples were taken by a syringe through a septum as shown in Figure 3-3 or a schematic diagram in Figure 3-4.

3.3 Gas collection

The gas collection was performed at every two weeks and completed in one day with three 45-minute-interval sampling periods; morning, afternoon and evening. At the beginning of each period, every chamber was covered, the time was recorded, and the first sample of that period was counted as at time zero (0 min.). During this 45-minute interval, gas samples were taken four times by a 20 ml syringes at every 15 minutes, and the samples were kept in a vacuum bottle for further analysis.

The measurements were done along the plant growth cycle as shown in Figures 3-5, 3-6 and 3-7.

3.4 Methane analysis

Methane concentration in the air sample was determined by using a gas chromatograph (GC) equipped with a flame ionization detector (FID). Methane emission fluxes, F, were calculated from the measured concentration inside the chambers as follows [Parashar *et al.,* 1996; Singh *et al.*, 1998].

$$F = \frac{BV_{STD} \times dC \times 16 \times 1000 \times 60}{10^4 \times 22400 \times A \times dt} \quad \left({}^{mg}\!\big/_{m^2 \cdot h} \right) \qquad (3\text{-}1)$$

$$BV_{STD} = \frac{BV \times B.P. \times 273}{(273+T) \times 760} \quad (\text{Vol. of air in chamber, cm}^3) \qquad (3\text{-}2)$$

where

F = Methane flux ($mg \cdot m^{-2} \cdot h^{-1}$)

BV = Volume of chamber above flooding water (cm^3)

$B.P.$ = Barometric pressure (mmHg)

T = Air temperature inside chamber (^oC)

A = Cross-section area of chamber (m^2)

dC = Difference of methane concentration at *0* and *t* minute (ppmV)

dt = Duration time (minute)

Assumptions:

- Barometric pressure (*B.P.*) is constant and equals to 760 mmHg through all experiment.
- Air temperature inside chamber (*T*) is assumed equivalent to the air temperature outside chamber at the time of measurement.

3.5 Soil sampling and soil parameters

Three soil samples at different depth (surface, above tillage border, and below tillage border) from each plot are collected in the same experiment day. Soil moisture by volume, water content by weight, and pH were measured from these soil samples.

3.5.1 pH

Forty gram of soil sample was added into 100 ml of distillated water (2:5 dilution of soil:water) and shaked for 1 hour. The pH value in each soil sample was immediately analyzed by a pH meter.

3.5.2 Soil moisture

About forty grams of wet soil were brought into an oven at 120^{o}C for one day. After that dry soil was weighted. The water content by weight was calculated by

$$\text{Water content (\%w/w)} = \left(\frac{\text{wet soil weight - dry soil weight}}{\text{wet soil weight}}\right) \times 100 \qquad (3\text{-}3)$$

3.6 Other parameters

Air and soil temperatures in the experiment day were measured by a thermocouple every minute before the measurement in the morning started and until the evening where measurement was finished. For upland fields, soil temperatures at two different depths (1 and 5 cm) were measured while in rice paddy field, water temperature and soil temperature at 5 cm depth were measured by the same equipment.

3.7 Data analysis

In this work, data analysis could be divided into two parts.

3.7.1 Formation of mathematic correlation

The aim of this part was the formation of mathematical correlation between methane flux from vegetation areas and the potential influencing parameters. This was achieved by using the linear regression analysis. The goodness of each relationship between methane flux and a parameter is shown by R-square (R^2) which measures how accurate the model is in explaining the variation of the data.

R-square is defined as the ratio of the sum of squares of the regression (SSR) and the total sum of squares (STT) as shown below:

$$R^2 = \frac{SSR}{SST} \tag{3-4}$$

where

$$SSR = \sum_{i=1}^{n} \omega_i (\hat{y}_i - \bar{y}_i)^2 \tag{3-5}$$

$$SST = \sum_{i=1}^{n} \omega_i (y_i - \bar{y}_i)^2 \tag{3-6}$$

$\hat{y}_i$ = the predicted value of y_i

$\bar{y}_i$ = the average value of y_i

y_i = the value of each y_i

R-square can take on any value between 0 and 1, with a value closer to 1 indicating a better fit. For instance, R^2 value of 0.8 means that the fit explains 80% of the total variation in the data about the average [The MathWorks, 2004]. The higher value of R-square indicates better a relationship of methane flux and each specific parameter.

3.7.2 Determination of global warming potential

This part dealt with the determination of global warming potential from vegetation area in comparison with industry. The methane flux from vegetation areas were converted to global warming potential (mass of CO_2 per area) so as to be able to compare with the emission from industrial area. Combustion of various types of fuel in power plants due to industrial activities was used as a model study (as a representative of industrial source of greenhouse gas) in this work. In the last section, to conclude on the effect of agriculture on greenhouse gas emission, greenhouse gas fluxes (carbon dioxide, methane, and nitrous oxide) from vegetation areas were also converted to global warming potential by the same method.

Table 3-1 Activities on the rice paddy field.

Activity	Period
Tillage and adding chemical fertilizer	May 9th, 2003
Submerging	May 11th, 2003
Transplanting	May 26th, 2003
Harvesting	Oct 20th, 2003

Flooding period = 163 days, Cropping period = 148 days

Table 3-2 Growing season of wheat and maize in the selected plots

Vegetation	Growing season
Wheat (Triticum aestivum)	November 2002 - June 2003
Maize (Zea mays L.)	July 2003 - October 2003

Cultivating period of wheat = 230 days, Cultivating period of maize = 94 days

Table 3-3 Area plots for this study

Plot	Area (m^2)	Tillage depth (cm)	Additives
No. 1 (TM)	805	15 - 20	Manure & Chemical
No. 2 (NTM)	805	5 - 10	Manure & Chemical
No. 3 (TF)	805	15 - 20	Chemical
No. 4 (NTF)	805	5 - 10	Chemical

Table 3-4 Details of chemical and manure fertilizers in wheat fields.

Plot	Mineral contents (%)				Total amount (kg/1000m^2)
	H_2O	N	P_2O_5	K_2O	
TM and NTM					
- Chemical		14	14	14	36
- Manure	64	0.68	0.15	0.70	1900
TF and NTF					
- Chemical		14	14	14	100

The additives were applied in November 2002 and February 2003.

Table 3-5 Details of chemical and manure fertilizers in maize fields.

Plot	Mineral contents (%)				Total amount (kg/1000m^2)
	H_2O	N	P_2O_5	K_2O	
TM and NTM					
- Chemical		14	14	14	36
- Manure	64	0.68	0.15	0.70	2200
TF and NTF					
- Chemical		14	14	14	143

The additives were applied in July 2003.

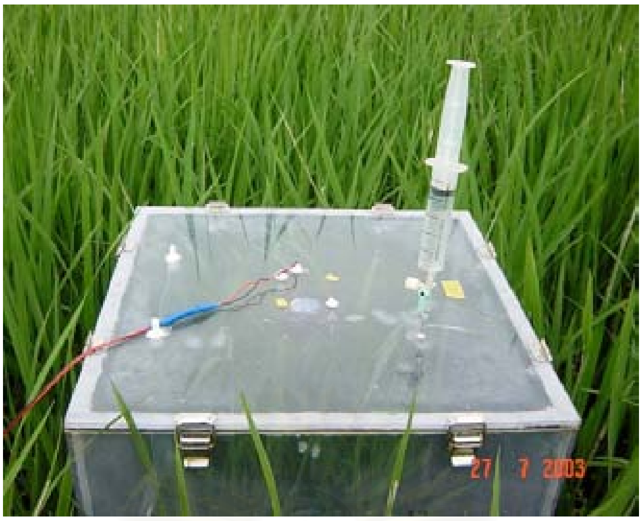


Figure 3-1 The chamber for rice paddy field

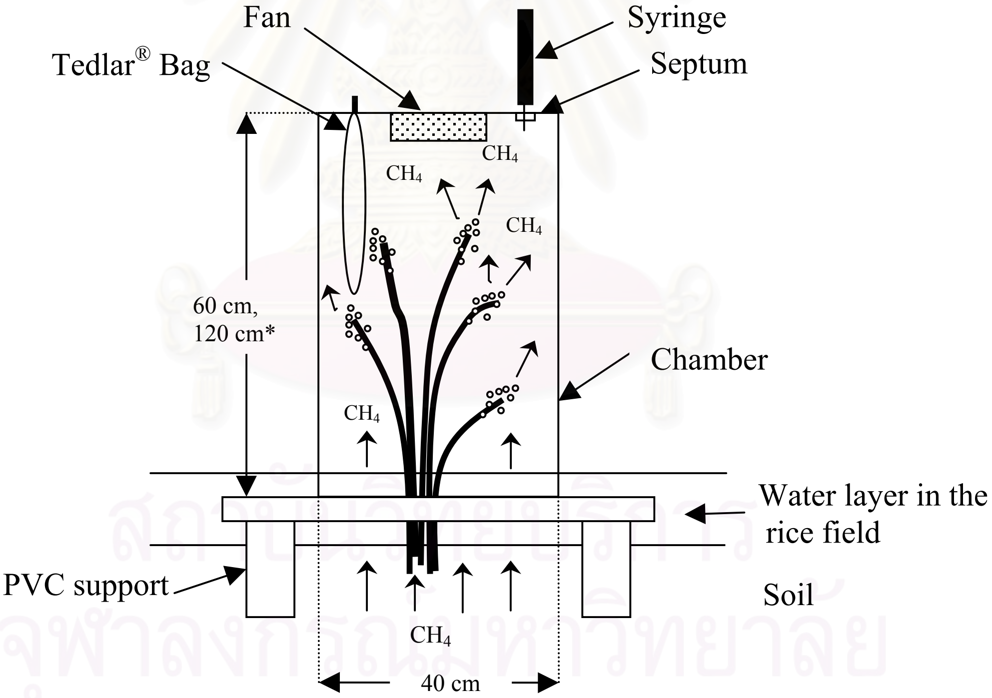


Figure 3-2 The schematic diagram of chamber for rice paddy field

* The height of the chamber could be varied according to the height of the rice.

Figure 3-3 The chamber for wheat and maize fields

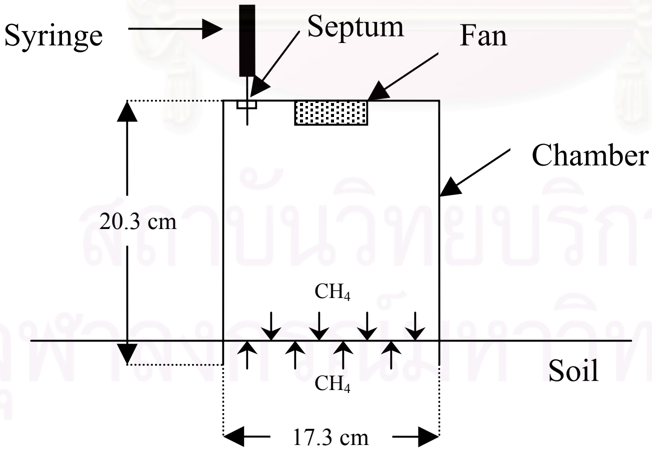


Figure 3-4 The schematic diagram of chamber for wheat and maize fields

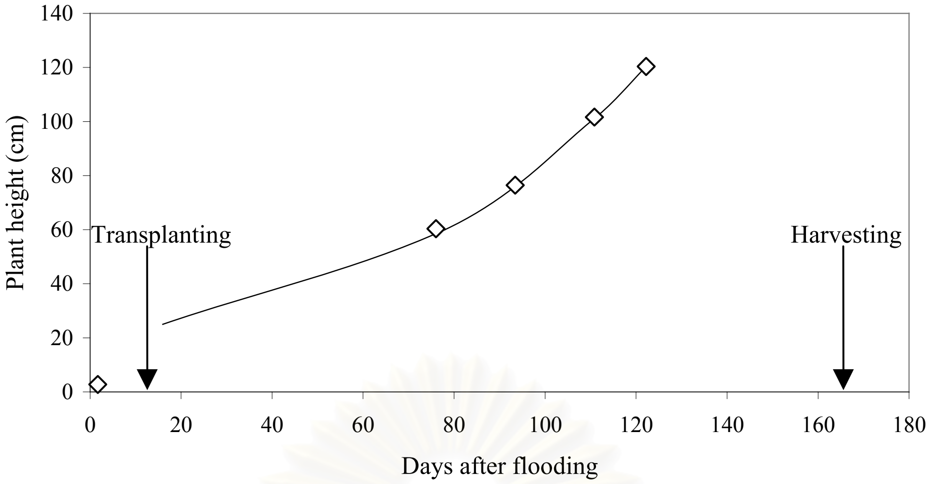


Figure 3-5 Growth of rice starting from May 11th, 2003. (◇ means the experiment day)

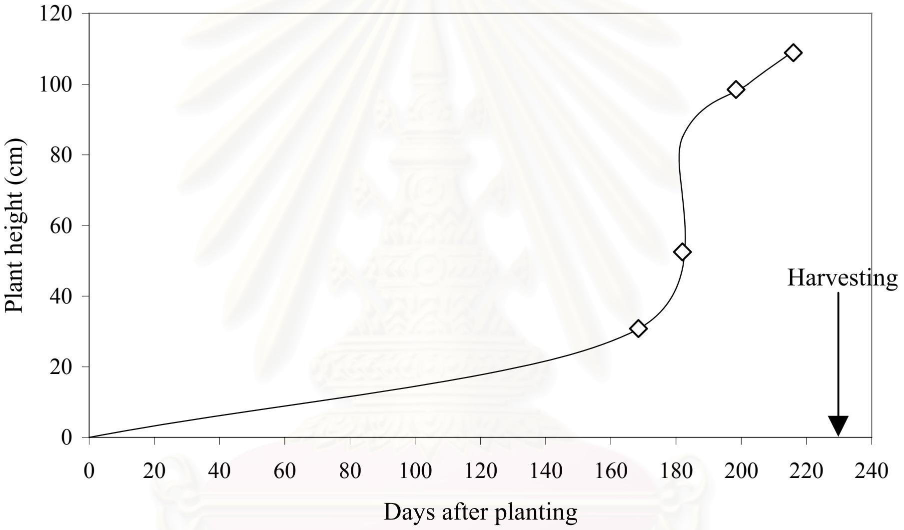


Figure 3-6 Growth of wheat starting from Nov 1st, 2002. (◇ means the experiment day)

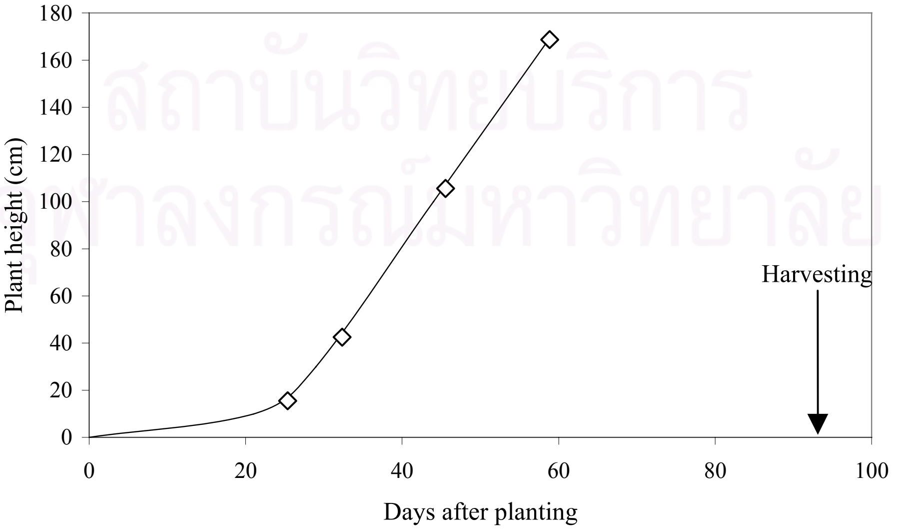


Figure 3-7 Growth of maize starting from July 9th, 2003. (◇ means the experiment day)

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Diurnal variation of methane flux

4.1.1 Irrigated field

Experimental results from rice paddy fields revealed that there was a slight diurnal variation in methane flux. Figure 4-1 illustrates that the same trend for the diurnal variation in methane flux could be observed, *i.e.* fluxes in the morning were usually lower than those in the afternoon or in the evening, while those in the afternoon and evening were more or less the same. For instance, the results obtained from Sep 9th, 2003 in Figure 4-2 showed the amount of methane released by this area ranged from 0.51 to 0.77 $mgm^{-2}h^{-1}$ with an average flux of 0.65 $mgm^{-2}h^{-1}$ and a variation of methane flux in a day shown by the coefficient of variance at 0.21 (see in Appendix B). In this figure, the lowest flux was observed in the morning where the highest was in the afternoon and the flux in the evening was found to be lower than that in the afternoon. This finding agreed well with the report from Yagi and his colleagues in 1994 who stated that minimum flux occurred in the early morning and the maximum flux occurred in the afternoon. This diurnal variation was believed to occur due to the accumulation of heat in the soil and therefore the flux in the morning was always found to be the lowest in the day. The high flux was obtained when there was adequate accumulation of heat in the soil which could be around afternoon or evening. This was due to the effect of some environmental parameters such as temperature, etc., that enhanced the production and emission of methane [Wang *et al.*, 1994]. Note that the actual flux in each measuring day was not in the same range as the experiment was uncontrolled and there might be some other parameters that affected the generation of methane. Hence, only the trend of this methane emission was used in the discussion.

Methane fluxes from rice paddy fields without plant were given in Figure 4-3 which shows that the diurnal variation had the same trend as in the area with plant. In the morning, methane fluxes were low and became higher in the afternoon. However, fluxes in the evening were found to be lower than that in the afternoon. For the sake of comparison between irrigated field with and without plant, the data from Sep 9th, 2003 was selected for elaboration and shown in Figure 4-4. The area without plant emitted methane in the range of 0.083 to 0.219 $mgm^{-2}h^{-1}$ (with the average value of 0.129 $mgm^{-2}h^{-1}$), with the highest flux in the afternoon and the minimal in the morning (similar to those from the area with plant in the same day). The data of Sep 9^{th}, 2003 showed that the coefficient of variance was about 0.6 which was higher than that of methane flux from the area with plant (see in Appendix B). This meant the diurnal variation in the area without plant was more pronounced than that with plant. However, since the fluxes from the area without plant was much lower than that from the area with plant, this diurnal variation was considered insignificant. The differences in methane fluxes from areas with and without plant shall be discussed later.

4.1.2 Upland field

In case of upland areas (wheat and maize fields), Figures 4-5 and 4-7 illustrate that methane fluxes of all measuring days from these areas had similar trend, but on different loading levels. There was a gradual increase in methane generation with a higher flux in the afternoon than in the morning. This was, again, thought to be due to the accumulation of heat in a day as mentioned in the previous section. Figures 4-6 and 4-8 emphasized this finding by plotting methane flux together with environmental temperatures. Soil temperature seemed to be the most significant parameter controlling the flux of methane. These plots illustrate that soil temperature gradually increased from morning to afternoon and this resulted in an increase in methane flux. In addition, the evening soil temperature was slightly lower than the afternoon and the methane flux also followed the same trend. Note that methane flux in the evening was not always lower than that in the afternoon (see Figures 4-5 and 4-7). This depended significantly on the soil temperature.

4.1.3 Concluding remarks

There seemed to exist a diurnal variation of methane fluxes from all vegetation areas. High flux was often observed in the afternoon or in the evening whilst low flux was in the morning. This variation was believed to take place due to the accumulation of heat in the soil. However, this variation was quite small especially for area without plant and when compared with the variation in the area with plant which was in a much greater extent. Hence, the use of average daily flux should be adequate in representing the methane flux from each vegetation area.

4.2 Comparison of methane flux between irrigated and upland fields

Normally, there are two types of bacteria in any soils that deal with methane production and consumption. These are methanogenic and methanotrophic bacteria, respectively.

Each bacteria is active under different environmental conditions. Methanogen is anaerobic bacteria while methanotroph is aerobic. The conditions provided by irrigated and upland fields were quite different in terms of available oxygen. Flooding water above the paddy soil inhibited the atmospheric oxygen transportation into the soil. This led to the lack of oxygen concentration in that soil and affected the decrease in the redox potential (Eh) [Lindau *et al.*, 1994]. Under this anaerobic condition, methane could be more produced by methanogenic bacteria than consumed by methanotrophic bacteria. This caused the positive methane flux from a rice paddy field as shown in Figure 4-2 which implied that methane was emitted from this area.

The upland soil conditions were markedly different from paddy soil because there was more oxygen available through the mass transfer with the open air. This aerobic condition rendered methanotrophic bacteria more active than methanogenic. Some methane produced by methanogen in upland soil might well be the carbon source for methanotroph and was converted to carbon dioxide. This methane consumption reduced the concentration of methane in the soil and caused the transfer of methane from the atmosphere into the soil. As a result, negative values of methane flux from both wheat and maize fields were observed in Figures 4-6 and 4-8.

4.3 Pathway of methane transportation from soil to the atmosphere

The comparison between methane flux from area with plant (Figure 4-2) and without plant (Figure 4-4) demonstrated that the area with plant emitted methane in a significantly higher quantity. Methane flux from area without plant was only 19.8% of that from area with plant. This was because the difference in a mechanism of methane transportation from soil to the atmosphere. Rice plant took important role as a main transportation route for methane from soil to the atmosphere. Nouchi and his colleagues' research in 1990 described this mechanism as the transportation through the shoots via lysigenous intercellular spaces and aerenchyma, before a release to the atmosphere. Schütz *et al.* (1989) also reported that in the area that had no plant, the transportation by ebullition and diffusion contributed only about 10% of the overall methane emission (in the area with plant).

To illustrate the contribution on ebullition and diffusion, the following discussion was conducted. Firstly, the ebullition mechanism was mentioned by Schütz and his associates in 1991 to be the transportation via gas bubble formation. This can only take place when methane reaches its supersaturated condition in the water and the partial pressure of methane exceeds the hydrostatic pressure. This mechanism was unlikely to occur in rice paddy because methane was not produced in large enough quantity such that its saturation was readhe. Thus very little amount of bubbles were formed and this could be neglected from consideration.

In the case of diffusion, this mechanism was restricted by vapor-liquid equilibrium of methane at the interface of ambient air and flooding water. To solve this phase equilibrium problem, the methane concentrations in both vapor (air) and liquid (water) phases were needed. From the experiment, the concentration in water was not measured, thereby Henry's law was employed to estimate the concentration in liquid phase from the gas phase concentration (measurable). This should be applicable as methane can only be sparingly soluble in water. The solubility of methane in water at 20°C is 25 mgl^{-1} [Physical & Theoretical Chemistry Laboratory, Oxford University, 2003], and the Henry's constant of methane is 1.34 $mmol(l\ atm)^{-1}$ [Lewis and Evans, 2001]. From the experimental results, the initial methane concentration in the air (at time zero in each measuring period) was about 2,000 ppb and the final (after 45 minutes of collection time) was about 10,000 ppb. Thus the initial and final partial pressures of methane were $2{,}000\times 10^{-9}$ and $10{,}000\times10^{-9}$ atm, respectively. The concentration of methane in water could be calculated from:

$$C_{CH_4} = H_{CH_4} P_{CH_4} \tag{4-1}$$

Initial condition; methane content was equal to 2000 ppb.

$$C_{CH_4} = \left(1.34\times10^{-3}\,\frac{mol}{l\cdot atm}\right)\left(10{,}000\times10^{-9}\,atm\right)\left(16{,}000\,\frac{mg}{mol}\right)$$

$$C_{CH_4} = 4.288\times10^{-5}\,{}^{mg}\!/_{l}$$

Final condition; methane content was equal to 10000 ppb.

$$C_{CH_4} = \left(1.34\times10^{-3}\,\frac{mol}{l\cdot atm}\right)\left(10{,}000\times10^{-9}\,atm\right)\left(16{,}000\,\frac{mg}{mol}\right)$$

$$C_{CH_4} = 2.144\times10^{-4}\,{}^{mg}\!/_{l}$$

From these calculations, the amount of methane in water along a measuring period was very small compared to the saturated methane content (25 mgl^{-1}) This implied that more methane could still be dissolved in the water and in other words, water acted as a buffer for methane that was emitted from the soil and prevented this methane from entering the atmosphere. Hence, most of the methane flux should come from the transportation through the rice plant.

In case of wheat and maize fields, the experimental setup could not cover the upland plants; hence, the pathway of methane through the plant could not be discussed here. However, negative methane emission obtained from experiment illustrated that the total transport from atmosphere to soil was more significant than the transport from soil to atmosphere. In this case, soil acted as a sink for methane and the transport of methane from atmosphere to soil could take place due to several mechanisms *e.g.* convection, dispersion, diffusion, etc.

4.4 Effect of plant growth on methane flux

4.4.1 Irrigated field

Table 4-1 shows methane flux from a rice paddy field in a growing season of 2003 (May-September). Methane was found to be emitted in a very small amount (0.001 $mgm^{-2}h^{-1}$) before this area was flooded. After flooding, the level of methane flux was gradually increased with the maximum methane emission of 2.13 $mgm^{-2}h^{-1}$ in the grain-developing stage. This result strongly supported the assumption that flooding was a significant factor for methane emission from a rice paddy field. As shown in Table 4-1, methane flux after flooding increased continually from transplanting, booting, and reached maximum load at grain-developing stage. As plant grew up, the quantity of carbon dioxide released by its root respiration and the quantity of root exudates excreted as hydrocarbons increased. These carbon dioxide and hydrocarbons were main carbon sources for methane production of methanogen in the soil. This methane was transported through the plant structure to the atmosphere.

At the end of the grain-developing stage, methane flux started to be steadily decreased through the grain-ripening (0.65 $mgm^{-2}h^{-1}$) and harvesting stages. During the grain-developing stage, rice enhanced its activities in order to create important parts of rice plant such as grain. However, after this stage, the rate of respiration declined which caused the reduction in carbon dioxide and hydrocarbons generations. Subsequently, the reduction in methane production rate could be seen. For this experiment, in terms of methane production and emission, the most significant stage was grain-developing stage.

4.4.2 Upland field

Figure 4-9 shows seasonal methane flux from a wheat field of the four plots with different land treatments. Negative methane fluxes were always obtained from the vegetation upland area along this period. For wheat field, it should be noted that wheat was cultivated in November 2002. The growth of the wheat passed through the winter time where the measurement could not be conducted. The measurement was started some time in April 2003 which was about 6 months after the cultivation. Figure 4-9, as a result, only presents data during the last three months of wheat growth where a slight increase in methane flux with time was observed. Nonetheless, it should be noted that as the methane flux tended to rise gradually with wheat plant growth, the environmental temperature was also increased as shown in Figure 4-9. Hence, the increase in methane flux might be due to either wheat plant growth or temperature.

In the case of maize field, the measurement could be performed for the whole harvesting cycle from July to nearly the harvesting season in October (Figure 4-10). Maize field provided negative methane flux along the growing period, where methane flux was observed to slightly decrease. In this specific case, the environmental temperature was also found to decrease gradually during the growth cycle. Thus, the effect of plant growth on methane generation might not be as strong as that of temperature.

4.4.3 Concluding remarks

Methane emission from a rice paddy field varied along the growing season. As rice plant grew, the quantity of methane released was changed. The highest methane flux occurred in the grain-developing stage. In addition, the variation of methane flux in upland fields did not depend strongly on the plant growth.

To compare the methane flux in a growing season between each vegetation area, a rice paddy field was only the area that produced and emitted methane into the atmosphere (4,508 mgm^{-2}) while upland fields including wheat and maize fields was the area that consumed and absorbed methane into the soil. The latter areas had more or less similar values of methane uptakes (59 and 40 mgm^{-2}, respectively). It could be said that a rice paddy field was a significant methane source, whereas upland fields acted as a methane sink.

4.5 Effect of soil treatment on methane flux

Because there was merely one chosen plot in a rice paddy field, the difference in soil treatment was not concerned in this area. In upland areas including wheat and maize fields, there were four plantation plots with different soil treatments. Soil treatment here included the tillage practice, and the use of fertilizer. Thus, only upland fields are mentioned in this topic. Moreover, methane emission from only maize field was investigated here because the experiment in wheat field was not carried out through out the entire growth period (as mention in the previous section), and the effect of tillage practice and fertilizer might not be clear with a 6-month delay experiment.

4.5.1 Tillage

Theoretically, tillage allows more oxygen transfer from the atmosphere into the soil. When the soil is rich in oxygen content, the oxidation of methane is likely to occur and a decrease in methane flux will be apparent. Table 4-2 shows the comparison between methane fluxes from the area with deep-tilled (TF) and with shallow-tilled (NTF) practices. In a growing season in 2003, methane flux from the area deeply tilled (TF) was -48.62 mgm^{-2} whilst that from the shallow-tilled area (NTF) was -37.33 mgm^{-2}. These figures indicated that the shallow-tilled area (NTF) generated more methane flux than the deep-tilled area (TF), in other words, in the shallow-tilled area, methane tended to be emitted rather than absorbed. This was due to the difference in oxygen content in soil between these two plots. Also demonstrated in Table 4-2, results from the other two areas (deep-tilled, TM and shallow-tilled, NTM) were apparently opposite to the previous case, *i.e.* methane flux from the shallow-tilled area (NTM), at about -37.31 mgm^{-2}, was lower than that from the deep-tilled one (-34.86 mgm^{-2}). This was believed to occur due to the presence of other growth factors. The soil moisture in the TM area was found to be greater than that in the NTM plot. This high moisture was also the condition more suitable for methanogen than methanotroph and this might be the reason for the finding as described above.

4.5.2 Fertilizer

The effect of fertilizer was observed from the experiments in the plots with the addition of manure (TM for deep-tilled, and NTM for shallow-tilled). It is noted that all plots were conditioned by chemical fertilizers but these two special plots were also conditioned with manure. From Table 4-2, methane fluxes from two 20-cm-depth-tilled plots (TM and TF) in a maize field showed that with manure additive, TM plot emitted more methane from soil, hence, the methane flux from TM plot with the flux of about -34.16 mgm^{-2} was higher than that from TF plot (-48.62 mgm^{-2}). The manure additive acted as a carbon source for methanogenic bacteria in the soil which was subsequently converted to methane. This resulted in a higher methane flux from the TM than from TF plots. This finding was in good agreement with the report of Yagi and Minami (1990) who stated that adding manure to Japanese rice paddies increased methane emission. Although there was a manifest difference in deep-tilled areas, there was not much distinction in two slightly tilled plots (NTM and NTF) in a maize field. As shown in Table 4-2, methane fluxes from these NTM and NTF plots were -37.31 and -37.33 mgm^{-2}, respectively. This might be because the methanogen lived deeper into the soil than the tilled layer (5-10 cm depth from the surface) to ensure anaerobic condition; consequently, methane-producing bacteria in NTM plot could not utilize this added carbon source (manure). This resulted in no difference in methane fluxes between NTM and NTF areas.

4.6 Effect of environmental conditions

In this section, several environmental parameters were measured independently in order to determine whether there were relationships between them and methane flux. It should be mentioned here, however, that this was an uncontrolled experiment as it was conducted in the actual vegetation field.

4.6.1 Temperature

4.6.1.1 Irrigated field

In the rice paddy field, the environmental temperature was measured in three different positions including air, flooding water, and soil. Air temperature was found to be between 25-33^{o}C which was slightly higher than water temperature (23-29^{o}C) and soil temperature (22-27^{o}C). Figures 4-11(a) and (b) illustrate that there was no direct relationship between air and water temperatures and methane flux from this area. In contrast, Figure 4-11(c) indicates that there might exist a direct relationship between soil temperature and methane flux (R^2 = 0.663, shown in Appendix B). This result was in good agreement with the findings from Khaili and Rasmussen, 1991; Holzapfel-Pschon *et al.*, 1986, and Yamane and Sato, 1967. It is possible that the increase in soil temperature stimulated microbial activities in soil, especially under this flooding condition, and led to higher methane emission rate.

4.6.1.2 Upland field

In wheat and maize fields, the temperature of air, soil at 1, and 5 cm depth ranged from 16 to 37°C, 13 to 33°C, and 13 to 30°C, respectively. Figures 4-12(a) and 4-13(a) illustrate that methane flux tended to increase slightly as air temperature inclined (R^2 = 0.223 and 0.149, respectively). However, the low R-squared values suggested that the relationship between methane flux and air temperature might not be precise. Similarly, the influence of soil temperature (both at 1 and 5 cm depth) on methane flux was very slight. There seemed be an upward trend of methane flux with soil temperature but the experimental results had high degree of scattering. Perhaps, a wider range of temperature would make the results become clearer, but within the range of temperature examined in this work, soil temperature was concluded to exert only slight influence on methane flux.

4.6.1.3 Concluding remarks

Experimental results implied that the variation of soil temperature had some effect on methane flux in both irrigated and upland fields. Nevertheless, the increase in methane flux in upland field due to soil temperature might not be as strongly pronounced as that in the paddy field. In the upland field, the methane flux was, in fact, negative which meant that this was methane uptake due to soil activities. The increase in soil temperature was found to reduce the uptake rate where about half of methane uptake was reduced with a 10°C increase in soil temperature. In a paddy field, however, only a 2°C increase in soil temperature led to as much as three times higher methane flux. This consequence was supported by a research of Crill *et al.* in 1994 and Sitaula *et al.* in 1995 which reported that there was less temperature dependence of methane uptake compared to that of methane production. Some researchers, *e.g.* Steudler and colleagues (1989) reported that methane uptake showed no correlation with the soil temperature.

4.6.2 pH

4.6.2.1 Irrigated field

Figure 4-14(a) illustrates that soil pH dropped from 6.62 to 6.12 after the area was flooded due to the alkalinity in paddy soils [Bouwnam, 1990]. During the flooding period, pH of paddy soil (6.06 – 6.18) did not show wide variation with the pH of water layer. As a result, as shown in Figure 4-15(a), the relationship between methane emission and soil pH was difficult to conclude. The pH of flooding water in this rice paddy field was, on the other hand, found to vary in a wider range, from 6.88 in grain-developing stage to

9.67 in booting stage (Figure 4-14(b)). However, a very low R-squared value ($R^2 = 0.005$) indicated that there was no relationship between methane flux and water pH.

4.6.2.2 Upland field

In case of upland field, the seasonal variation of soil pH at different positions such as soil surface, 5 cm above and below tillage border were shown in Figure 4-16. No significant changes of soil pH in these three different measuring positions were observed. The plots fertilized only by chemical fertilizer (TF and NTF) were slightly more acidic than other plots that fertilized by both manure and chemical fertilizer (TM and NTM). This meant that manure additive affected soil properties by raising soil pH. As shown in Figure 4-17, it seems that there was no tendency of methane flux on soil pH occurring in upland fields Moreover, from low R-squared values as reported in Appendix B, it was concluded here that there was no relationship between methane flux and pH of soil in all positions.

4.6.3 Soil moisture

For the reason that the paddy soil was covered by the flooding water at all the cultivation time, this soil was always saturated with water. Thus, the soil moisture in paddy soil was not taken as a parameter for evaluation, and only that in upland soil is considered here.

In among soil moisture from three different positions including soil surface, 5 cm above and below tillage layer, the highest water content was found at the deepest position which was at 5 cm below tillage layer as shown in Figure 4-18. And the smallest amount was at soil surface. This implied that the deeper position of soil sampling contained the larger soil-water content. Moreover, the soil moistures in all plots, *i.e.* TM, NTM, TF, and NTF, were not much different and all were in the same range of 30-45% by weight.

Figure 4-19 demonstrates the relationship between methane flux and soil moisture in various vegetation fields. It was found that methane flux increased with the increase in soil moisture. Moreover, the relationship for wheat field was more precise than that of maize field (see R-squared value in Appendix B). Soil moisture reflects the quantity of water in soil and, can also be used to refer to the fraction of air in the soil. Provided that soil fraction is constant, a higher soil moisture meant a lower air content, and also a lower available oxygen for microbial activities. As mentioned in Sections 4.2 and 4.5.1, under low oxygen concentration in soil or anaerobic condition, methanogen could be more active than methanotroph, and methane tended to be produced and emitted rather than be consumed and absorbed. Therefore, methane flux was found to be higher at high soil moisture that at lower soil moisture as depicted in Figure 4-19.

4.7 Comparison between agricultural and industrial emission of methane

Up to now, it becomes clear that there were actually emissions of greenhouse gases from agricultural areas. This conclusion agreed well with research findings from other researchers [Boonyanopakun, 2002; Freibauer, 2003; Lin *et al.*, 1997]. It is the aim of this work to further evaluate the extent of the greenhouse gas or, rather, the global warming potential from agriculture. This will be accomplished by comparing the global warming potential from agricultural methane emission with that caused by industries. Several industrial activities such as power plant, cement production, asphalt production were reported to be important sources of greenhouse gases (carbon dioxide, methane, nitrous oxide, etc.) [El-Fadel *et al.*, 2001; Kadam, 2002; Kram *et al.*, 2000]. Most of the greenhouse gases emitted from industries are from the combustion of fuel. Turning fuel into energy requires that fuel is decomposed using oxidizing agent such as oxygen, and carbon content in the fuel is converted to carbon dioxide, the most significant greenhouse gas. One major fuel uptake industry is the electricity generation which converts energy from fuel combustion into electricity, the most important form of energy employed by almost all other industrial activities. To enable further utilization of research outcome from this work, actual situation on power generation in Thailand (industrial sector) was considered as a model study for comparison purpose.

The following assumptions were made for the calculation in this section:

- Natural gas, lignite, and fuel oil are used as the main fuels for the power plants with 365 operating days a year.
- The efficiency of the power plants by using natural gas, lignite, and fuel oil as fuels was 45, 40, and 50%, respectively [Energy Policy and Planning Office, Ministry of Energy, Royal Thai Government, 1999].
- The carbon content in natural gas, lignite, and fuel oil is 70.64, 84.03, and 87.5%, respectively [Babcock and Wilcox, 1975].
- 99.9% of carbon in natural gas and 99% of that in lignite and fuel oil are converted to carbon dioxide [USEPA, 1995].
- The heating value of natural gas, lignite, and fuel oil is 51, 34, and 44 MJ/kg, respectively [Babcock and Wilcox, 1975].

- There was the emission of greenhouse gases from rice paddy field only in growing season (approx. 5 month in one year). No greenhouse gases were emitted from field during the rest of a year.

According to the Energy Policy and Planning Office, in 2001, the total electricity produced in Thailand was about 11,800 MW. Table 4-5 indicates that power plants based on the use of natural gas, lignite, and fuel oil produced 7,500, 1,600, and 500 MW of electricity, respectively. It was estimated that about 18.6 Tg of carbon dioxide was generated and released from power plants into the atmosphere (see Table 4-5 and calculation in Appendix C). However, the Thailand Load Forecasting Subcommittee reported in 2002 that industries consumed the electricity approximately 45% of the overall power demands. Therefore, industrial activities or all power plants for industrial sector could potentially release approximately 8,400 Gg of carbon dioxide.

To compare with the emission from agricultural area, a rice paddy field was selected as a study case. From the experiment, seasonal methane flux from a rice paddy field was about 2.6 gm^{-2}. In order to compare this emission flux with that of industry, it was required that the unit of greenhouse gases is normalized. It is a common practice to display the extent of greenhouse gases in terms of carbon dioxide equivalent. The Global Warming Potential (GWP) index as reported in Table 2-2 was, at this point, used to convert methane to carbon dioxide equivalent.

The GWP denoted the potential of each greenhouse gas in raising the average earth temperature compared to carbon dioxide [IPCC, 1992]. By using this GWP, the quantity of all greenhouse gases is changed and displayed in terms of carbon dioxide equivalent which can be used for comparing the amount of greenhouse gases from different sources or even from the same source that emits various types of greenhouse gases. The GWPs of carbon dioxide, methane, and nitrous oxide are 1, 24, and 310, respectively. For example, methane is reported to have GWP of 24 which means that a molecule of methane can increase the earth temperature as effective as 24 molecules of carbon dioxide or one kilogram of methane has the same effect on the earth temperature as 66 kilogram of carbon dioxide. Additionally, the amount of carbon dioxide that provides the same result of increase in the earth temperature as one kilogram of nitrous oxide is 310 kilogram (since they have the same molecular weight.).

The above conversion suggested that 2.6 gm^{-2} of methane flux was equivalent to 172 gm^{-2} of carbon dioxide. As Thailand possesses approximately 21,850 km^2 of rice paddy field, the total methane emission from this area was approximately 3,750 Gg (as carbon dioxide). This was simply equivalent to 40% of the total quantity of greenhouse gas emitted from the power plants for industrial sector in Thailand.

The result indicated that rice paddy fields in Thailand acted as a source of methane which was a cause of global warming problem. However, to determine the effect of agriculture such as rice paddy fields on environmental problems, other greenhouse gases including carbon dioxide and nitrous oxide should be taken into account. In the next section, total greenhouse gas emission from agricultural areas would be discussed.

4.8 Greenhouse gas from agricultural areas

As mentioned in the literature part (Sections 1.1 and 2.1), greenhouse effect was a cause of global warming problem which gives a tendency to increase the earth temperature. Thus, global warming problem could result from the proliferation of greenhouse gases content in the atmosphere including carbon dioxide, methane, nitrous oxide, etc. Although this experiment focused only on the methane emission from an agricultural area, these cultivation areas also involved with the emissions of other greenhouse gases, particularly carbon dioxide and nitrous oxide. To quantitatively evaluate the effect of greenhouse gases from agricultural areas on global warming problem, the quantities of different greenhouse gases must be converted into the same unit by using the GWP as mentioned in the previous section.

4.8.1 Irrigated field

To evaluate the greenhouse gas fluxes from a rice paddy, the data of other greenhouse gas fluxes were needed. Carbon dioxide flux was obtained from Miyata *et al.*, 2000 who dealt with the cultivation of rice “IREX96” with mineral fertilizer from May till October 1996. This research revealed that, in one day, the photosynthesis of rice plant consumed about 44 gm^{-2} of carbon dioxide. This meant that this amount of carbon dioxide was absorbed into this rice paddy field. However, carbon dioxide was released from this area due to the respiration of plant, and this quantity of carbon dioxide emission was about 13 $gm^{-2}d^{-1}$. Thus, the net flux of carbon dioxide in a rice paddy field was -31 $gm^{-2}d^{-1}$.

Under the assumption of no difference in methane and nitrous oxide fluxes in the day and night times, it was found in this work that methane was emitted at about 30 $mgm^{-2}d^{-1}$ along a growing season of 2003. Furthermore, Xiang reported in 1994 that nitrous oxide was emitted in a rice paddy field in Bangkok with rice cultivar species “RD23” from November 1993 until March 1994 at a rate of about 0.11 $mgm^{-2}d^{-1}$.

To convert these amounts of greenhouse gas fluxes to carbon dioxide equivalent flux, the GWPs as shown in Table 4-3 were employed and the carbon dioxide equivalents for methane and nitrous oxide were 2 $gm^{-2}d^{-1}$ and 34 $mgm^{-2}d^{-1}$, respectively. Let us consider this problem in two aspects. Firstly, the carbon dioxide consumption in the rice paddy was ignored. This was to investigate the potential of global warming effect from the rice paddy. In this case, the total carbon dioxide equivalent was 15 $gm^{-2}d^{-1}$. The second scenario took into account the carbon dioxide consumption due to rice photosynthesis. This was to evaluate the actual problem regarding the greenhouse gas emission from this area. Interestingly, the amount of carbon dioxide required for photosynthesis exceeded the total amount of greenhouse gases (in terms of carbon dioxide equivalent), and the net carbon dioxide flux was -28 $gm^{-2}d^{-1}$. This means that rice paddy took up greenhouse gases more than emitted them.

4.8.2 Upland field

Only TF plot of a wheat field was chosen as a case study in this topic. The data of carbon dioxide and nitrous oxide was obtained from Boonyanopakun (2002) who carried out experiment in the same agricultural area as this work but in a cultivating season of 2002. The fluxes of carbon dioxide and nitrous oxide were 16264 and 0.30 $mgm^{-2}d^{-1}$, respectively. Then, all fluxes of greenhouse gases were converted to carbon dioxide equivalent and the results are shown in Table 4-4. The net flux of greenhouse gases from this plot or the summation of carbon dioxide equivalent fluxes was equal to about 16.3 $gm^{-2}d^{-1}$. Thus far, there was no report on carbon dioxide requirement for photosynthesis in the wheat field, and therefore the evaluation of actual global warming potential could not be complete.

Table 4-1 Seasonal methane fluxes from a rice paddy field from May to September 2003

Date	Growth stage	CH_4 flux[a] ($mgm^{-2}h^{-1}$)	CH_4 flux[b] ($mgm^{-2}h^{-1}$)
7th May 2003	Before flooding	0.001	-
26th July 2003	Booting stage	1.156	-
27th July 2003	Booting stage	1.097	-
7th August 2003	Grain-developing stage	2.130	0.073
28th August 2003	Grain-developing stage	1.308	0.045
9th September 2003	Grain-ripening stage	0.654	0.129

a – Methane flux from the area with plant.

b – Methane flux from the area without plant.

Table 4-2 Methane emission (mgm^{-2}) from each vegetation area in a growing season of 2003

Treatment	Vegetation	
	Wheat	Maize
TM	-68.47	-34.86
NTM	-48.51	-37.31
TF	-59.09	-48.62
NTF	-58.01	-37.33

Table 4-3 Greenhouse gases flux from a rice paddy field

Greenhouse gas	Flux ($mgm^{-2}d^{-1}$)		CO_2 equivalent ($mgm^{-2}d^{-1}$)	
	Emission	Absorption	Emission	Absorption
Carbon dioxide	13250[a]	43750[a]	13250	43750
Methane	30.46[b]	-	2010.36	-
Nitrous oxide	0.11[c]	-	34.10	-

a – Miyata *et al.*, 2000.

b – This work.

c – Xiang, 1994.

Table 4-4 Greenhouse gases flux from a TF plot of a wheat field

Greenhouse gas	Flux ($mgm^{-2}d^{-1}$)	CO_2 equivalent ($mgm^{-2}d^{-1}$)
Carbon dioxide	16264[a]	16264
Methane	-0.26[b]	-17.16
Nitrous oxide	0.30[a]	93

a – Boonyanopakun, 2002.

b – This work.

Table 4-5 Characteristics of fuels (natural gas, lignite, fuel oil) used in power plants in Thailand in 2001

Characteristic	Types of fuel				
	Natural gas	Lignite	Fuel oil	Others	Total
Carbon content[a] (%)	70.64	84.03	87.5	-	-
Converting to CO_2[b] (%)	99.9	99.0	99.0	-	-
Heating value[a] (MJ/kg)	51.22	34.03	44.11	-	-
Used quantity[c] (kg)	10.36×10^9	13.20×10^9	0.63×10^9	-	-
Produced energy[c] (MW)	7479	1588	447	2303	11817
Efficiency[c] (%)	≈ 45	≈ 40	≈ 50	-	-
CO_2 emission (Tg)	7.32	10.98	0.28	-	18.57

a – Babcock and Wilcox, 1975.
b – USEPA, 1995.
C – Energy Policy and Planning Office, Ministry of Energy, Royal Thai Government, 1999.

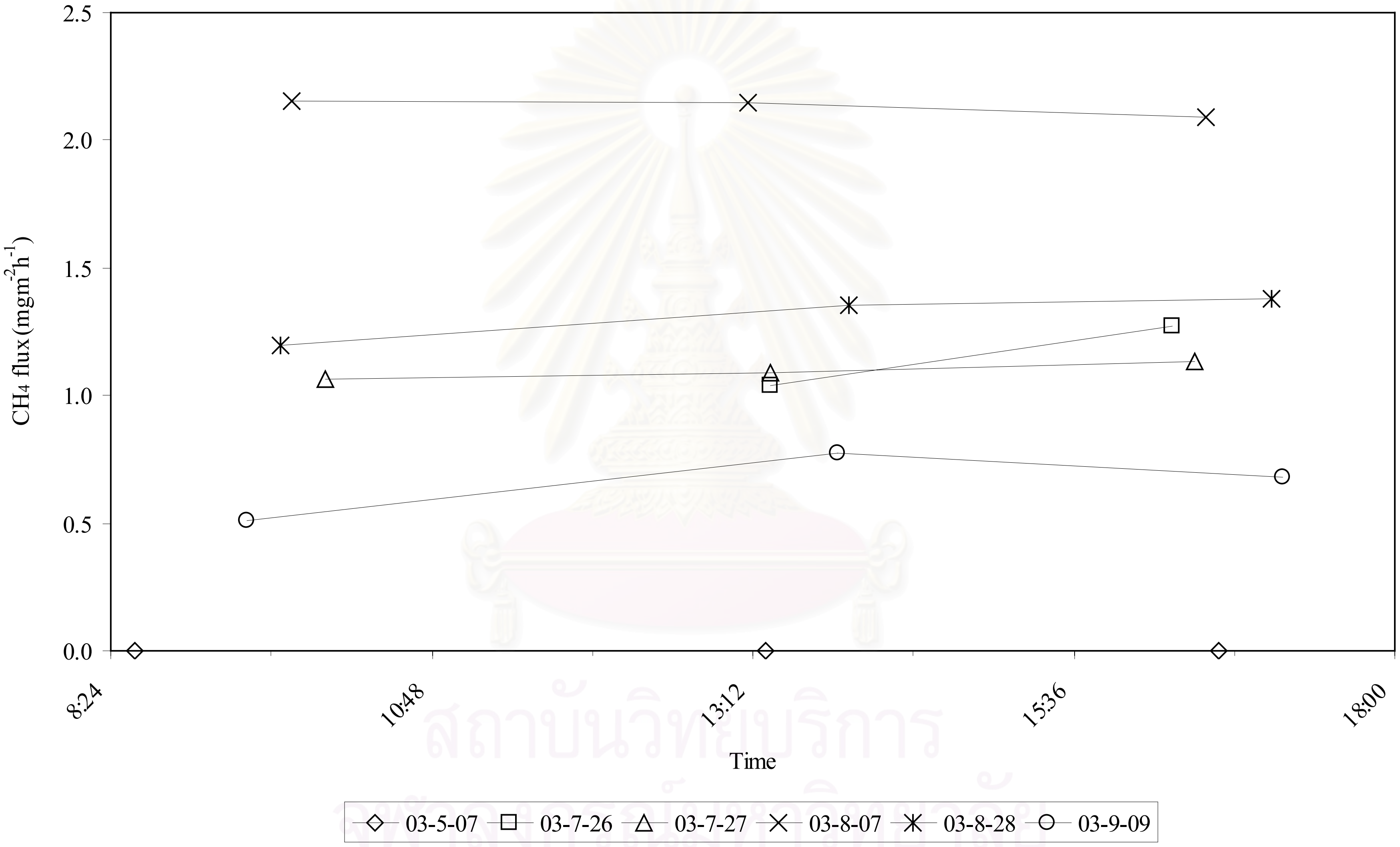


Figure 4-1 Diurnal methane fluxes from a rice paddy field with plant

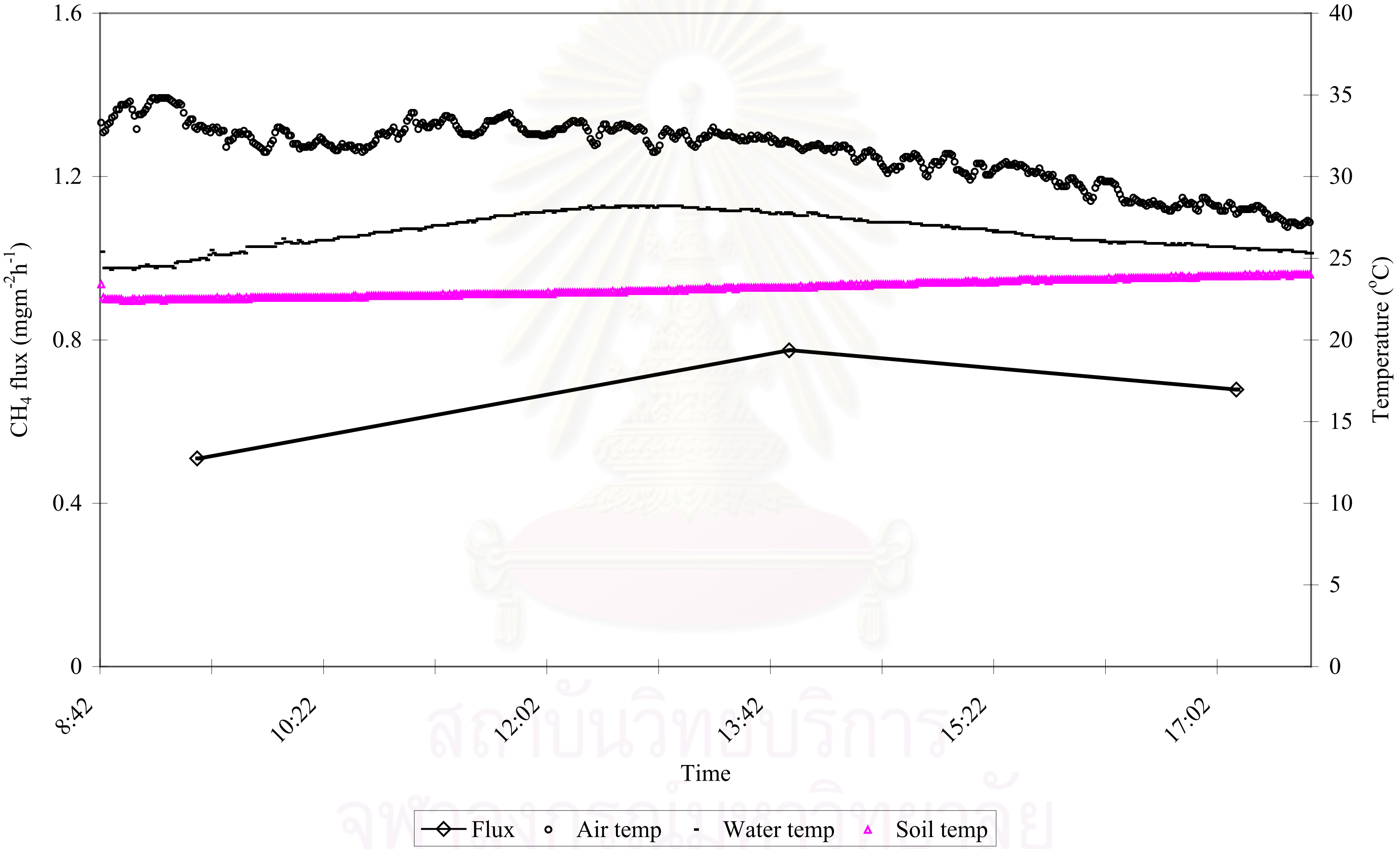


Figure 4-2 Diurnal methane flux from a rice paddy field with plant on Sep 9th, 2003

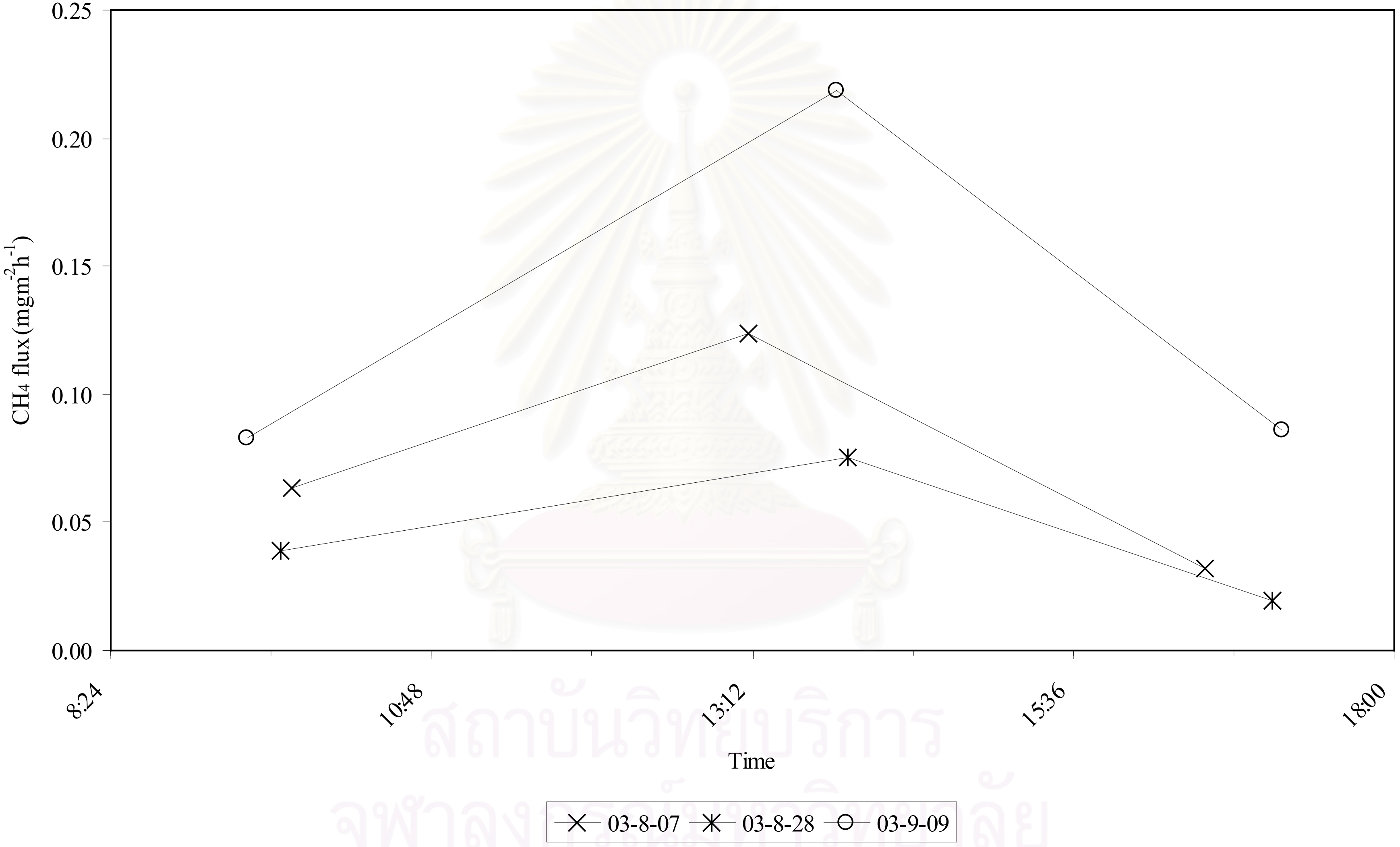


Figure 4-3 Diurnal methane fluxes from a rice paddy field without plant

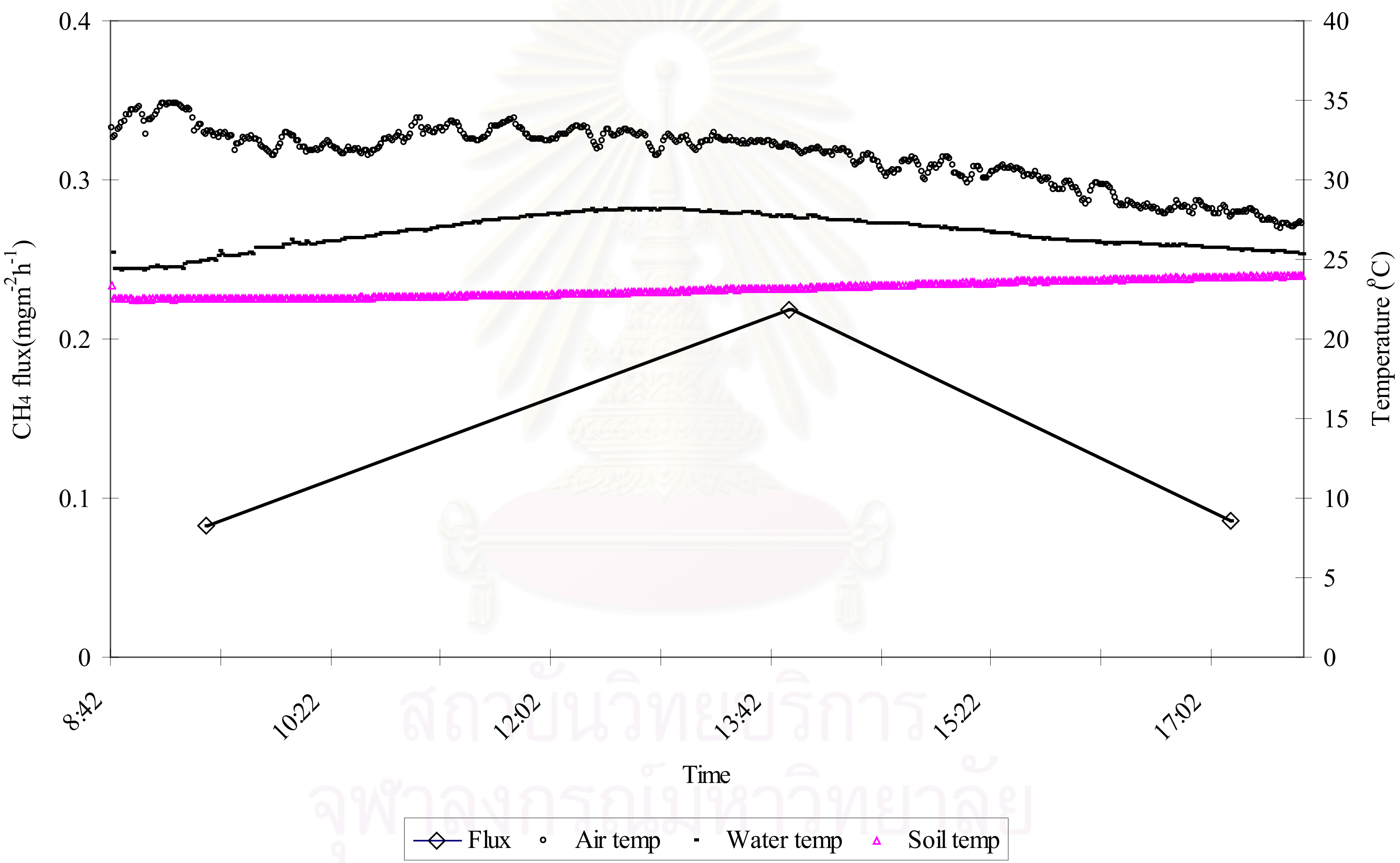


Figure 4-4 Diurnal methane flux from a rice paddy field without plant on Sep 9th, 2003

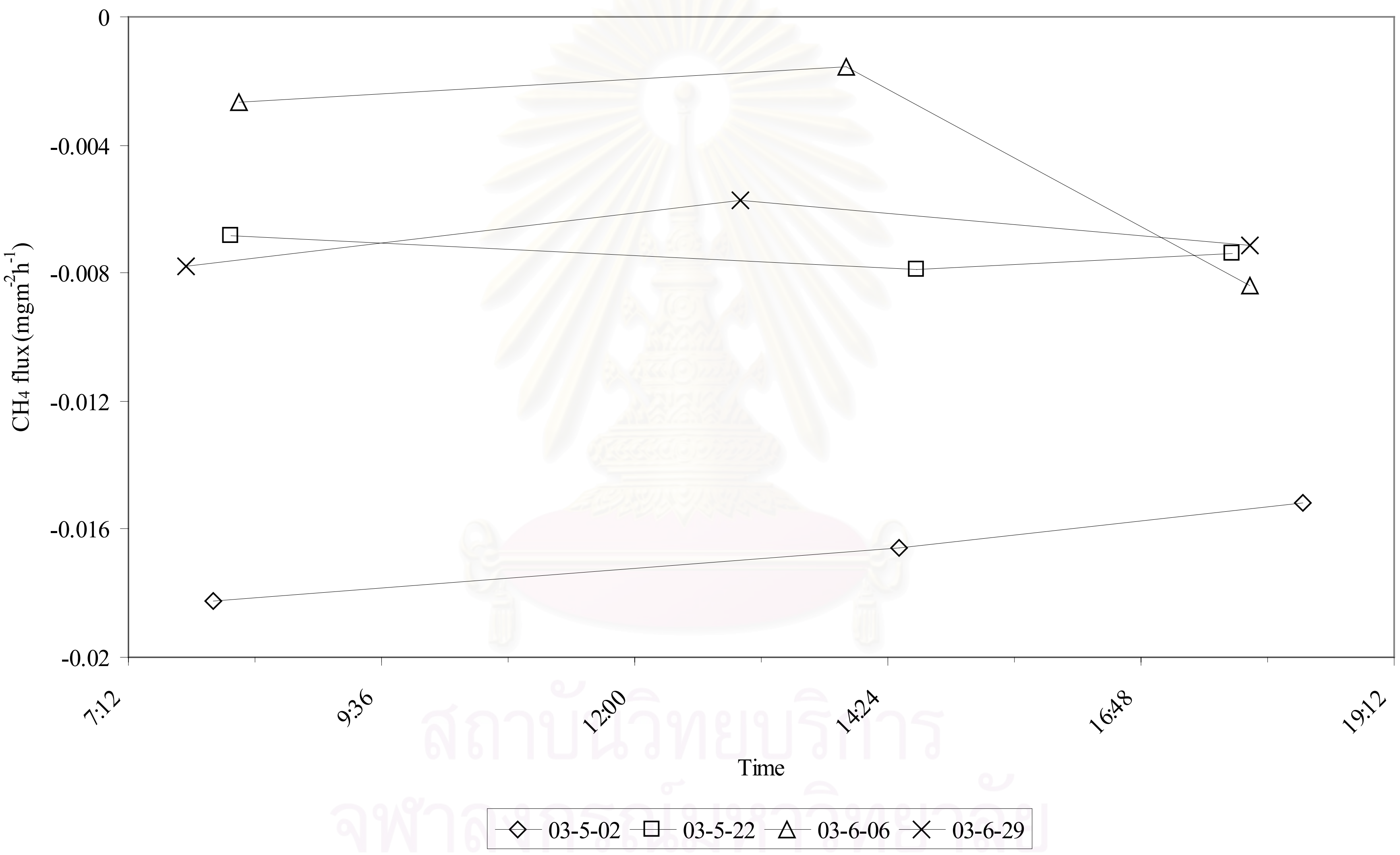


Figure 4-5 Diurnal methane fluxes from a wheat field

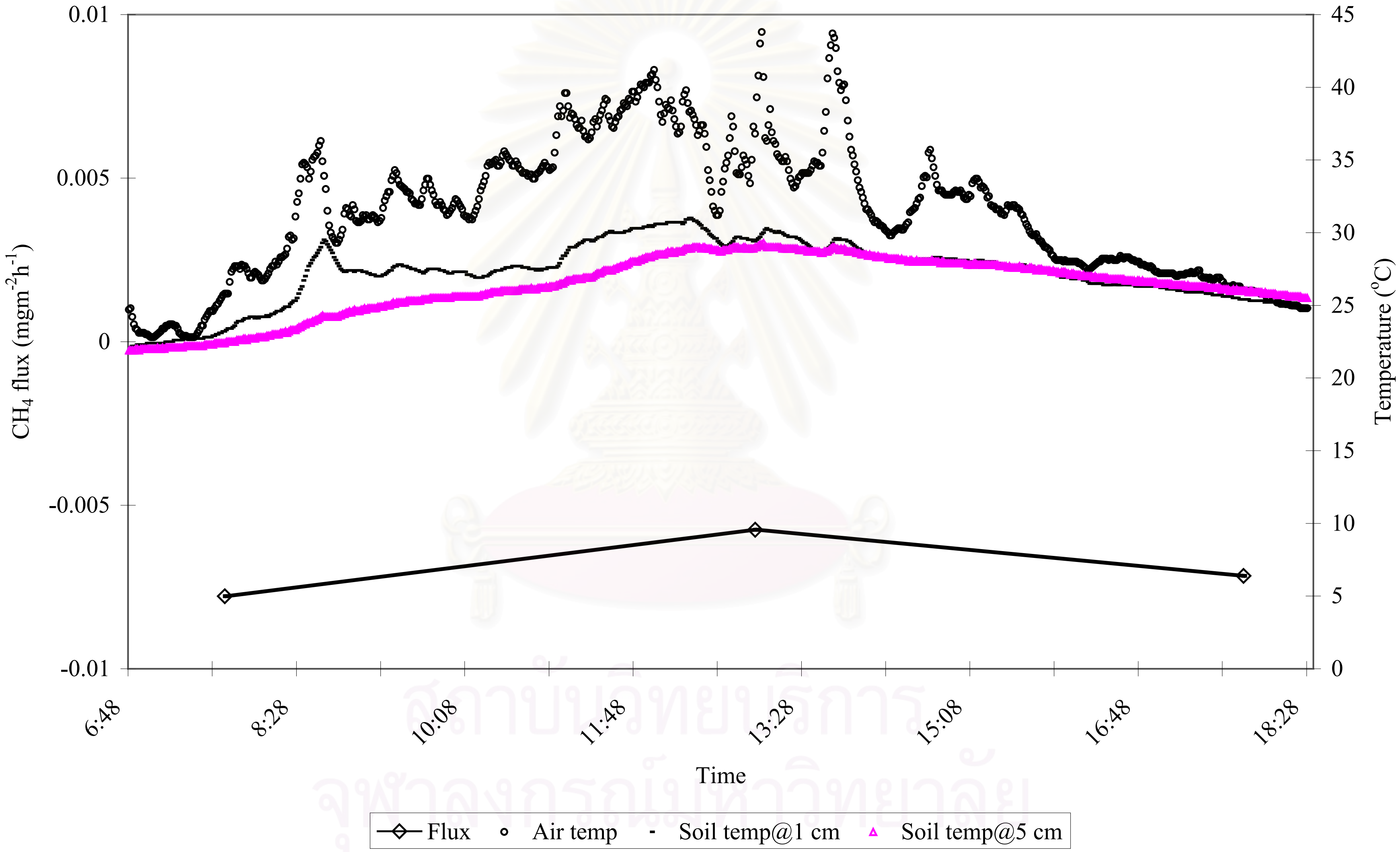


Figure 4-6 Diurnal methane flux from a wheat field on June 29th, 2003

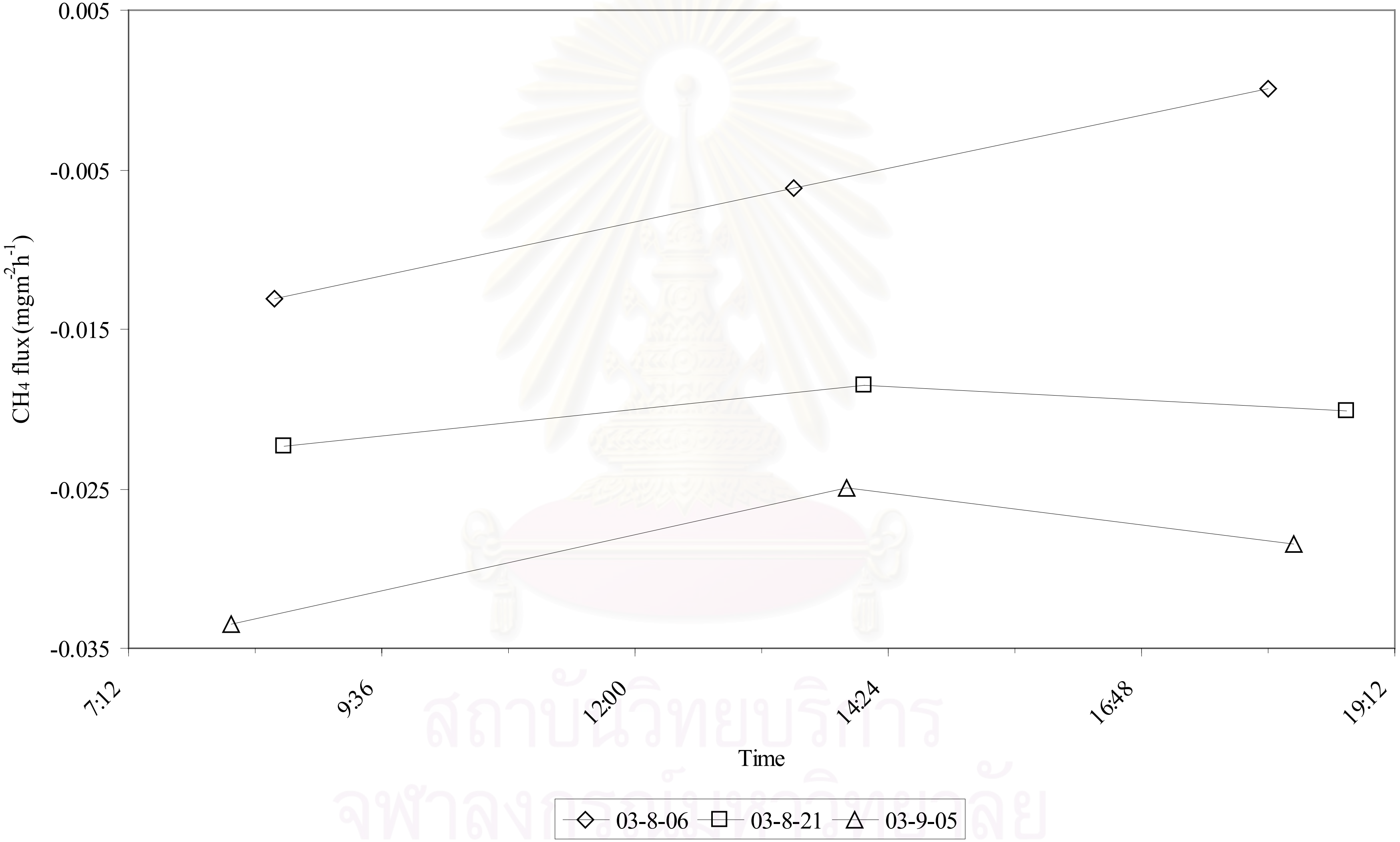


Figure 4-7 Diurnal methane fluxes from a maize field

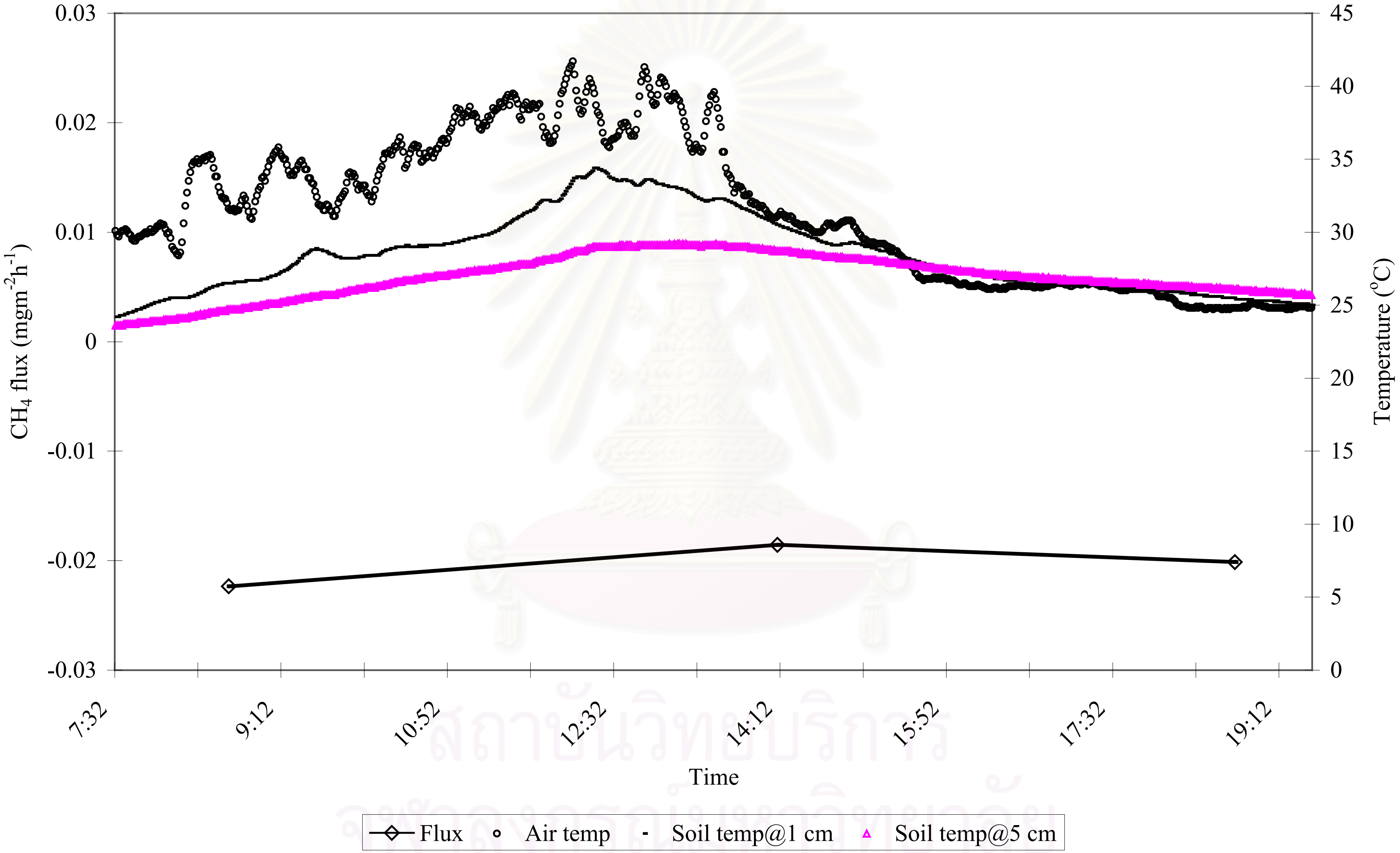


Figure 4-8 Diurnal methane flux from a maize field on Aug 21st, 2003

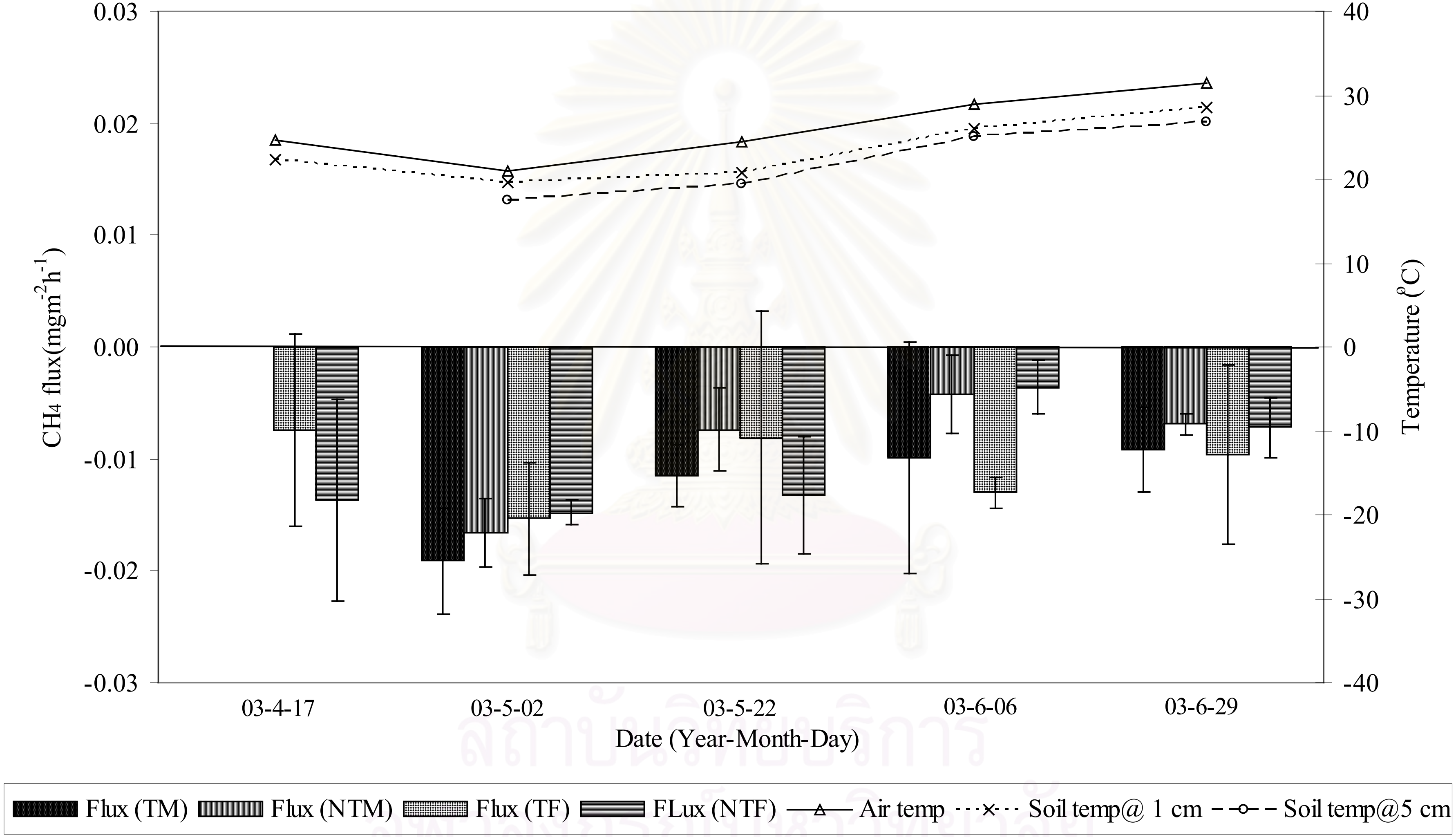


Figure 4-9 Seasonal methane flux from a wheat field in a cultivating period of 2003

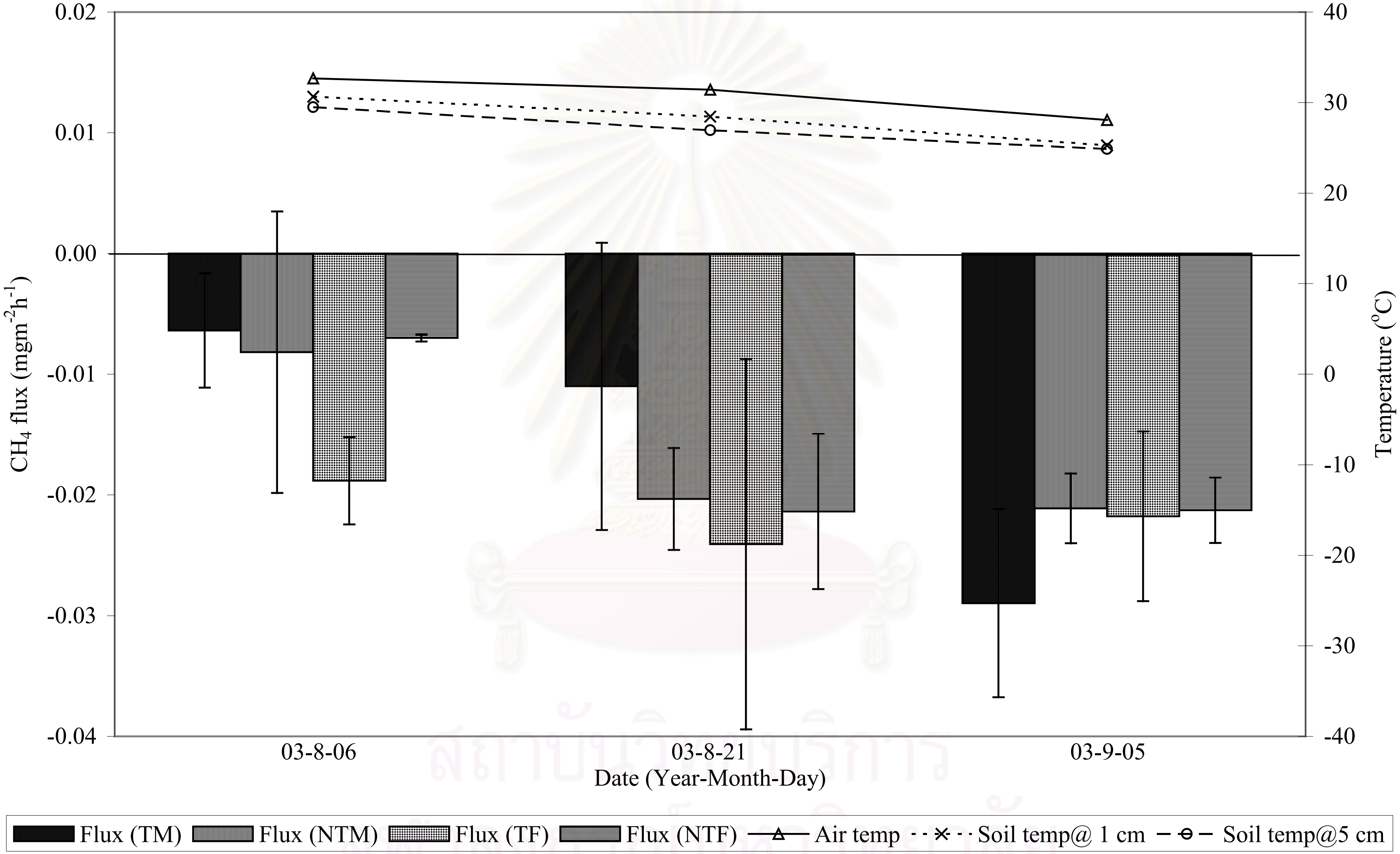


Figure 4-10 Seasonal methane flux from a maize field in a cultivating period of 2003

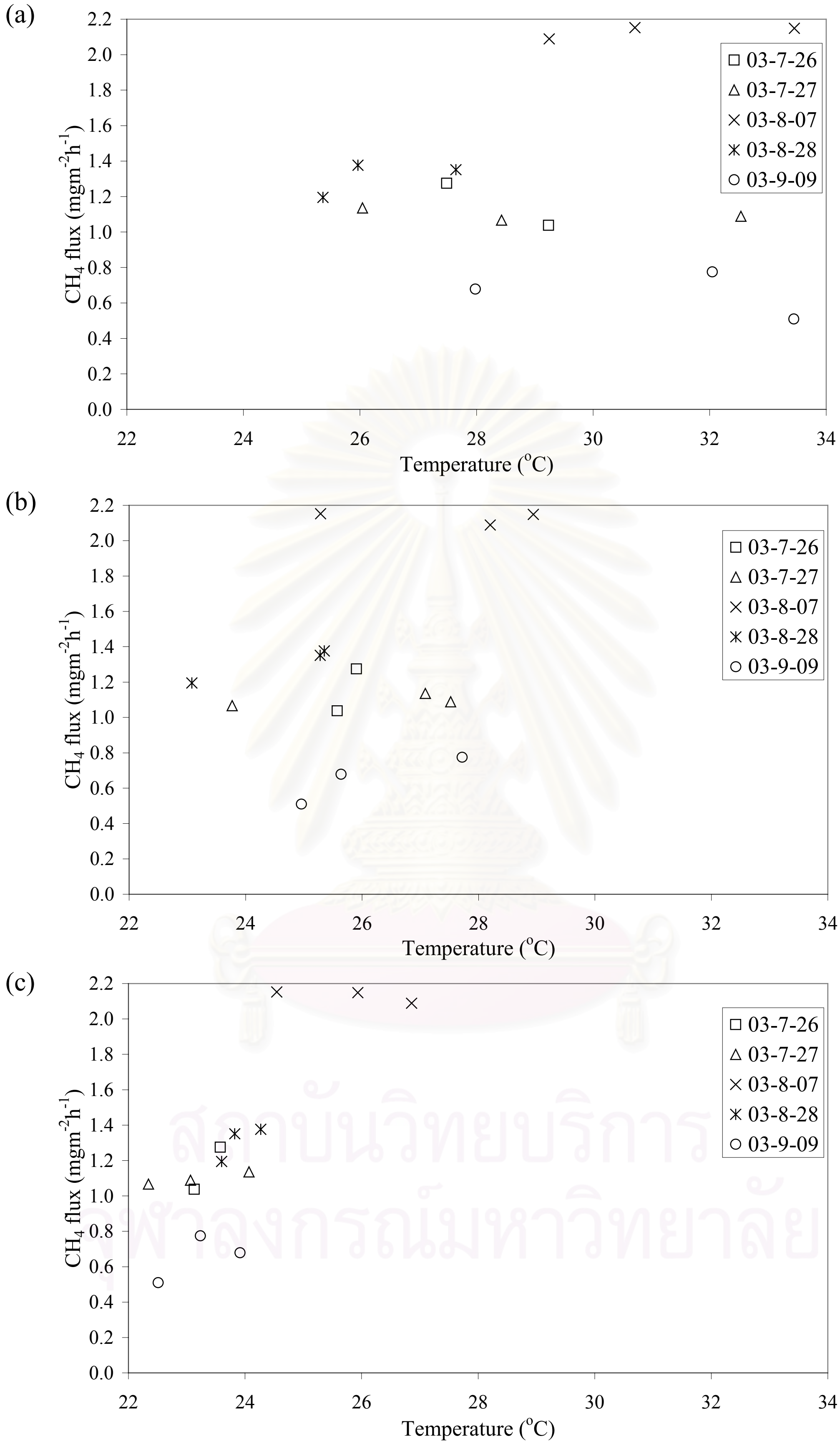


Figure 4-11 The relationship between methane flux and environmental temperature in a rice paddy field a) air temperature, b) water temperature, and c) soil temperature

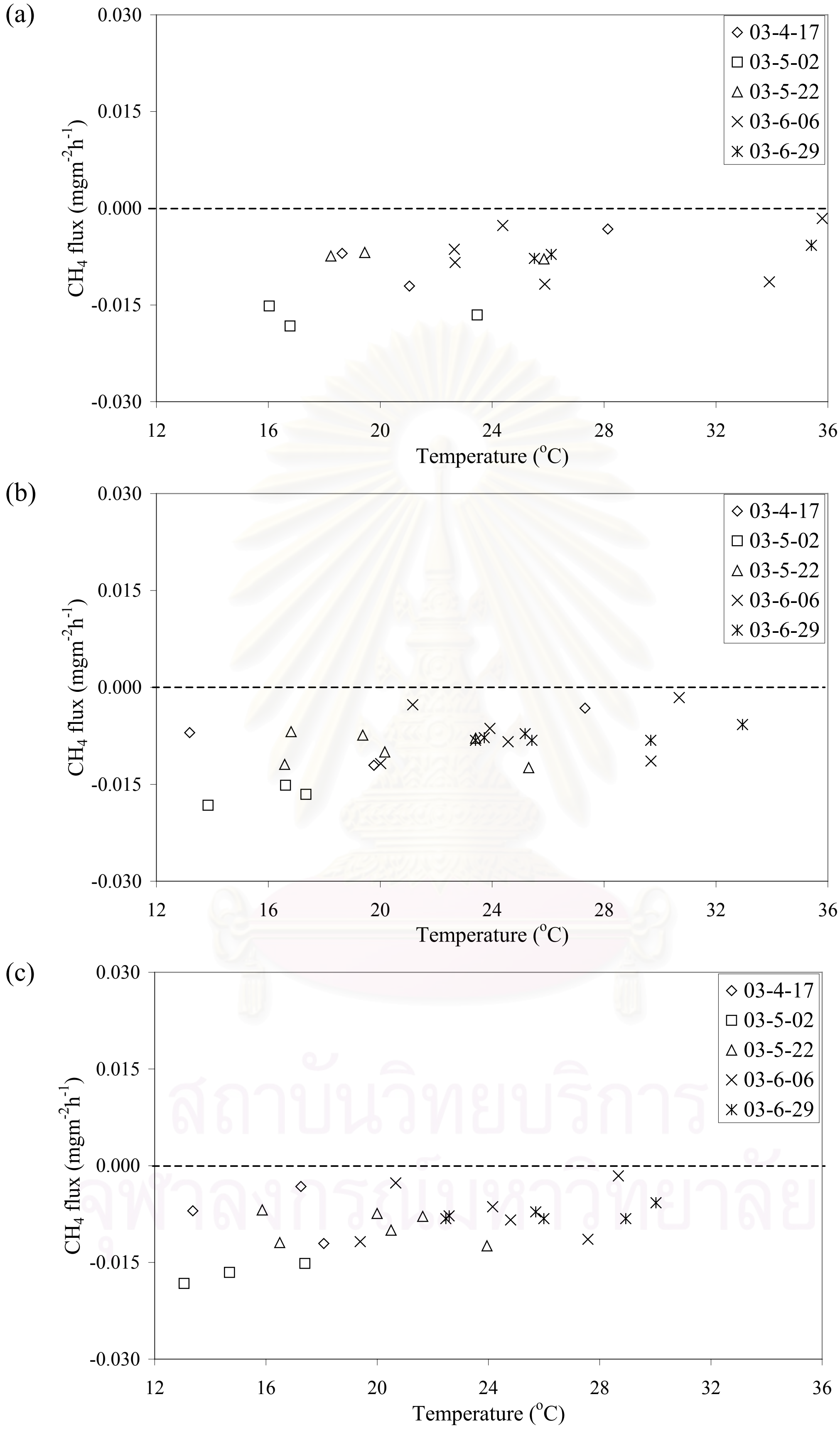


Figure 4-12 The relationship between methane flux and environmental temperature in a wheat field a) air temperature, b) soil temperature at 1 cm depth, and c) soil temperature at 5 cm depth

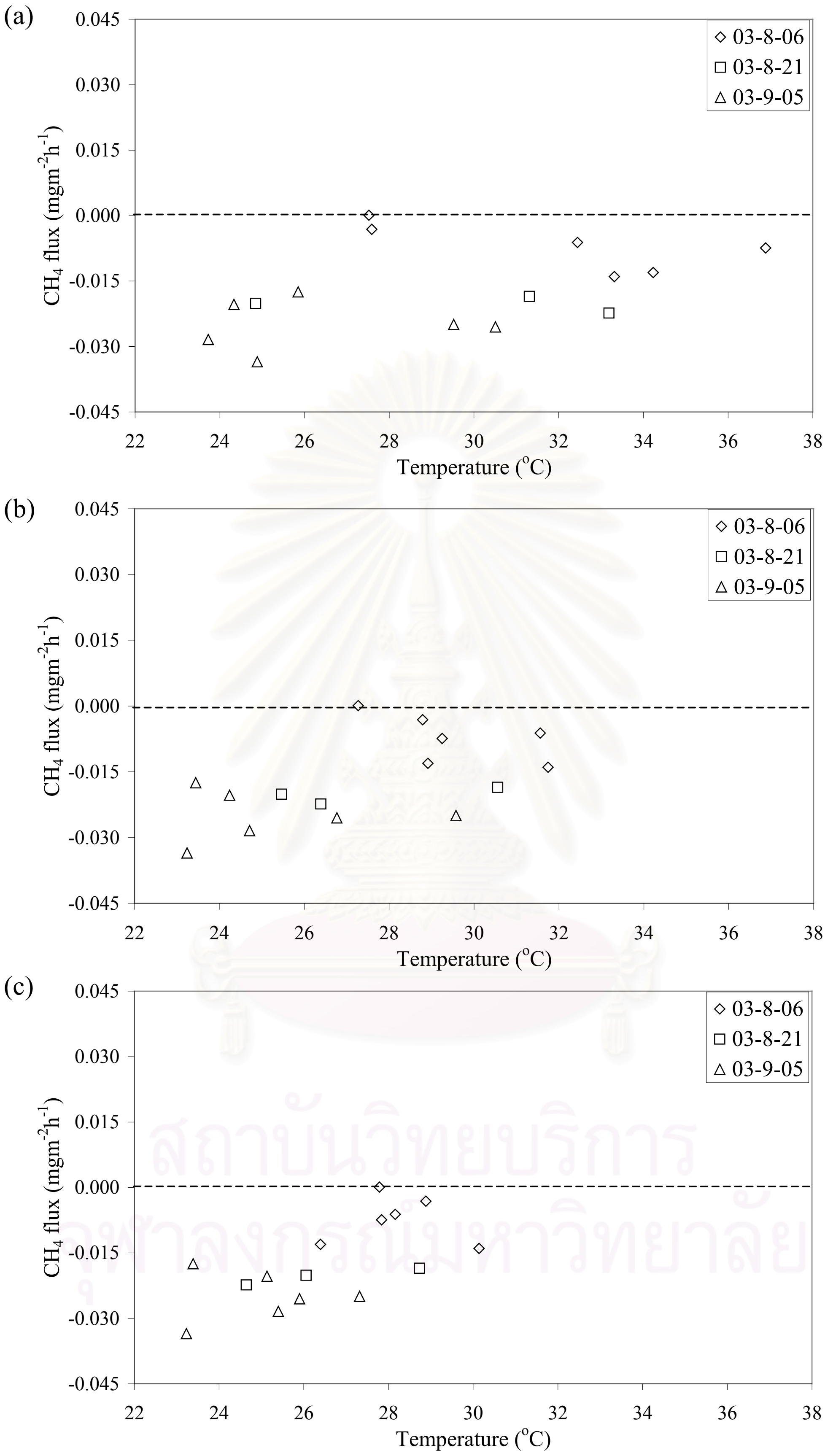
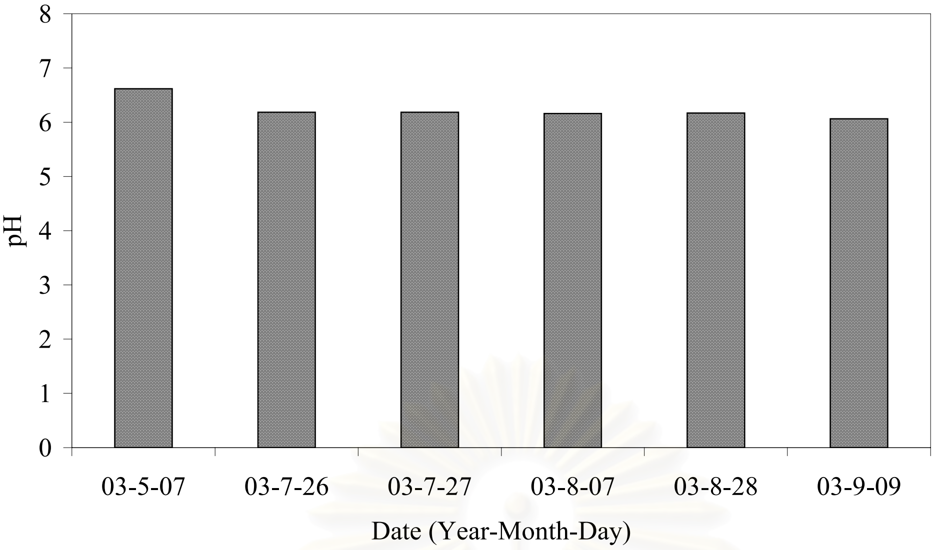


Figure 4-13 The relationship between methane flux and environmental temperature in a maize field a) air temperature, b) soil temperature at 1 cm depth, and c) soil temperature at 5 cm depth

(a)



(b)

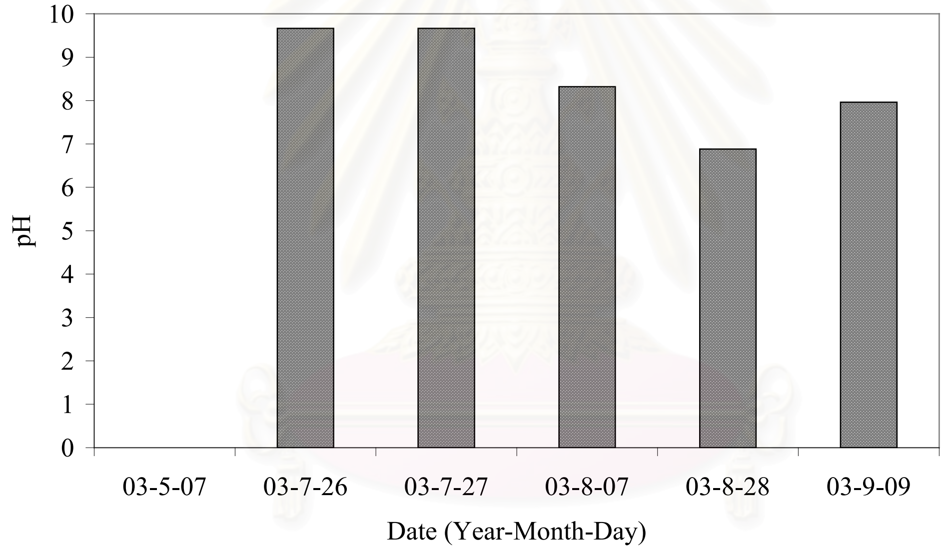


Figure 4-14 The seasonal pH change in a rice paddy field a) soil pH, and b) water pH

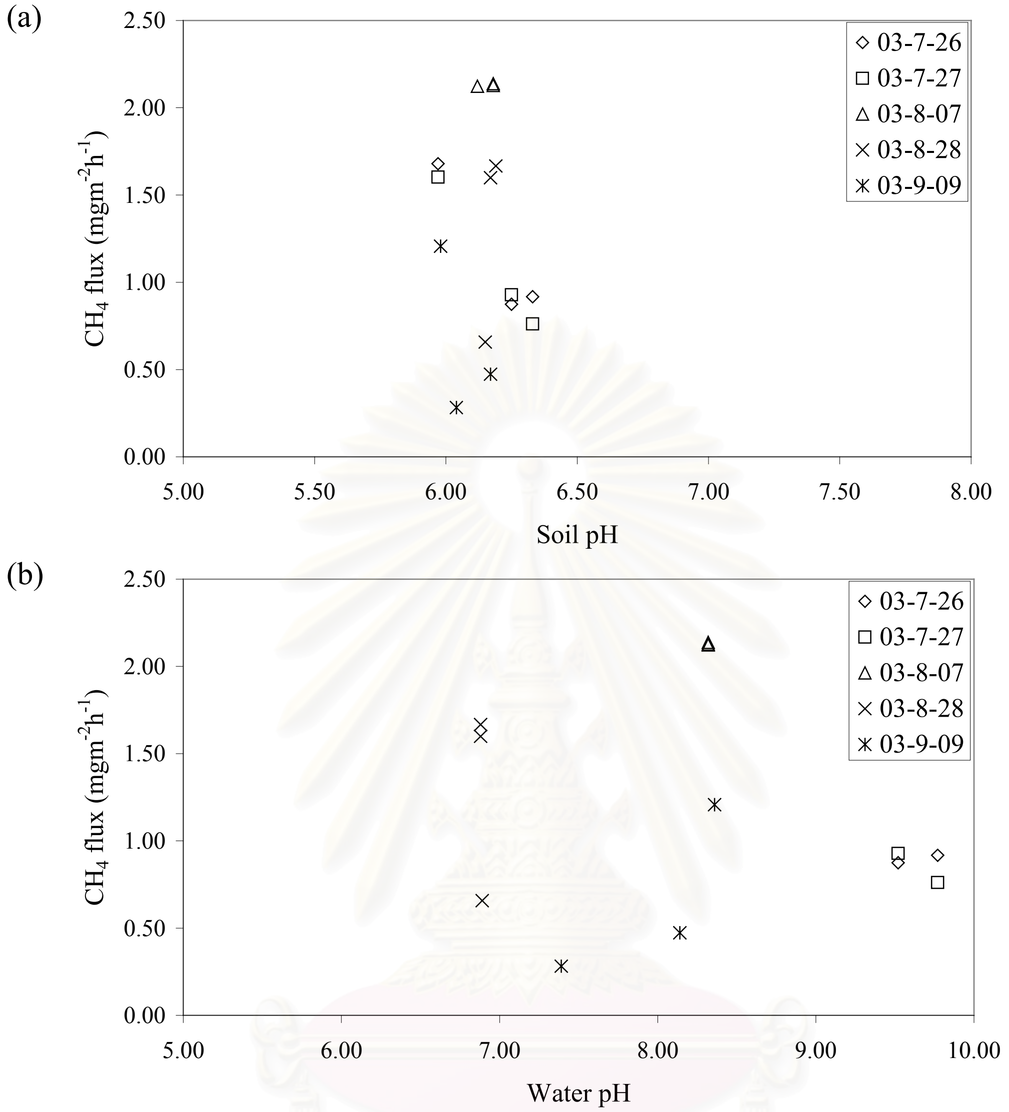


Figure 4-15 The relationship between methane flux and pH in a rice paddy field a) soil pH, and b) water pH

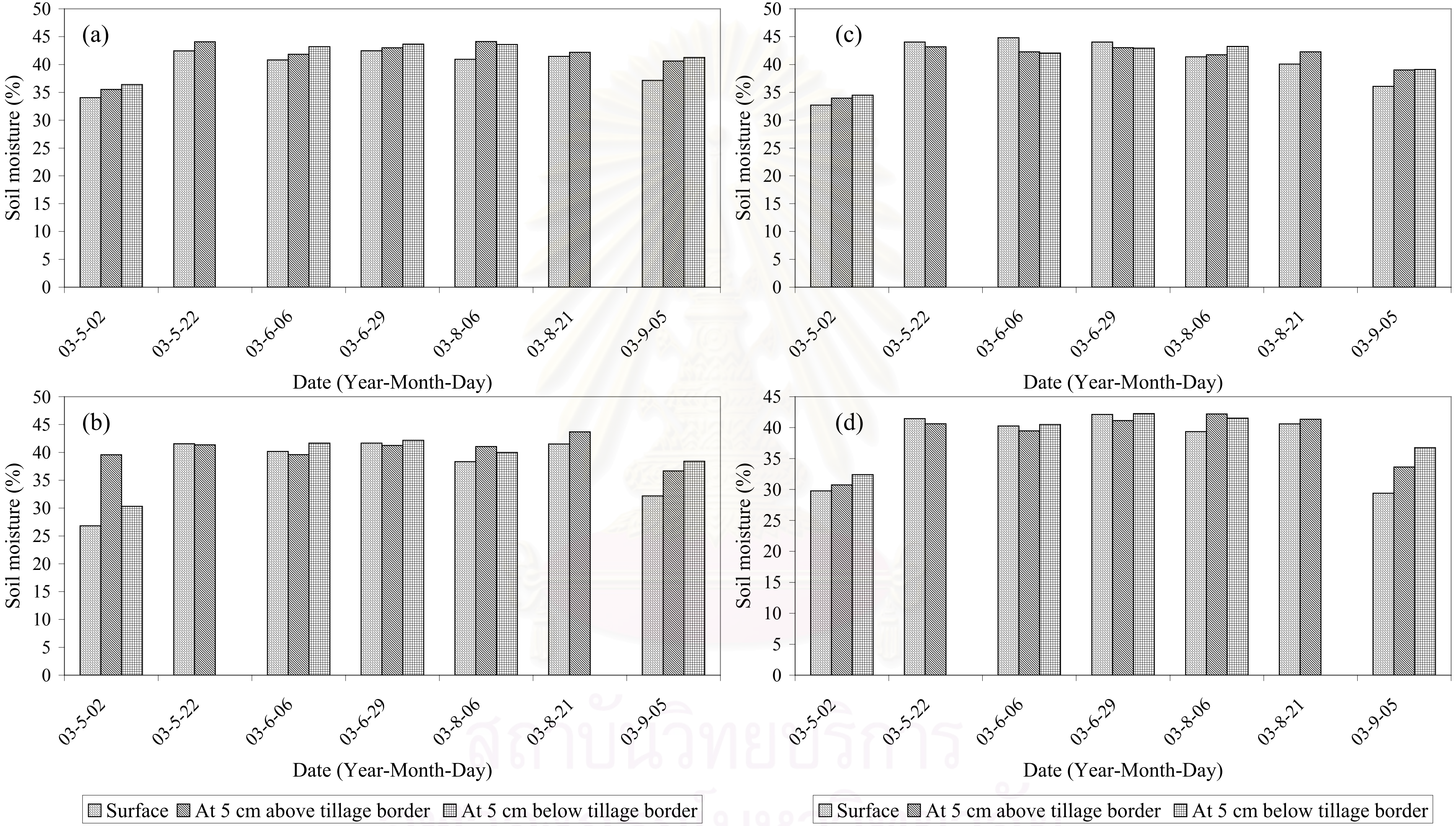


Figure 4-18 The seasonal change of soil moisture in an upland field a) TM area, b) NTM area, c) TF area, and d) NTF area

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The irrigated field acted as a source of methane whereas the upland field was a sink.
2. A rice paddy field with flooding water provided anaerobic condition which was suitable for methane production by methanogen. Thus, methane was produced and emitted from a rice paddy field. On the other hand, the aerobic condition in upland area promoted methane utilization by methanotroph which converted methane to carbon dioxide. This caused methane uptake in upland field.
3. There were three main pathways of methane emission from paddy soil to the atmosphere: (i) diffusion, (ii) ebullition, and (iii) transportation through the rice plant. The most significant pathway was the transportation through the rice plant which accounted for about 80% of total methane emission from a rice paddy field.
4. In terms of methane production and emission, the most significant growth stage of rice plant was grain-developing stage. This was due to the increase in the root respiration and the quantity of root excretion. While, in upland field, no relationship between methane flux and plant growth was found.
5. The soil treatment had effect on methane flux in an upland area. For example, the different level of tillage provided the difference in oxygen content in the soil. The deep-tilled area contained more oxygen content and promoted the aerobic methane utilization, whilst less oxygen in shallow-tilled area led to a lower methane utilization rate. Furthermore, the addition of manure into the soil enhanced methane production.
6. The environmental conditions had effect on methane flux such as soil temperature, and soil moisture. The increase in soil temperature raised methane flux from irrigated and upland fields. However, this temperature effect in a rice paddy field was more pronounced than in an upland field. Moreover, high soil moisture often was found to have higher methane flux.
7. The amount of methane emitted from whole irrigated fields in Thailand was equivalent to approximately 40% of the total quantity of greenhouse gas released from the power plants for industrial sector in Thailand.

8. In terms of overall greenhouse gases emission, a rice paddy field was found to absorb greenhouse gases rather than to emit them. The net flux was -28 $gm^{-2}d^{-1}$.

5.2 Contribution

This work was among the first that provided critical analysis of methane emission from agricultural area. This is important as it directly concerned with the global worming potential, and the management of greenhouse gases will be crucial in the reduction of the greenhouse gases. Although it was finally found that the net greenhouse gas emitted from agricultural area was negative indicating that agricultural area absorbed greenhouse gases in a higher quantity than emitted them out, methane flux from rice paddy field was certainly released and will be exposed to the environment. Future work should then be conducted with the focus on the reduction of this mechanism. Results from this work suggested that, with a proper treatment of agricultural area, the flux of methane flrom the soil could be manipulated.

5.3 Recommendations

1. To complete the work in this area, there are still a few other aspects that should be given attention. Firstly, the night time emission of methane should be measured to complete the cycle of methane production in one day.
2. Due to the limitation of closed chamber technique, experiment could only be performed for a short period of time. A new, nondestruction measurement of gases from industrial area should be researched and developed. A continuous data will be very useful for analyzing data.

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APPENDICES

APPENDIX A

ABBREVIATIONS

d = day

g = gram

Gg = 10^3 ton

GWP = Global warming potential

ha = 10^4 m^2

IPCC = the Intergovernmental Panel on Climate Change

l = liter

m = meter

mg = 10^{-3} g

micron = 10^{-6} m

MW = 10^6 watt

Tg = 10^6 ton

y = year

APPENDIX B

Table B-1 Average CH_4 flux, standard deviation, and coefficient of variance of CH_4 flux from each area

Area	Average CH_4 flux ($mgm^{-2}h^{-1}$)	Standard deviation ($mgm^{-2}h^{-1}$)	Coefficient of variance
Paddy field (with plant)[a]	0.654	0.134	0.21
Paddy field (without plant)[a]	0.129	0.078	0.60
Wheat field[b]	-0.007	0.001	0.15
Maize field[c]	-0.020	0.002	0.09

a – the data of 9th September 2003.
b – the data of 29th June 2003.
c – the data of 21st August 2003.

Table B-2 The slope, intercept, and R-squared value of the linear relationship between methane flux and temperatures in a rice paddy field

Parameter	CH_4 flux		
	Slope	Intercept	R-squared value
Air temp.	0.010	0.993	0.003
Water temp.	0.114	-1.684	0.132
Soil temp.	0.346	-6.994	0.663

Table B-3 The slope, intercept, and R-squared value of the linear relationship between methane flux and temperatures in wheat and maize fields

Parameter	CH_4 flux					
	Wheat			Maize		
	Slope	Intercept	R-squared value	Slope	Intercept	R-squared value
Air temp.	0.223	-0.018	0.223	0.001	-0.043	0.149
Soil temp. at 1 cm depth	0.000	-0.018	0.269	0.002	-0.067	0.283
Soil temp. at 5 cm depth	0.000	-0.017	0.201	0.003	-0.097	0.405

Table B-4 The slope, intercept, and R-squared value of the linear relationship between methane flux and pH in a rice paddy field

Parameter	CH_4 flux		
	Slope	Intercept	R-squared value
Soil pH	-1.076	7.885	0.042
Water pH	-0.012	1.371	0.005

Table B-5 The slope, intercept, and R-squared value of the linear relationship between methane flux and soil pH in wheat and maize fields

Parameter	CH_4 flux					
	Wheat			Maize		
	Slope	Intercept	R-squared value	Slope	Intercept	R-squared value
Surface soil	-0.001	-0.005	0.033	-0.002	-0.043	0.032
@5 cm above tillage border	-0.001	-0.004	0.035	-0.001	-0.012	0.006
@5 cm below tillage border	-0.002	-0.000	0.033	-0.000	-0.015	0.000

Table B-6 The slope, intercept, and R-squared value of the linear relationship between methane flux and soil moisture in wheat and maize fields

Parameter	CH_4 flux					
	Wheat			Maize		
	Slope	Intercept	R-squared value	Slope	Intercept	R-squared value
Surface soil	0.001	-0.035	0.562	0.001	-0.062	0.376
@5 cm above tillage border	0.001	-0.042	0.418	0.000	-0.021	0.000
@5 cm below tillage border	0.001	-0.041	0.505	0.002	-0.097	0.306

APPENDIX C

1. Finding the emission of carbon dioxide by natural gas combustion from power plants

   From the assumptions:

   - The carbon content in the coal is 70.64%.
   - 99.9% of carbon in natural gas is converted to carbon dioxide.

$$\textit{Carbon content in natural} = (0.7065)\left(14.36 \times 10^{9}\,kg\right) = 10.14 \times 10^{9}\,kg$$

$$\textit{Emitted carbon dioxide} = (0.999)\left(10.14 \times 10^{9}\,kg\right) = 10.13 \times 10^{9}\,kg$$

Thus, in one year, there is 10.13 Tg of carbon dioxide emitted due to natural gas combustion from power plants in Thailand.

The amounts of carbon dioxide emitted due to lignite and fuel oil combustion are also calculated by the same method. It is estimated that carbon dioxide due to lignite and fuel oil combustion is released about 10.98 and 0.28 Tg, respectively.

2. Finding the amount of carbon dioxide emitted from power plants in Thailand.

The total amount of carbon dioxide emitted from power plants in Thailand is calculated by:

$$\textit{Total carbon dioxide emitted} = (10.13 + 10.98 + 0.28) \times 10^{9} = 21.39 \times 10^{9}\,kg$$

Due to industrial activities, the total amount of carbon dioxide emitted from power plants in Thailand is calculated by:

$$\textit{Total carbon dioxide emitted} = (0.45)\left(21.39 \times 10^{9}\right) = 9.62 \times 10^{9}\,kg$$

APPENDIX D

APPENDIX E

PSU-UNS International Conference 2003
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METHANE EMISSION FROM VEGETATION AREA AND ITS CONTRIBUTION TO GLOBAL WARMING PROBLEM

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ABSTRACT

Vegetation in flooded area such as rice field could emit methane in such a significant quantity that might have affected the global warming problem. A higher soil temperature was found to increase the methane emission flux. The quantity of greenhouse gases emitted from the rice paddies was found to be quite significant in comparison with that from industry. Methane emission from 21850 km^2 of rice field was estimated to introduce global warming potential in the same level as the 1000MW coal fired power plant.

KEYWORDS

Greenhouse, rice paddy, forest, upland, industry

1. INTRODUCTION

Global warming problem has been taken seriously as one of the major environmental issues. There are several reports which stated that the ground level temperature of the earth increased steadily with time over the last 150 years (Hansen *et al.*, 1981; Lean *et al.*, 1995).

Methane is one of the most important greenhouse gases. According to Lyman (1990), methane contributed as much as 18% to the global warming problem, the second only to carbon dioxide. Although the warming potential of methane is 24 times that of carbon dioxide (IPCC, 1990; IPCC, 1992), the contribution of methane is less due to a lower quantity of methane emitted. The major source of carbon dioxide emission is the combustion of various types of fuels (Augenbraun *et al.*, 1999b) whilst sources of methane are rather diversified (see Fig.1). Methane is naturally produced from methanogenic microorganisms which live under anaerobic conditions (Schütz *et al.*, 1991; Sass *et al.*, 1992; Yagi, 1996). Therefore areas that promoted anaerobic environments such as natural wetlands were usually found to emit large quantity of methane (Schütz *et al.*, 1991; Augenbraun *et al.*, 1999a).

Statistically, methane concentration in the atmosphere increased steadily with time from 1984 to 1994 and its increasing trend was still observed since then. (The University of Oregon, 1994) This increase was, apart from wetlands, believed to be the results from human activities (anthropogenic sources). Such human activities could be classified into two main groups, i.e. Enteric fermentation and rice paddies, (IPCC, 1990, 1992, 1994, Khalil and Shearer, 1993) and industry such as natural gas losses and coal mining (Bouwman, 1990).

The objective of this work was two-fold. Firstly, the effect of types of vegetation on methane emission was investigated. This information allowed one to determine the significance of the methane emission from vegetation areas by evaluating their contribution to the global warming problem. It would be interesting to compare the extent at which the vegetation contributed to the global warming problem in comparison with the industry and this was the second objective of this work.

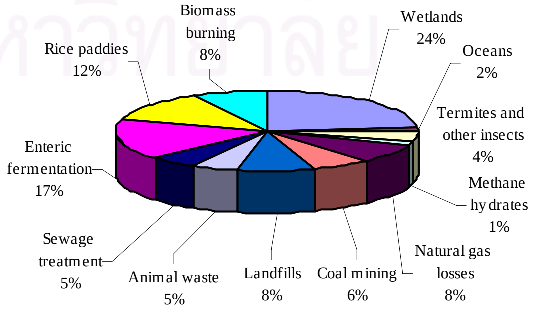

Fig.1 Methane sources (IPCC, 1990, 1992, 1994; Khalil and Shearer, 1993)

2. AGRICULTURE AND METHANE PRODUCTION

Table 1 summarizes data on methane emission fluxes from low land areas (flooded rice paddy fields). It can be seen that the emission flux of methane from these various areas varied significantly. This was due to differences in the cultivation practices such as species of rice in each plot, the fertilizing and tillage methods, and perhaps the quality of water (e.g. temperature, pH, etc.).

Table 1 Methane emission fluxes from rice paddies

Type	Area	CH_4 flux ($mgm^{-2}d^{-1}$)
Lowland	Ayutthaya, Thailand[a]	67-977
Lowland	Chaing mai, Thailand[b]	40-600
Lowland	Pathumthani, Thailand[c]	17-222
Lowland	New Delhi, India[d]	13-30
Lowland	Tsukuba, Japan[e]	8-104
Lowland	Kanto, Japan[f]	34-117
Lowland	The Philippines[g]	18-443
Lowland	Louisiana, USA[h]	298-467
Lowland	Texas, USA[i]	13-151
Lowland	California, USA[j]	12-510
Upland	Chaing mai, Thailand[b]	32-58
Floating	Ayutthaya, Thailand[a]	42-409

a: Tiawyuenyong, 1994
b: Kanchanasuntorn, 1994
c: Jermsawatdipong *et al.*, 1994
d: Mitra *et al.*, 1999
e: Nouchi *et al.*, 1994
f: Yagi *et al.*, 1996
g: van der Gon and Neue, 1994
h: Lindau *et al.*, 1993
i: Sass *et al.*, 1992
j: Cicerone *et al.*, 1992

Fig.2 is the results from our experiment carried out in Fuchu, Japan, which illustrated that, within the same cultivation area, a large fraction of methane was emitted through the intercellular spaces and aerenchyma and not from other area without rice. Methane was generated from the microbial activities in the soil and was emitted to the atmosphere. This information confirmed that the easiest way for methane to escape to the atmosphere was through the intercellular spaces and aerenchyma. In the area without rice, methane might also be emitted from the soil but, despite its relatively low solubility, most of the emitted methane could be well dissolved into the water. Therefore a low emission flux was observed.

In addition, Fig.2 depicts that methane emissions from rice paddies were in a range from 0.5 to 2 mg m^{-2} h^{-1} (or 12 to 24 mg m^{-2} d^{-1}). This agreed well with some of the reported fluxes but was quite low compared to the fluxes obtained from the cultivation area in Thailand. Table 1 indicates that even the upland rice field in Thailand emitted a significant level of methane, almost at the same level as the emission from our flooded experiment. The reason for this large difference is still unknown and has to be investigated further.

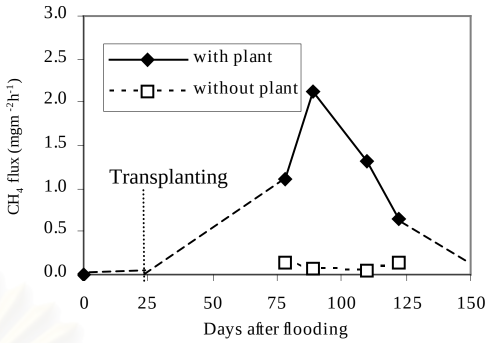

Fig.2 Methane flux from rice paddy field

Our experiments on rice paddies also revealed that methane emission rate did not vary much with the fertilizer nor tillage practices. The primary factor that influenced methane flux was the soil temperature. Fig.3 indicated that there existed almost a linear relationship between soil temperature and methane emission flux. It might be possible that methanogenic microorganisms worked better at elevated temperature. However, it should be noted that the temperature in the experiment could not be controlled but the soil temperature was regularly monitored along with the emission rate.

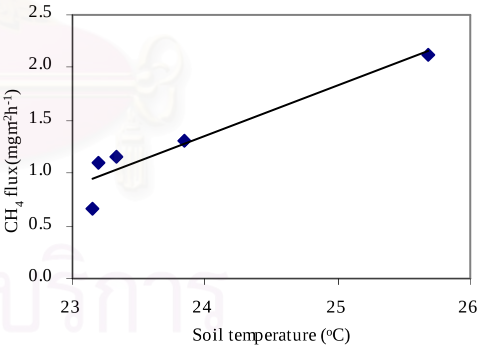

Fig.3 Effect of soil temperature on methane flux from rice paddy field

Methane emission rates from dry vegetation area are summarized in Table 2. The emissions of methane from these areas were significantly less than that obtained from the rice paddies where the maximum was found to be only 2 mg m^{-2} d^{-1}. Most data indicated that these areas actually acted as a methane sink. The water content in soil, however, could affect this methane sink. Fig.4 indicated that methane absorption capacity of soil decreased with an increase in soil water content. It was believed that water content in soil promoted the condition suitable for the growth of methanogenic bacteria.

Methane generated from these microorganisms could then cancel out the absorption capability of the area and a lower methane absorption rate was observed.

Table 2 Methane fluxes from vegetation areas

Crop	Area	Treatment	CH_4 flux ($mgm^{-2}d^{-1}$)
Mustard[a]	India	-	2.00
Chickpea[a]	India	-	0.43
Blackgram[a]	India	-	0.36
Dryland rice[b]	India	Control	-4.80
		NPK	-3.31
		NPK+WS	-1.78
Lentil[b]	India	Control	-9.00
		NPK	-8.35
		NPK+WS	-6.31
Wheat[c]	Japan	T-M	-0.34
		NT-M	-0.24
		T-F	-0.29
		NT-F	-0.24
Corn[c]	Japan	T-M	-0.38
		NT-M	-0.38
		T-F	-0.48
		NT-F	-0.29

a: Adhya *et al.*, 2000
b: Singh *et al.*, 1998
c: This work.
NPK: Fertilizer with nitrogen, phosphorus, and potassium.
WS: Wheat straw
T: Tillage depth at 15-20 cm. NT: Tillage depth at 5-10 cm.
M: Manure fertilizer. F: Manure and chemical fertilizer.

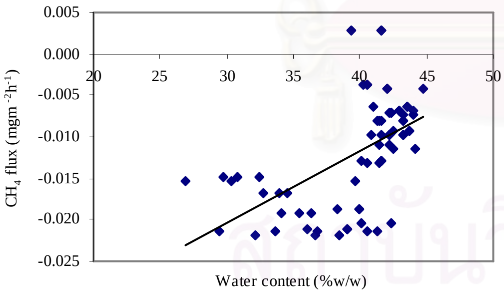

Fig.4 Effect of water content in soil on methane emission flux from upland cultivation area

Natural areas such as forests were often found to be a methane sink (except the wetland) in a greater extent than the upland cultivation area. Examples of such areas with their corresponding methane fluxes are given in Table 3. This, in turn, can be interpreted that the deforestation could result in less methane absorption capacity. Therefore altering the forest into the agricultural area can effectively result in a warmer atmosphere particularly when the vegetation is to be cultivated in the irrigated flooding area.

Table 3 Methane fluxes from natural areas

Type	Area	Period	CH_4 flux ($mgm^{-2}d^{-1}$)
Shorea forest[a]	India	Rainy	-4.32
		Winner	-11.52
		Summer	-6.96
Acacia forest[a]	India	Rainy	-4.80
		Winner	-14.16
		Summer	-10.08
Boswellia forest[a]	India	Rainy	-5.76
		Winner	-16.08
		Summer	-12.00
Savanna[a]	India	Rainy	-5.76
		Winner	-18.96
		Summer	-14.16
Cypress forest[b]	Japan	-	-3.06
Deciduous forest[c]	Japan	-	-4.58
Cedar forest[c]	Japan	-	-5.80
Cypress and cedar forest[c]	Japan	-	-1.80

a: Singh *et al.*, 1998
b: Nobuaki *et al.*, 2003
c: Shigehiro *et al.*, 2000

3. DISCUSSION ON GLOBAL WARMING POTENTIAL

In this section, we confined our scope to the methane emission fluxes from rice paddy fields as emissions from other areas could be considered relatively insignificant when compared to the rice paddy. Hence, their influences on global warming problem could also be regarded as immaterial. The global warming problem was measured in terms of carbon dioxide equivalent (kg CO_2) of the associated activities.

Most of the greenhouse gas emitted from industry is from the combustion of fuel. Turning fuel into energy requires that fuel is decomposed using oxidizing agent such as oxygen and almost all carbon content in the fuel is converted to carbon dioxide, the most significant greenhouse gas. One major fuel uptake industry is the electricity generation where the energy from fuel combustion is used to produce electricity. In this work, a 1000MW coal fire power plant was selected as a model study for comparison purpose. The following assumptions were made for the calculation in this section:

- Bituminous coal is used as fuel for the power plant with 365 operating days in a year.
- The efficiency of the power plant is 80%.
- The carbon content in the coal is 84.03% (Babcock and Wilcox, 1975)
- 99% of carbon in coal with dry and ash-free basis is converted to carbon dioxide. (USEPA)

- The heating value for the bitumenous coal is 34 MJ/kg (Babcock and Wilcox, 1975)
- There is methane emission from rice paddy field only in growing season (approx. 5 months in one year). No methane is emitted from field during the rest of a year.

With this assumption, it was estimated that to produce 1000MW, in one year, 963 Gg of CO_2 was produced and emitted into the atmosphere. This was equivalent to the methane emission from 5610 km^2 of rice paddy field. In other words, the total rice field in Thailand possesses approximately 21850 km^2 and the total methane emission from this area is equivalent to 3750 Gg CO_2. This is simply equal to the greenhouse gas emitted from as many as three to four 1000MW power plants.

4. CONCLUSIONS

This article emphasized the contribution of agriculture on the global warming potential. Specific agricultural activities such as rice cultivation could lead to a large quantity of greenhouse gas, or methane, emitted to the atmosphere. The magnitude of greenhouse gases from rice paddies was found to be comparable to the CO_2 generating industry such as a large coal fire power plant. This work, however, have not attempted to consider CO_2 absorption capacity of the plants. CO_2 is consumed in photosynthesis of the plant and this CO_2 uptake should be included into the evaluation and this will be carried out as our further work.

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