CHAPTER 2

LITERATURE REVIEW

Climate change is not a new phenomenon that occurred in the world. Global climate has been changed consistently overtime. Studies shown that recent changes in climate are influenced by human activities, which led to the increase of GHGs. GHGs are unneeded by products of the activities that cause global climate change and methane is one of those greenhouse gases.

2.1 Greenhouse Gases

Recent atmospheric measurements indicate that concentrations of GHGs are increasing (Matthew *et al.*, 1995). These GHGs include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chlorofluoro-carbons (CFCs) and others trace gases, which capable of trapping heat of the long-wave radiation. GHGs cause a global phenomenon known as greenhouse effect, which affects global climate change (Taylor and MacCracken, 1990). GHGs are found naturally in the earth's atmosphere in small quantities but it is very important in term of the earth's climate and human being. CO_2, CH_4, and N_2O emission are directly related to agricultural activities. In 1990, the estimated global emission of CO_2, CH_4, and N_2O into the atmosphere were 167,100.0; 535.0; and 15.0 million tonnes, respectively (Prather, 1994) and taking global warming into account 50%, 15%, and 9%, respectively (Department of the Environment and Local Government, 1998).

Carbon dioxide is responsible for 50% of the human causes to global warming. Current concentration of CO_2 is 355 ppm (Singh and Padilla, 1995). The major sources of CO_2 are fossil fuel burning and deforestation. It remains in the atmosphere for 500 years. Industrial countries account for about 76% of annual emission. Annual concentration is increased by 0.4% of atmospheric CO_2 concentration (Miller, 1992).

Methane is second to carbon dioxide in term of heating up the atmosphere. Even annual CO_2 accumulating in the atmosphere is much larger than that of CH_4, but each molecule of CH_4 is about 21 times more effective in warming the troposphere than a molecule of CO_2. It remains in the troposphere for 7 – 10 years. Methane is produced by groups of bacteria that decompose organic matter in anaerobic condition. The methane sources are paddy field, waterlogged soils, bogs, marshes landfills, burning of forest and grasslands, the guts of termites, ruminant animals. Swamps and wetlands systems have the highest soil carbon as compared to other systems, therefore they pose a suitable environment for methanogenic bacteria to produce methane.

At the global scale, methane gas increases by 1% annually. The atmospheric methane concentration of 1.72 ppmV is more than doubled its pre-industrial value of about 0.8 ppmV (Khalil and Rasmussen, 1987). The wetland soils including rice paddies contribute between 15 to 45% to methane pool in the atmosphere, whereas non-wetland soils contribute between 3 to 10% to the methane sink of the atmosphere (Segers and Kenger, 1997).

Chlorofluorocarbons (CFCs) is responsible for 14-20% of the human causes to global warming, CFCs also deplete ozone layer in the stratosphere (10-50 km above the earth's surface). The main sources are leaking of air conditioners and refrigerators, evaporation of industrial solvents, production of plastic foams, and propellants in aerosol spray cans. CFCs remains in the atmosphere for 60-400 years and generally its' global warming potential (GWP) 10,000 to 20,000 times the impact per molecule as compared to CO_2. Increase of annual concentration is 6.0%. Because of high global warming potential and its' ability to deplete ozone layer, Montreal Protocol had forced to control its' emission since 1986. The GHGs under the Protocol are CFC-11, CFC-12, CFC-113, CFC-114 and CFC-115. The Protocol was signed by more than 35 industrial countries including the United States. By ratification of this Protocol CFCs emission were reduced 20% below 1986 level by

1994 and a total 50% by 1998. Compare to other greenhouse gases CFCs are easier to be reduced because they are absolute man-made gases, but unfortunately they can remain for long time in the atmosphere (Masters, 1991).

N_2O is responsible for 9% of the global warming. It is released from the breakdown of nitrogen fertilizer in soil, livestock wastes, and by biomass burning. Its' concentration in the atmosphere is about 0.3 ppm (Masters, 1991) and average stay for 150 years in the troposphere . Beside global warming ability, it also depletes ozone layer in the stratosphere. The global warming potential per a molecule of this gas is about 310 times as compared to CO_2. It is increased by 0.4% of atmospheric concentration annually. The GWP of N_2O is about 310 times that of CO_2.

Atmospheric ozone (O_3) is formed by oxygen drifted upward and it react with incoming ultraviolet radiation and converted to ozone. This gas is separated into two parts. First part, mass of O_3 acts as a greenhouse gas in the tropospheric layer. Its concentration is about 0.01 ppm (Masters, 1991), and contributes for 8% of the global warming. Second part, mass of O_3 acts as a short wavelength filter in the stratosphere layer (10-50 km above global surface). Short wavelength, ultraviolet energy is absorbed by this earth's protective layer, causing the air to be heated in this layer.

2.2 Greenhouse Effect

A virtual ocean of the air coating the earth and extending upward is known as "*atmosphere*". The atmosphere is made up of nitrogen, oxygen, and other trace gases, which are important in environmental science studies. When the Sun supplies an enormous amount of heat energy to the earth with and average of 1,372 watt per square meter, more than half of this energy is absorbed and reflected by the atmosphere. However the amount reaching the earth surface is still about 154 watts per square meter (Masters, 1991). Visible light passes through almost undiminished, while ultraviolet radiation is absorbed by the ozone layer. Infrared radiation is mostly absorbed by CO_2 and water (H_2O). Most of the incoming solar radiation is in the visible light region of the electromagnetic wave band. The energy remitted by the earth is mainly infrared radiation (long wave one).

Infrared radiation is an important factor determining the mean temperature of the earth's surface and its climates. It is normally reflected back to outer space, however, some is trapped in the troposphere (Figure 2.1). The amount of heat energy trapped depends mostly on the concentration of various heat-trapping gases in the troposphere layer known as "*greenhouse gases*". The average surface temperature and the climate of the earth are the result of a number of interacting factors and the chemical composition in the troposphere. If the increase of the GHGs concentrations in the atmosphere are faster than they are removed, the earth's mean surface temperature will be increased. Vise versa, if the decrease of their concentrations faster than they are emitted, mean surface temperature of the earth will be dropped (Miller, 1992).

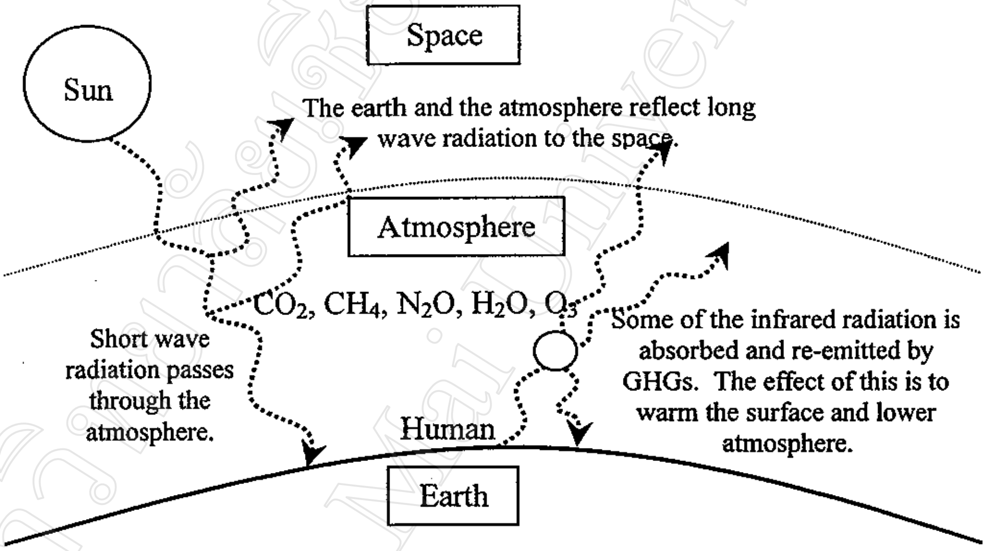

Figure 2.1 Schematic representation of increasing and out going radiation (Masters, 1991).

2.3 Impacts of Greenhouse Effect

Even there is a number of uncertainties in the evaluation of GHGs emission but there are enough evidences (Khalil and Rasmussen, 1987; Masters, 1991; Miller, 1992) to predict that global climate is changing by anthropogenic activities. The Intergovernmental Panel on Climate Change (IPCC) and the United Nations Framework Convention on Climate Change (UNFCCC) predicted that in the next 100 years (the year 2100) global mean temperature will be increased by 1.5 – 4.5 °C. And the mean sea level will increase 15 – 95 cm due to melting of the ice caps in the North and South Poles. The regional temperature changes may differ in region by region. The existing forest and vegetation areas possible changes due to changing of temperature and water availability (TEI, 1997).

2.4 Estimating GHGs Emission

2.4.1 At the Global Level

At the global level, in 1990, the estimated values of CO_2, CH_4 and N_2O were 167,100.00, 535.00, and 15.00 Tg, respectively. The contributions of these gases to global warming were 50%, 15% and 9%, respectively (Department of the Environment and Local Government, 1998; Prather, 1994).

2.4.2 Thailand Case

In 1990, Thailand emitted 208.50, 5.61 and 0.04 Tg of CO_2, CH_4 and N_2O, which is equal to 1.25%, 1.05% and 0.27% of the global scale, respectively (TEI, 1997). Major sources of CO_2 consist of land used change and forestry, all energy sector (fuel combustion and fugitive emission from fuel) and industrial processes, which contribute to emit CO_2 by 55.57%, 39.71% and 4.72%, respectively. Land use change and forestry sector also uptake CO_2 for photosynthesis activity by 12.91% of the total emitted CO_2. It implies that CO_2 can be reduced by increase the area or promotion consumption activity of these sectors. Land use change and forestry is also the major source of N_2O via biomass burning, which contributed for 52.56% of total N_2O emission followed by agricultural and industrial sectors for 45.35% and 2.08%, respectively. Of the total 5.61 Tg of methane emitted from terrestrial of Thailand, agricultural sector is the major source, it contributed 87.2% of the emission. Flooded rice cultivation is the most significant producer, produced by 4.4 Tg or 78.4% of total methane production. Others agricultural sources are enteric fermentation animals, manure management, and field burning of agricultural residue. Beside agricultural sector, transportation, industrial processes, waste management, and forest and grassland conservation are also classified as methane sources (TEI, 1997).

2.5 Significant of Methane Gas

Methane is an important GHG, which is enhanced to emit into the atmosphere by both natural and human activities. The global annual emission to the atmosphere is estimated to be 535.00 Tg. Thailand emitted 5.61 Tg of CH_4 to the atmosphere (in 1990) equivalent to 117.60 Tg of CO_2 (GWP of methane is equal to 21 times of CO_2). The major sources are agriculture, all energy categories, waste, and land use change and forestry (biomass burning), which emitted CH_4 into the atmosphere 4.89, 0.49, 0.15 and 0.03 Tg, respectively. Agricultural category consists of rice cultivation, enteric fermentation, and manure management which contributed to emit methane to the atmosphere 4.41; 0.33; and 0.15 Tg, respectively (TEI, 1997).

Methane is emitted from environment in the field both terrestrial and aquatic, whether natural or agricultural, depend on the biological processes by which CH_4 is produced or consumed. The net CH_4 emission from a system is the result of methanogenic bacteria (production) and methanotrophic bacteria activities (consumption). Therefore, for better estimation of net emission, their production and consumption rates within a system are important task to be quantified.

2.5.1 Methane Emission and Factors Affecting

Methane emission

Methane is a natural biogas, which formed from fermentation or decomposition processes of plant and animal biomass under anaerobic condition, e.g., flooded rice fields, wetlands (Figure 2.2). The estimate of CH_4 emission has a high degree of uncertainty, due to several factors such as soil types, soil temperature, field managements, type of fertilizers and mode of applications (Wassmann *et al.*, 1993). The net emission from an agricultural system is the result of production and consumption, and the net emission will be positive or negative depending on the relative magnitude of those processes (Knowles, 1993). Methane emission can be predicted from rice net productivity, cultivars' characters, soil texture, temperature, and organic matter amendments (Huang *et al.*, 1998). There is correlation between seasonal methane emission and the percentage sand in the soil (Sass *et al.*, 1994). Emission of methane gas from anaerobic condition, e.g., flooded soil in rice fields (Figure 2.2) to the atmosphere comprises of three channels (1) ebullition, (2) vascular transport, and (3) diffusion (Wang *et al.*, 1995).

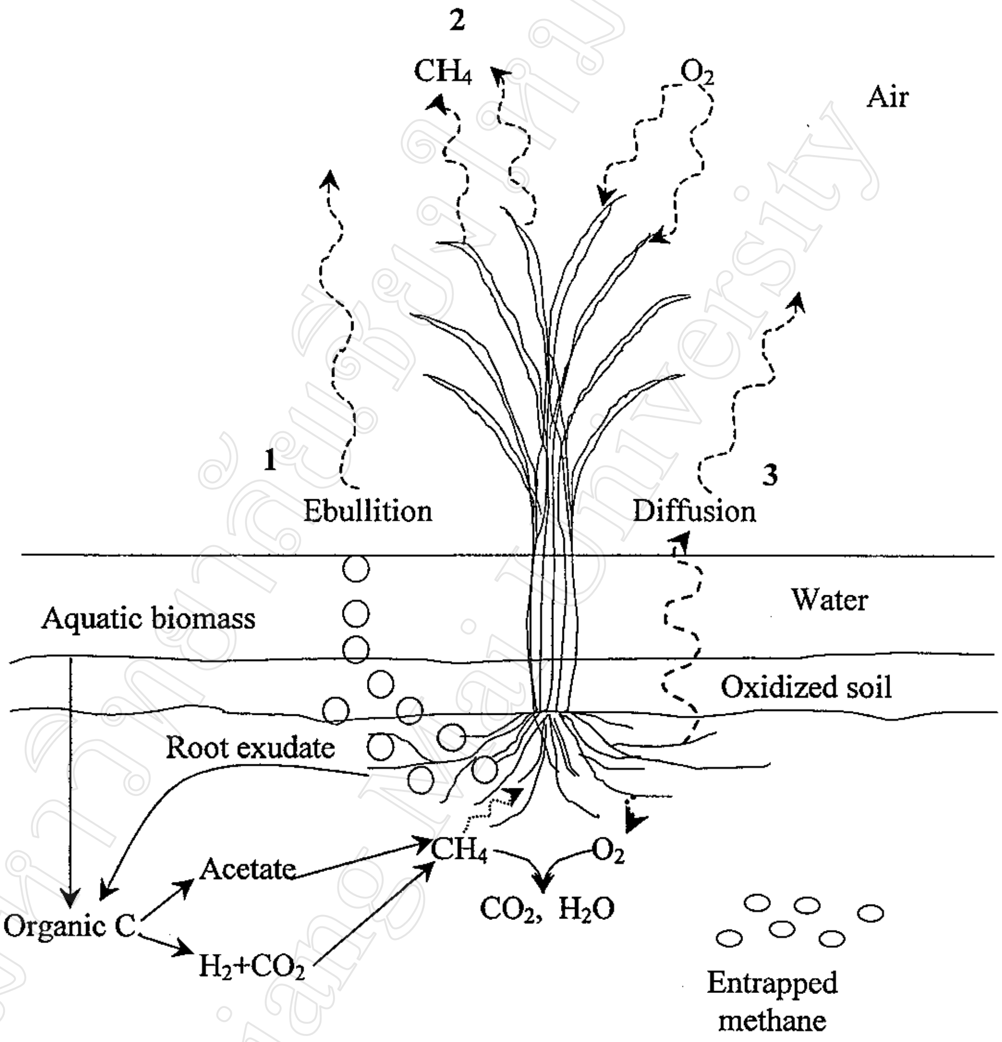

Figure 2.2 Schematic of methane emission from paddy field (Quiamco, 1996; Wang *et al.*, 1995)

Ebullition (bubbles)

When the partial pressure of entrapped CH_4 within flooded soil exceeds the hydrostratic pressure, bubbles will be formed and moved upward through water, water-air interface and the atmosphere. Chareonsilp *et al.* (1996) conducted an experiment to observe the proportion of ebullition to total of methane emission from deepwater rice field, they found that ebullition contributed 14 to 59% of total methane emission, depending on magnitude of methane production.

Vascular transport

Aerenchyma and intercellular gas-space system provides oxygen to the rice root, while other gases including CH_4 and CO_2 are able to use this transport system as well. CH_4 moves upward from production zone through aerenchyma and intercellular space of rice root via rice stem, stomata and finally emitted into the atmosphere. Higher emission rates were found in planted rice field than in those that unplanted (Wang *et al.*, 1995).

Diffusion

Methane, which dissolved in water, may diffuse from flooded soils layer, where is the production zone, through soil-water and water-air interface. However, the diffusion of gas in water is about 10,000 times slower than in air; therefore, gas diffusion almost stops when soils are flooded, so methane diffusion is very small portion compared to other two channels.

Factors Affecting on Methane Production

Four significant factors affecting on methane formation before emitting into the atmosphere are carbon sources, soil redox potential, soil pH and soil temperature

(Jermsawatdipong *et al.,* 1999). Both human activities and natural processes are contributors controlling these factors.

Carbon sources

Paddy soils under anaerobic condition have been recognized as the major methane producers. Three main carbon sources for methanogenic bacteria activities in flooded rice soils are included as follows;

(1) The soil organic matter such as plant biomass from previous crops or native SOM,

(2) The exogenous supply of organic materials to the soil, e.g., manure and compost,

(3) The leave and root litters, and root exudate from growing rice plants. Root exudates consist mainly of carbohydrate, organic acid, amino acid, and phenolic compound (Wang *et al.*, 1995).

The major sources of substrate providing carbon and energy for methanogenic bacteria are H_2+CO_2, acetate, formate, methylate amines, and methanol. The positive relationships of CH_4 emission with plant growth and organic matter addition have been found in rice paddies (Neue *et al.*, 1990; Sass *et al.*, 1990; Yagi and Minami, 1990).

Soil Oxidation-Reduction Potential (Eh)

Oxidation-Reduction (redox) Potential (Eh) determines oxidizing or reducing properties of a solution. Redox potential, measured in millivolts, is the potent difference between the metallic indicating electrode and constant voltage reference electrode immerge in a test solution. Redox potential measures the ability of a soil environment to supply electrons to an oxidizing agent, or to take up electrons from a reducing agent. When paddy soils are flooded, oxygen in the soil solution is consumed rapidly. Reduction of NO_3^- to NO_2^-, N_2O and N_2, Mn^{4+} to Mn^{2+}, Fe^{3+} to Fe^{2+}, SO_4^{2-} to S^{2-} and CO_2 to CH_4 occurs sequentially in the soil system. In wellaerated soils, redox potential ranges from 400 to 600 mV and in most reduced soils under anaerobic condition ranges from –300 to –100 mV. The critical Eh for CH_4 production has recently been measured in the range of -140 to -160 mv (Masscheleyn *et al.*, 1993; Wang *et al.*, 1993).

Soil pH

The soil pH is the negative logarithm to base 10 of the H ion activity. It is based on the ion product of pure water ($pH = -\log[H^+]$). Because pH is logarithmic, the H ion concentration in solution increases ten times when the pH is lower one unit (Quiamco, 1996). Methanogenic bacteria are pH sensitive organism, most of them grow over a relative narrow pH range (about 6-8) and the optimal pH is about 7 (Oremland and Capone, 1988). At pH below 5.8 and above 8.8, CH_4 production in the soil solution is almost completely inhibited. In pH range of 8.1 to 9.7, only few strains of alkaliphilic methanogen are active and produce CH_4 (Wang *et al.*, 1995). Some of alkaline and acidic soils produce more CH_4 than soils with near natural pH after the convergence of soil pH to 7 during anaerobic incubation. The application of rice straw and chemical fertilizers might have some influence on soil pH, and results in increase CH_4 production rates.

Soil Temperature

Soil temperature and CH_4 production generally has a positive relationship (Dunfield *et al.*, 1993). Incubation of soil samples in different temperatures (0-35 °C) found that the optimum temperature for both CH_4 production and consumption was 25 °C. CH_4 production is much more temperature sensitive (Q_{10} = 5.3-16) than CH_4 consumption (Q_{10} = 1.4-2.1). Jermsawatdipong *et al.* (1999) reported that methane production is doubled when soil temperature rose from 20 to 25 °C and methane production peaks at soil temperature reaches 37 °C. Methane oxidation in a Danish forest soil, Q_{10} (5-15 °C) was 1.35 and 1.36 of *insitu* and intact soil cores incubated in laboratory, respectively (Prieme and Christensen, 1997). Incubation of forest (mineral) soils under laboratory-controlled, moisture and temperature condition Q_{10}

(15-25 ^{o}C) of methane uptake was 1.11 indicates that methane uptake is controlled by physical processes (Bowden *et al.*, 1998).

2.5.2 Methane Production

Methane is the final gas product of biomass decomposition under anaerobic condition by several groups of microorganisms (Figure 2.3). Plant biomass is initially hydrolyzed by hydrolyzing microorganisms. Fermenters further ferment the obtained hydrolysis products. Products of the fermentation processes are acetate (fatty acid), alcohol, CO_2 and H_2, which are substrates for methane production. In nature, acetate, CO_2 and H_2 are major methane production substrates (Knowles, 1993).

Methanogenic bacteria are able to use many intermediate products for their activities and release methane into the atmosphere. The substrates used are H_2, CO_2, formate, methanol, methylamine, dimethylamine, trimethylamine, and acetate.

The rice plant enhances CH_4 emission by providing substrates for methanogenesis in the form of root and leaf litter, and root exudates. However, the vascular system decreases CH_4 emission by allowing O_2 transport into the rice rhizosphere to increase the rate of CH_4 oxidation and reduce CH_4 production (Wang *et al.*, 1995).

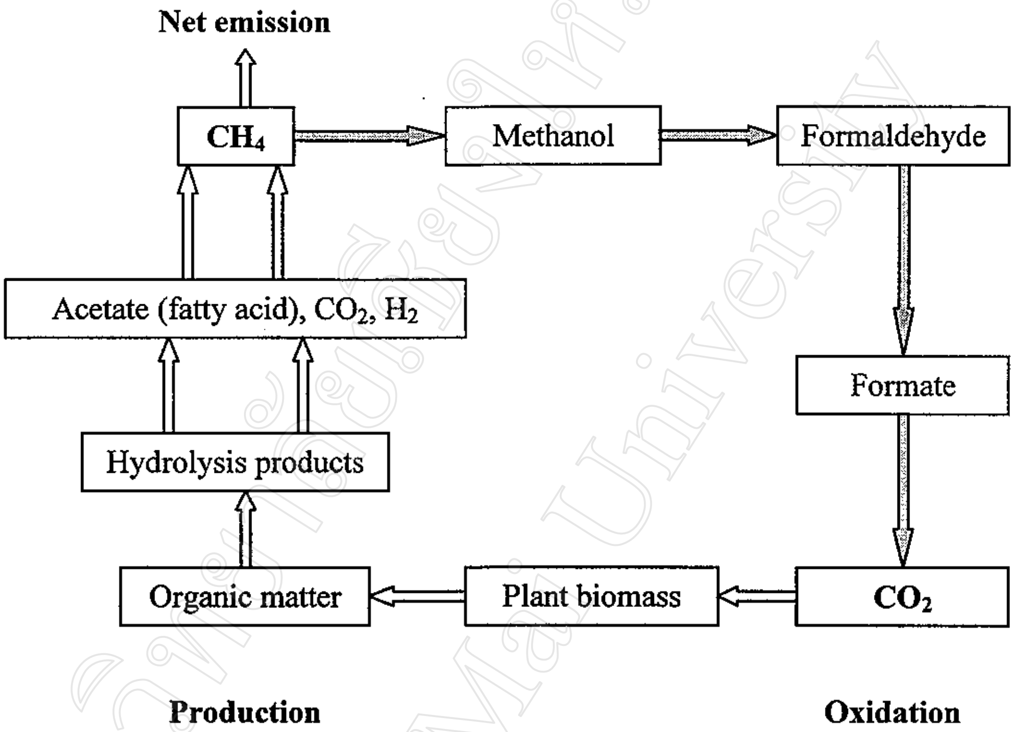

Figure 2.3 Some pathways of methane production and methane consumption (Knowles, 1993).

In Figure 2.3, plant biomass is firstly hydrolyzed by hydrolyzing microorganisms, then further fermented to form acetate (fatty acid), alcohol, CO_2 and H_2, which are substrates for methane production. And the pathway of methane oxidation (consumption) to release CO_2 into the atmosphere, the first step of methane oxidation is the reaction of monooxygenase enzyme and methane and a molecular of O_2. The product of this reaction is methanol, which further oxidized to formaldehyde, formate and CO_2 as a final product (Knowles, 1993).

2.5.3 Methane Consumption

The induction of CH_4 oxidation process, consumption processes was affected by physio-chemical soil variables such as soil pH, temperature, soil moisture, NH_4^+ and Cu^{2+} concentrations, and aggregate size. The optimum environmental conditions for oxidation activity were soil water content of 20-30% H_2O; pH 6.7-8.1; soil temperature 25-30 °C, NH_4^+ concentration in soil water phase of 12-61mm. Cu^{2+} inhibited the induction of CH_4 oxidation activity (Bender and Conrad, 1995). Gulledge and Schimel (1998) studied on moisture controlling atmospheric CH_4 consumption and CO_2 production in diverse Alaskan soils. They found the maximum atmospheric CH_4 consumption occurred between 20-40% of water holding capacity (WHC) in all soils with an average of 34% WHC. The optimum water potential for CH_4 oxidation was –0.3 to –0.2 MPa in upland soils, and –0.2 MPa in wetland soils.

Sitaula *et al.* (1995) studied the effect of N fertilization and soil acidification on the uptake of atmospheric CH_4 and soil CH_4 concentration. They conducted an experiment in lysimeter soil from a 100 years old Scot pine forest in Norway. Nitrogen application rates were varied between 30 and 90 kg N ha^{-1} y^{-1}. The two N application rates resulted in CH_4 uptake 85 $\pm$ 3% and 62 $\pm$ 2% of the control, respectively. Assessment of the individual effects of moisture and temperature on CH_4 oxidation showed that moisture was the primary controlling factors in CH_4 sink soils at AS2 and BS2 (boreal soils), while temperature was more important in CH_4 source soils at LB. They also found the lowest CH_4 oxidation rates in the combination of the highest moisture content and lowest temperature of each soil. Conversely, combination of optimum moisture content with the highest soil temperature consistently gave the highest CH_4 oxidation rate (Whalen and Reeburgh, 1996).

Comparison of CH_4 oxidation rate from woodland, arable and set aside (not woodland or agricultural area and it was left) on a loamy sand soils in eastern Scotland found that the oxidation rates in the arable soil were less than half the corresponding rate in the woodland soil. The oxidation rates in the set aside soil were lower than the arable soil. There was negative correlation between CH_4 oxidation and moisture content ($P<0.001$) in the wetland soil and positive correlation between CH_4 oxidation and soil temperature ($P < 0.001$) in the set aside soil. A negative correlation between ammonium concentration and CH_4 oxidation rate in woodland soil ($P < 0.001$), indicated that ammonium was inhibitor of CH_4 oxidation activity (Dobbie and Smith, 1996). Prieme and Christensen (1997) measured seasonal and spatial variation of methane oxidation in Danish spruce forest. They found that the average daily CH_4 oxidation rates ranged from 27.1 to 57.7 μg CH_4 m^{-2} h^{-1} and there is positive correlation with the soil temperature ($P < 0.001$) with Q_{10} (5 – 15 °C) of 1.35 and 1.36 for in situ and in laboratory, respectively.

CH_4 flux was measured from four Indian land use types: dry land, irrigated rice, seasonal dry forest and savanna. Maximum CH_4 consumption was observed during the winter season at all sites in the rate of 0.46-0.95 mg m^{-2} h^{-1}. And minimum was found during the rainy season range from 0.17-0.32 mg m^{-2} h^{-1}. Seasonal methane flux was found in the irrigated rice fields. Paddies fields emitted CH_4 in the range 2.14-8.23 mg m^{-2} h^{-1}during rice growing season while the dry land rice soil consumed 0.12-0.90 mg m^{-2} h^{-1} (Singh *et al.*, 1998).

2.6 Impact of CH_4 on Agricultural Systems

There are no research or any evidences indicating that CH_4 is directly harmful to agricultural systems. Indirectly, it contributes (about 15%) to warm the atmosphere. Weather and soil characteristics are both direct and indirect effect on agricultural systems. By theoretical and numerical, the global average temperature will rise by 1.5 to 4.5 °C in the 21st century (Taylor and MacCracker, 1990). Increase of temperature is one significant affecting factor on agricultural systems. The effects are;

1. Soil organic matter and soil nutrients decrease due to high decomposition rate and increasing the solubility of soil minerals, easy to be lost by leaching, unless dry matter production rate is increased (Buol *et al.,* 1990).

2. Crop growth duration will be shorter by speeding up development processes (Matthews, 1995) causing decrease of grain yields (Allen *et al.*, 1995). Rice grain yields decline roughly 10% per 1 °C increase of temperature above 28/21 °C (day/night) because increase in number of unfilled grains (Baker *et al.*, 1995). Matthews *et al.* (1995) found that every 1 °C of increasing temperature, the rice grain yields declined 6.7 to 7.4%, while decreasing by 7.3 to 9.5% of soybean grain yields occurred when temperature increase 4 °C (Jone *et al.*, 1995).
3. According to a prediction by IPCC mentioned earlier, the agricultural land adjacent to the sea might be reduced due to the rise of sea level. Change of precipitation and longer season is directly effect on agricultural system, however it still not clears both spatial and temporal effect.

2.7 Modeling of Methane Production and Consumption

Modeling is a powerful tool to make systematic understanding of a system. A few models of methane emission from rice field were constructed in China. Simulation results indicated that methane fluxes was highly related to rice growth, and decomposition of soil organic matter. Temperature and soil organic matters are two factors controlling the variation of methane emission from paddy field during a growing season (Aiju *et al.*, No date). Modeling of methane fluxes from grassland on peat soils was constructed. The finding was that the soil could act both as a net source and as a net sink of methane. The contribution of the soil to the methane flux still large, due to the factors and processes that effect on the fluxes are not well known (Segers *et al.*, 1998). Cao *et al.* (1995) constructed a model of methane emission from rice fields. They found that methane emission from rice field is an ecosystem processes closely couple with rice growth and soil organic matter decomposition. The model consists of rice growth function, organic decomposition processes, and methane oxidation at rice rhizosphere sub-model. However, there is no model of methane consumption in non-wetland soils.