温帯域と熱帯域の水田におけるメタンと二酸化炭素の動態

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Methane and carbon dioxide dynamics in temperate and tropical rice paddy fields

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Chapter 1

Introduction

Historical ice core data has revealed unprecedented increases in the atmospheric greenhouse gas (GHG) concentrations since 1750 owing to human activities (IPCC, 2013). The increases in GHGs have contributed to global climate change, in particular, increases in global mean surface temperature from 1951 to 2010 (IPCC, 2013). The major GHGs causing global surface warming are carbon dioxide (CO_2) and methane (CH_4) (IPCC, 2013). The increase in atmospheric CO_2 is the largest contributor to the global surface warming, with atmospheric CH_4 accounting for more than half of the global surface warming by CO_2 (IPCC, 2013). Accurate assessments of CO_2 and CH_4 emissions are required to better understand global carbon cycles and to help forecast global climate change in the future (Kirschke et al., 2013; Le Quéré et al., 2015).

The Agriculture, Forestry and Other Land Use (AFOLU) sector accounts for 24 % of global anthropogenic GHGs emissions. Rice paddy fields, which possibly emit 25-300 Tg CH_4 per year, are one of the dominant anthropogenic CH_4 sources (IPCC, 2013; Bridgham et al., 2013), but they also serve as CO_2 sinks on the yearly budget basis (Campbell et al., 2001; Ono, 2008; Alberto et al., 2012, 2014, 2015; Hatala et al, 2013; Bhattacharyya et al., 2014). Although the amount of CH_4 emission from rice paddy fields is generally small relative to the amount of CO_2 uptake (Knox et al., 2015), the global warming potential of CH_4 is 34 times greater than that of CO_2 over a time horizon of 100 years (IPCC, 2013). Therefore, CH_4 emission offsets the mitigation effect of CO_2 uptake (Knox et al., 2015). In order to elucidate whether rice paddy fields act as an overall source or a sink for GHGs, a net GHG budget needs to be assessed by measuring both CH_4 and CO_2 fluxes (emission/uptake rates). Furthermore, better understanding is needed of the processes and regulating factors in order to estimate CH_4 and CO_2 budgets more accurately (Bridgham et al., 2013; King et al., 2015).

Methane emission in rice paddy fields increases during rice growth periods (Buendia et al., 1997;

Alberto et al., 2014, 2015). During this time, rice paddy fields are generally flooded by irrigation water, which increases CH_4 production by methanogenesis that prefers anaerobic soil conditions. Soil CH_4 is mainly released into the atmosphere by three pathways: via rice plants, bubble ebullition through paddy water, and molecular diffusion between atmosphere and flooded water (Schütz et al. 1989). Estimates of the plant-mediated pathway range from 48-85 % of total CH_4 emission (Wassmann and Aulakh, 2000). Another study also showed that when rice straw was plowed into paddy soil, CH_4 emissions via bubble ebullition through paddy water contributed to 35-62 % of total CH_4 emission (Wassmann et al., 1996).

Carbon dioxide uptake also mainly occurs during the rice cultivation season (Campbell et al., 2001; Saito et al., 2005; Ono, 2008; Alberto et al., 2012, 2015; Bhattacharyya et al., 2014). Throughout the rice cultivation season, CO_2 exchanges in rice paddy fields are mainly conducted by photosynthesis of rice plants and aquatic plants in the floodwater and by ecosystem respiration of rice plants, aquatic plants and soil microorganisms (Miyata et al., 2000; Koizumi et al., 2001). The CO_2 uptake by plant photosynthesis is generally larger than the CO_2 emission by ecosystem respiration, which results in rice paddy fields being a CO_2 sink (Campbell et al., 2001; Saito et al., 2005; Ono, 2008; Alberto et al., 2012, 2015; Bhattacharyya et al., 2014).

The major rice cultivation area extends from tropical to cool-temperate climate zones in the world. The different climate zones lead to differences in meteorological and soil conditions, and also cultivation management, which consequently change the seasonal CH_4 and CO_2 flux dynamics, and so the CH_4 and CO_2 budgets. This may possibly mean that rice paddy fields in some climate regions are overall sources of GHG whereas in other climate regions they are sinks for GHGs. In addition, CH_4 emission dynamics in tropical rice paddy fields is not yet well understood due to the limited number of field studies (Melton et al., 2013; Bridgham et al., 2013).

Based on the abovementioned background, I carried out field experiments with two main objectives: (1) to evaluate seasonal CH_4 and CO_2 flux dynamics and total GHG budgets, obtained as the sum of CH_4 and CO_2 budgets, in rice paddy fields in temperate Japan and tropical Thailand, and (2) to investigate the dynamics and mechanism of CH_4 emission in detail in rice paddy fields in

tropical Thailand. The controlling factors for GHG dynamics and budgets were examined in both climate areas, and field experiments were conducted at around heading and flowering stages when CH_4 emission is usually large.

Chapter 2

Methane and Carbon dioxide fluxes in temperate and tropical rice paddy fields

2.1 Abstract

This field study investigated the seasonal dynamics of CO_2 and CH_4 fluxes, CO_2 and CH_4 budgets and the net GHG (CO_2 and CH_4) budget for the cultivation period in rice paddy fields in temperate Japan and tropical Thailand so as to clarify whether rice paddy fields in each climate region act as sources or sinks for GHG. The factors controlling the differences in fluxes and budgets of CH_4 and CO_2 in the temperate and tropical climatic regions were also examined. The CH_4 and CO_2 fluxes were measured using eddy covariance and hyperbolic relaxed eddy accumulation methods. The seasonal CO_2 fluxes in Japan usually showed the negative values throughout the rice-cropping season. The seasonal CO_2 fluxes in Thailand also showed negative values for most of the rice growth period except for the initial period of up to 30 days from transplanting. The positive CO_2 flux during the initial stage in Thailand was due to large CO_2 emission by respiration of rice plants and soil microorganisms and by CO_2 ebullition through flooded water compared with the CO_2 uptake by plant photosynthesis. Carbon dioxide budgets in both countries revealed that the rice paddy fields served as a sink for CO_2, but that the strength of CO_2 sink in Thailand was only about half of that in Japan. The weaker CO_2 sink in tropical Thailand was mainly derived from the large CO_2 emission under the high air temperature conditions relative to temperate Japan. The seasonal CH_4 flux dynamics in Japan depended on field water management and plant growth, whereas in Thailand there was high CH_4 emission throughout the measuring period due to the continuous flooding conditions. Methane budgets in both countries showed that rice paddy fields in tropical Thailand served as a stronger CH_4 source relative to those in temperate Japan. The net GHG budget, obtained as the sum of the CH_4 and CO_2 budgets, confirmed that the rice paddy fields during the rice growth period in temperate Japan acted as

an overall sink for GHG whereas those in Thailand acted as a sources of GHG.

2.2 Introduction

The Agriculture, Forestry and Other Land Use (AFOLU) sector accounts for 24 % of global anthropogenic greenhouse gas emission (IPCC, 2013). The major greenhouse gases from agricultural sources are CO_2 and CH_4 (IPCC, 2013). CH_4 has 34 times higher global warming potential than CO_2 over a time horizon of 100 years (IPCC, 2013). In particular, rice paddy fields are one of the major anthropogenic sources of CH_4 (IPCC, 2013) whereas they generally act as sinks for CO_2 (Ono, 2008; Alberto et al., 2012; Hatala et al, 2013; Bhattacharyya et al., 2014). Although CH_4 emission is lower than CO_2 uptake, the higher GWP of CH_4 reduces the mitigating effect on global warming of the CO_2 uptake (Knox et al., 2015). In order to clarify whether rice paddy fields act as a net source or sink of greenhouse gases, CH_4 and CO_2 fluxes (emission/uptake rates) need to be simultaneously measured in rice paddy fields to assess the net GHG budget, obtained as the sum of the CH_4 and CO_2 budgets (McMillan et al., 2007; Bhattacharyya et al., 2014).

Methane emission mainly occurs during the rice growth period. During the rice cultivation season, rice paddy fields are generally flooded by irrigation water, triggering active production of CH_4 by methanogenesis under anaerobic soil condition. The soil CH_4 under flooded conditions is released via rice plants, via bubble ebullition from the paddy soil, and via molecular diffusion from the floodwater. In particular, the plant-mediated pathway accounts for 48-85 % of total CH_4 emission (Wassmann and Aulakh, 2000).

Also, CO_2 uptake generally increases during the rice-cropping season (Campbell et al., 2001; Ono, 2008; Alberto et al., 2012, 2015; Bhattacharyya et al., 2014). Rice and aquatic plants in paddy fields absorb atmospheric CO_2 during photosynthesis while the same plants and also soil microorganisms emit CO_2 into the atmosphere by their respiration (ecosystem respiration) (Miyata et al., 2000; Koizumi et al., 2001). The CO_2 flux by plant photosynthesis generally exceeds that of ecosystem respiration, leading to rice paddy fields being sinks for CO_2 (Campbell et al., 2001; Ono, 2008;

Alberto et al., 2012, 2015; Bhattacharyya et al., 2014).

The cultivating areas of rice range from tropical regions to cool-temperate regions throughout the world, which varies the magnitudes of CH_4 emission and CO_2 uptake under the different climatic/field conditions and the associated field management (Miyata et al., 2005; McMillan et al., 2007; Hatala et al, 2013; Bhattacharyya et al., 2014; Alberto et al., 2014, 2015). Thus, CH_4 and CO_2 fluxes need to be measured in rice paddy fields in different climate zones in order to assess the net GHG budget in each climatic zone and to elucidate the factors regulating the GHG dynamics and budgets in each climatic region.

Methane and CO_2 fluxes in rice paddy fields have been mainly measured using chamber methods and micrometeorological methods (Cicerone and Shetter, 1981; Yagi et al., 1996; Wassmann et al., 2000; Miyata et al., 2000, 2005; Toprayoon et al., 2005; Ono, 2008; Xie et al., 2010; Alberto et al., 2012; Hatala et al, 2013; Bhattacharyya et al., 2014). Although the chamber method is suitable for determining the difference between sites or between treatments, the chamber measurements disturb the natural air condition. In addition, chambers have small measurement areas which makes it difficult to obtain spatially-representative gas flux in rice paddy fields (Simpson et al., 1995; Miyata et al., 2000; Hirano, 2001) because CH_4 emission spatially varies even within the same rice field (Sass et al., 2002; Oo et al., 2013, 2015). In contrast to the chamber measurements, micrometeorological methods can provide spatially representative gas fluxes over a large upwind area without disturbing natural conditions. Thus, the application of the micrometeorological methods to rice paddy fields has been recently conducted in order to measure fluxes of CH_4 and CO_2 and to assess net GHG budget more accurately (Miyata et al., 2005; McMillan et al., 2007; Takimoto et al., 2010; Hatala et al, 2013; Bhattacharyya et al., 2014; Alberto et al., 2014, 2015; Knox et al., 2015).

Flux-gradient, eddy covariance (EC) and relaxed eddy accumulation (REA) methods are the major micrometeorological methods that have been utilized in CH_4 flux measurements in rice paddies (Simpson et al., 1995; Harazono et al., 1996; Hamotani et al., 1997; Miyata et al., 2000, 2005; McMillan et al., 2007; Takimoto et al., 2010; Hatala et al, 2013; Alberto et al., 2014; Iwata et al., 2014; Komiya et al., 2014). The flux-gradient method needs to measure the vertical profiles of wind

velocity and CH_4 concentration whereas the EC and REA methods only need to measure those parameters at one height. The EC method can measure the turbulent fluctuations of vertical wind velocity (w) and CH_4 concentration at over 10 Hz (0.1 s) intervals, which can provide reliable flux data (Harazono et al., 1996). Recent development of a CH_4 gas analyzer for the EC method has enabled many researchers to measure CH_4 flux in rice paddy fields using the EC method (Meijide et al., 2011; Hatala et al, 2013; Bhattacharyya et al., 2014; Iwata et al., 2014; Alberto et al., 2014, 2015). Meijide et al. (2011) reported that further research with EC method is required to evaluate more accurate CH_4 budgets in rice paddy fields. The REA method measures CH_4 flux from the difference in CH_4 concentration between updraft and downdraft air stored for fixed time. Thus, the REA method can measure CH_4 concentration at wide intervals. Komiya et al. (2014) showed that valid CH_4 fluxes could be obtained in rice paddy fields using the REA method. In addition, Bowling et al. (1999) improved the REA method to develop the hyperbolic REA (HREA) method to improve the precision of gas fluxes by maximizing the concentration difference between updraft and downdraft air. Ueyama et al. (2013) reported that the HREA method could measure CH_4 fluxes precisely in a forest site.

The EC method has been utilized for micrometeorological CO_2 flux measurements in rice paddy fields (Miyata et al., 2000, 2005; Ono, 2008; Alberto et al., 2012, 2014, 2015; Hatala et al, 2013; Bhattacharyya et al., 2014) because CO_2 gas analyzers for the EC method were developed early. Since the CO_2 budget for a rice growth period varies at different sites around the world (Ono, 2008; Alberto et al., 2012, 2014, 2015; Bhattacharyya et al., 2014; Zhao, 2014), further field studies are needed using the EC method to clarify the regulating factors that contribute to the differences in CO_2 budgets.

Therefore, this study examined the seasonal dynamics of CH_4 and CO_2, and net CO_2 budgets in temperate (Japan) and tropical (Thailand) rice paddy fields using the EC and HREA methods.

2.3 Materials and Methods

2.3.1 Site description

Field experiments were conducted during rice-cropping seasons in rice farm paddy fields in Hiratsuka (35° 21' 46"N, 139° 20' 17"E), Kanagawa prefecture, Japan in 2013 and at Kamphaeng Saen campus (14° 00' 33"N, 99° 59' 03"E), Kasetsart University in Nakhon Pathom Province, Thailand in 2014. The paddy soil in Japan was a clay loam (clay 34.0 %, silt 32.0 % and sand 34.0 %) and that in Thailand was a clay (clay 65.7 %, silt 23.3 % and sand 11.0 %). The soil pH in Japan and Thailand were 6.12 and 5.98, respectively. The specific management practices in both countries are shown in Table 2.1, 2.2. Two rice varieties “Koshihikari” and “Nikomaru” were cultivated in the Japanese rice paddy fields. “Koshihikari” was cultivated in most of the rice paddy fields whereas “Nikomaru” was experimentally grown in only one rice paddy field by the farmer. In each field, 3-5 seedlings of each rice variety per hill were transplanted on June 5 in 2013. The Thailand rice paddies were transplanted with 4-5 seedlings of the rice cultivar “Homcholasit” per hill on June 30 in 2014. Rice straw was plowed into the rice paddy fields in Japan before April in 2013. In Thailand, weeds and weedy rice were plowed into rice paddy soil on June 17 and 26 in 2014. The Japanese paddy fields were flooded at a water depth of about 5 cm from May 31 to September 16, except for a midseason drainage period between July 18 and 24. In contrast to Japan, the Thailand rice paddies were permanently flooded (2 – 20 cm depth) during the field growing period from June 17 to October 28. In Japan the “Koshihikari” and “Nikomaru” rice varieties were harvested on September 29 and in mid-October in 2013, respectively. The unhulled rice yields of “Koshihikari” and “Nikomaru” were 4235.5 kg ha^{-1} and 4033.3 kg ha^{-1}, respectively. In Thailand, the harvest day of “Homcholasit” was October 28 in 2014, and the unhulled rice yield was 4375 kg ha^{-1}.

2.3.2 Environmental measurements

Net radiation in Japan and Thailand were measured with a net radiometers (Q7.1, REBS, Seattle, WA, USA) positioned horizontally 2.0 m and 5.0 m above the soil surface, respectively. Atmospheric pressure in both countries was measured using a barometer (MPXAZ6115A and MPXV7007DP, Freescale Inc., TX, USA). Air temperature in Japan was measured at 2.2 m (May – August 22, 2013)

height and then 2.7 m (August 22 – September 29, 2013) height with a temperature sensor (HMP155A, Vaisala Inc., Helsinki, Finland). In Thailand, air temperature was measured at 3.0 and 5.0 m heights with two temperature sensors (HMP45A, Vaisala Inc., Helsinki, Finland), respectively. Soil temperature (type T thermocouples) and soil redox potential (platinum-tipped electrodes) were measured at 0, 5 and 10 cm depths in the Japanese paddy soil and 0, 3, 9 and 15 cm depths in Thailand paddy soil, respectively.

2.3.3 CO_2 flux measurements

Fluxes of CO_2, water vapor (H_2O) and sensible heat were measured using the open-path eddy covariance method. The CO_2 flux by the eddy covariance method (F_{EC}, mg m^{-2} s^{-1}) is described by,

$$F_{EC} = \overline{\rho_d w r_c} = \overline{\rho_d} \cdot \overline{w' r_c'} \tag{2.1}$$

where ρ_d is dry air density (kg m^{-3}), and $\overline{w'r_c'}$ is the covariance of vertical wind speed (w; m s^{-1}) and CO_2 mixing ratio (r_c; mg kg^{-1}) relative to the dry air, and the overbar denotes the time averaging. The open-path CO_2/H_2O gas analyzer actually measures the mass density of CO_2/H_2O rather than mixing ratio of those due to the difficulties of measuring air pressure and temperature in atmospheric condition at the same sampling point of the gas analyzer (Kondo and Tsukamoto, 2012). Thus, the CO_2 flux by the open-path eddy covariance method (F_{OPEC}, mg m^{-2} s^{-1}) is obtained using the following equation (Kondo and Tsukamoto, 2012),

$$F_{OPEC} = \overline{\rho_d w r_c} = \overline{\rho_d w \frac{\rho_c}{\rho_d}} = \overline{w\rho_c} = \overline{w'\rho_c'} + \overline{w}\,\overline{\rho_c} \tag{2.2}$$

where ρ_c is the CO_2 density (mg m^{-3}) measured by the open-path CO_2/H_2O gas analyzer, and $\overline{w'\rho_c'}$ is the covariance of w and ρ_c. Although the mean vertical speed is generally assumed to be zero in turbulence transport (Webb et al., 1980), Webb et al. (1980) suggested this assumption wasn't satisfied under natural conditions where air density varies. Thus, Webb et al. (1980) proposed the Eq. (2.3) for F_{OPEC} using the ideal gas equation,

$$F_{OPEC} = \left(\overline{w'\rho_c'} + \frac{M_d}{M_v} \frac{\overline{\rho_c}}{\overline{\rho_d}} \overline{w'\rho_v'} + (1 + \frac{\overline{e}}{\overline{P}}) \frac{\overline{\rho_c}}{\overline{T}} \overline{w'T'} \right) \quad (2.3)$$

where M_d and M_v are the molecular weights (mg mol^{-1}) of dry air and H_2O, respectively, $\overline{w'\rho_v'}$ is the covariance of w and H_2O density (ρ_v; mg m^{-3}), e is vapor pressure (kPa), P is atmospheric pressure (kPa), T is ambient temperature (K), and $\overline{w'T'}$ is the covariance of w and T.

The vertical and horizontal wind velocities and sonic temperature (T_{sv}) were measured at 2.2 m height (May 31 to August 22, 2013) and 2.7 m (August 22 to September 29, 2013) in the Japanese rice paddy fields, and at 2.9 m in the Thailand paddy fields (June 15 to October 31, 2014) using a three dimensional sonic anemometer-thermometer (CSAT3A, Campbell Scientific, Inc., Logan, UT, USA). The open-path CO_2/H_2O gas analyzer (EC150, Campbell Scientific, Inc., Logan, UT, USA) measured the mass densities of CO_2 and H_2O at the almost same sampling point of CSAT3A. The output data from the CSAT3A and EC150 were sampled and recorded at 10 Hz (0.1 s) using a data logger (CR5000, Campbell Scientific, Inc., Logan, UT, USA).

Half-hourly fluxes of CO_2, H_2O and sensible heat were calculated using the Flux Calculator software (Ueyama et al., 2012). Before calculating these fluxes, the Flux Calculator software applied the following series of corrections; de-spiking of raw data, a double rotation method so as to assume the mean vertical wind speed as zero, and a time lag correction by finding the maximum covariance. The sensible heat flux, measured by the CSAT3A, was actually the covariance between w and T_{sv}, which contains the H_2O fluctuation, so that the H_2O effects was corrected as follows (Asiaflux, 2007),

$$\overline{w'T'} = \overline{w'T_{sv}'} - 0.514 \cdot \overline{T_{sv}} \cdot \overline{w'q'} \quad (2.4)$$

where q is the specific humidity, and $\overline{w'q'}$ was obtained by dividing $\overline{w'\rho_v'}$ by wet air density (ρ_v; mg m^{-3}). The CO_2 flux for 30 minutes was finally obtained by Eq. (2.3).

2.3.4 CH_4 flux measurements

Methane fluxes at the Japan and Thailand sites were measured with the closed-path EC and HREA

techniques, respectively. These techniques are described briefly below.

2.3.4.1 Closed-path EC method

The CH_4 flux by the closed-path EC method was measured using the CSAT3A sonic anemometer-thermometer and the CH_4/H_2O closed-path gas analyzer (G2301-f, Picarro Inc., Santa Clara, CA, USA). The CH_4/H_2O closed closed-path gas analyzer measures the mixing ratios (dry mole fractions) of CH_4 and H_2O in the cavity cell under constant pressure (140 Torr) and temperature (45 ^oC). Thus, the CH_4 flux doesn't need the Webb correction; Eq. (2.3). Therefore, the half-hourly CH_4 fluxes (F_{CPEC}, mg m^{-2} s^{-1}) were calculated using the following equation,

$$F_{CPEC} = \overline{\rho_d} \cdot \frac{M_c}{M_d} \cdot \overline{w' \chi_c'} \tag{2.5}$$

where M_c is the molecular weight of CH_4 (mg mol^{-1}), and $\overline{w'x_c'}$ is the covariance of w and the dry mole fraction of CH_4 (mol mol^{-1}). The CH_4/H_2O closed-path gas analyzer was kept in a shed fitted with an air conditioner, located around 10 m away from the CSAT3A. Air was continuously drawn into the measuring cavity cell through two filters (1.0 μm and 0.1 μm) and a 12-15 m tube at 6-8 L min^{-1} using a diaphragm pump placed downstream from the CH_4/H_2O closed-path gas analyzer. Prior to the CH_4 flux calculation, the Flux Calculator software corrected the raw data (by despiking, the double rotation method and the lag-time compensation) as well as calculating the CO_2 flux by the open-path EC method. The high frequency loss due to the sampling tube was corrected by the bandpass covariance method (Asiaflux, 2007).

2.3.4.2 HREA method

Methane and CO_2 fluxes in the Thailand rice paddy fields were measured using the HREA method. These fluxes (F_{HREA}, mg m^{-2} s^{-1}) by the HREA method are given as

$$F_{HREA} = B \cdot \sigma_w \cdot \frac{\overline{P} M_s}{R} \left(\frac{\overline{\chi_{s\_up}}}{\overline{T_{up}}} - \frac{\overline{\chi_{s\_down}}}{\overline{T_{down}}} \right) \quad (2.6)$$

where B is an empirical coefficient, M_s is the molecular weight of CH_4 or CO_2 (mg mol^{-1}), R is the gas constant (Pa m^3 K^{-1} mol^{-1}), $\overline{T_{up}}$ and $\overline{T_{down}}$ are the respective average temperatures of the sampled updraft and downdraft eddies, and $\overline{\chi_{s\_up}}$ and $\overline{\chi_{s\_down}}$ are the mean CH_4/CO_2 dry mole fractions in the respective sampled updraft and downdraft eddies. Although the REA method simply sampled the updraft ($w' > 0$) and downdraft ($w' < 0$) eddies, the HREA method doesn't sample the air when the deviations in CH_4/CO_2 concentration are near 0 in order to increase the differences of CH_4/CO_2 concentrations between updraft and downdraft eddies. The sampling criterion (H) for the HREA method is defined as (Bowling et al., 1999),

$$H = \left| \left(\frac{w'}{\sigma_w} \right) \cdot \left(\frac{s'}{\sigma_s} \right) \right| \quad (2.7)$$

where s' is the scalar deviation, and σ_s is the scalar standard deviation. The sampled air is identified as an updraft eddy when H is higher than the threshold of H ($H_{threshold}$) and w' is positive, and identified as a downdraft eddy when H is higher than $H_{threshold}$ and w' is negative.

The HREA measuring system was developed by modifying the REA system of Komiya (2012). The HREA measuring system is shown in Fig. 2.1. The CR5000, CSAT3A and EC150 used in the open-path EC system controlled the separation of the updraft and downdraft air. The atmospheric turbulences of CO_2 and CH_4 can be assumed to be similar to those of T_{sv} and H_2O (Kaimal and Finnigan, 1994; Ueyama et al., 2013), so that from August 5 to September 16, 2014, s' was defined as the deviation of T_{sv} by CSAT3A. From September 16 to 28, 2014, s' was defined as the deviation of H_2O density by EC150. $H_{threshold}$ was determined as 1.1, following Bowling et al. (1999). The CR5000 instantly calculated w', s', σ_s and σ_w at 10 Hz using instantaneous 15-min moving windows (Ueyama et al., 2013), and determined whether the air was an updraft, downdraft or unsampled air based on the H and w' criteria described above. Once the air was judged as an updraft or downdraft eddy, the solenoid valve for the updraft or downdraft eddy opened to collect the air in separate

sampling bags (vinyl alcohol series polymer film, 10 L, GL science Inc., Tokyo, Japan). Between August 5 and 29, 2014, when the updraft or downdraft eddy solenoid valve was open, an air pump (TD-4N, Brailsford and Rye, NY, USA) continuously pumped the updraft or downdraft air samples into the appropriate air bag at 0.5 L min^{-1}, and also exhausted the uncollected air at 0.5 L min^{-1}. During this period, condensation was often observed in the sample and exhaust lines. Therefore, after August 29, the flow rates in the sample and exhaust lines were changed to 0.2 L min^{-1} by a flow meter and around 1.2-1.5 L min^{-1} without flow control, respectively, to reduce the condensation. The condensation water in the tubes was removed using high-purity compressed nitrogen gas at 1-5 day intervals. The updraft and downdraft air was stored in the sampling bags for 30 min to calculate half-hourly fluxes of CH_4 and CO_2. The stored air in each sampling bag was measured using a $CH_4/CO_2/H_2O$ gas analyzer (G2201-i, Picarro Inc., Santa Clara, CA, USA). The sampled air was dried using a reflux method with a membrane dryer (SWG-A01-06, Asahi Glass Engineering Co., Chiba, Japan) before it entered the $CH_4/CO_2/H_2O$ gas analyzer. After drying, the dry mole fraction of H_2O in the sample air was reduced to below 0.1 % v/v.

Values of $\overline{\chi_{s\_up}}$ and $\overline{\chi_{s\_down}}$ were calculated as the 1.5 min-averages of dry mole fractions of CH_4 and CO_2 before the end of analyzing the air sample in each bag. Assigning the CO_2 dry mole fractions in the updraft and downdraft eddies to $\overline{\chi_{s\_up}}$ and $\overline{\chi_{s\_down}}$, respectively, the B value was obtained by regressing $\sigma_w \cdot \frac{\overline{PM}_s}{R}\left(\frac{\overline{\chi_{s\_up}}}{\overline{T_{up}}} - \frac{\overline{\chi_{s\_down}}}{\overline{T_{down}}}\right)$ against the CO_2 flux by the open-path EC method. The B values were determined almost every week, and ranged between 0.18 and 0.38. The determined B values were considered to be valid because the weekly relationships between HREA and EC methods were significantly linear with r=0.86-0.97 ($p<0.001$, n=65-286, Fig. 2.2). The CH_4 fluxes by the HREA method were finally obtained using these B values.

2.3.5 Data selection and gap-filling

High quality flux data at both sites were selected as follows. When the prevailing wind direction was between 76 and 107 degrees in Japan, flux data were removed. In Thailand, flux data were discarded when the prevailing wind direction was either (0-80 or 280-360 degrees. Friction velocity (u^*) filtering was also applied to the flux data when u^* didn't exceed the threshold value ($u^*_{threshold}$, Japan: $u^*_{threshold}$ = 0.07, Thailand: $u^*_{threshold}$ = 0.05) under low turbulence conditions. The $u^*_{threshold}$ was decided as the value above which the increase of u^* contributed little to increasing the CO_2 fluxes (Takimoto et al., 2010). Moreover, CH_4 and CO_2 flux data were rejected during rainfall periods and when the signal strength of the EC150 was low (CO_2 signal strength < 0.7, H_2O signal strength < 0.7). A stationary test was also used to filter the flux data at both sites. Each set of half-hourly raw (10 Hz) data was divide into 6 intervals of 5 min, and the covariance ($\overline{w'\rho_c'}$ and $\overline{w'x_c'}$) for each 5 min interval was calculated using the Flux Calculator software. The average of the covariance at 5 min intervals within each 30 min dataset was compared with the half-hourly covariance. If the difference between both covariances was higher than 40 %, the flux data were discarded (Saito et al., 2005). In both countries, when the CO_2 flux data by the open-path EC method were rejected due to the stationary test, the CH_4 flux data were also rejected because CH_4 turbulence was assumed to be similar to CO_2 turbulence; the open-path EC method monitored CO_2 turbulence in real time with little high-frequency losses. Finally, footprint filtering was conducted using the footprint model (Kormann and Mexiner, 2001). Flux data were rejected when the flux represented less than 60 % of rice paddy field measurement area.

In order to calculate the budgets of CH_4 and CO_2 during the growth period at both sites, missing half-hourly fluxes of CH_4 and CO_2 were gap-filled using environmental drivers of these fluxes. The missing half-hourly CO_2 fluxes in the daytime were gap-filled using non-linear regression equations between half-hourly CO_2 flux and net radiation at 10-day intervals. Nighttime CO_2 fluxes are generally represented by the respiration of rice plants and soil. The ecosystem respiration rate (R_e) exponentially increases with increasing temperature as follows (Saito et al., 2005),

$$R_e = R_0 \exp(\ln(Q_{10}) \frac{T_{\mathrm{Re}}}{10}) \tag{2.8}$$

where R_0 is the respiration rate at 0 ºC, and Q_{10} is the factor by which CO_2 respiration rates increase when air temperature (T_{Re}, ºC) increases by 10 ºC. When T_{Re} was unavailable, soil temperature at 5 cm deep was used for T_{Re}. The missing nighttime CO_2 fluxes at each site were gap-filled using Eq. (2.8), obtained from the daily overnight averages of CO_2 fluxes and air temperature. CH_4 fluxes also have positive and exponential relationships with air or soil temperature (Takimoto et al., 2010; Meijide et al., 2011; Alberto et al., 2014). A significant relationship was found between the half-hourly log-CH_4 flux and air temperature at each site (Fig. 2.3), and the missing half-hourly CH_4 fluxes were estimated using the regression equation at each site.

2.3.6 CO_2 partitioning

Net ecosystem CO_2 exchange per day (NEE, g CO_2 m^{-2} day^{-1}), which was the daily total of CO_2 flux, was divided into daily gross primary production (GPP, g CO_2 m^{-2} day^{-1}) and net ecosystem respiration (R_e, g CO_2 m^{-2} day^{-1}) using the following equation (Ono, 2008),

$$NEE = -GPP + R_e \tag{2.9}$$

GPP represents the net photosynthesis by rice and aquatic plants. R_e comprises both nighttime respiration and daytime respiration. The daytime respiration rates were estimated using the nighttime relationship of Eq. (2.8), and R_e was calculated as the sum of daytime and nighttime respiration. GPP was determined by the difference of NEE and R_e.

2.3.7 Soil gas sampling

Soil gas samples were obtained using gas permeable silicon tubes. In Japan, soil gas at 5 cm deep near the rhizosphere was collected with a silicon tube (id = 20 mm; wall thickness = 2.8 mm; length = 500 mm) at intervals of about 1-2 weeks. In Thailand, soil gases were sampled at 3 and 9 cm depths underneath a rice-plant hill and under the space between rows of rice plants with four gas samplers using high permeable membrane (wall thickness = 0.4 mm) at 3-4 day intervals. The soil gas samplers

in Thailand are described in detail in Chapter 5. The soil gases in Japan were analyzed with a gas chromatograph-flame ionization detector (6890N, Agilent Technologies Inc., Santa Clara, CA, USA). The soil gases in Thailand were measured using the $CH_4/CO_2/H_2O$ gas analyzer as described by Komiya et al. (2015).

2.3.8 Dissolved carbon measurement

Soil solutions in the paddy soil at both sites were sampled using ceramic porous cups (Daiki Rika Kogyo Co., Ltd., Saitama, Japan). The porous cups were installed at 5 and 10 cm depths near the rhizosphere in Japan, and at 3 and 9 cm depths underneath a rice-plant hill and in the space between rice plants in Thailand. Soil solution samples were collected in pre-vacuumed vials using an extension tube from the porous cup. Soil solution at Japan and Thailand sites was sampled at 1-2 week and 3-4 day intervals, respectively. The dissolved carbon (TC) in each soil solution was analyzed by a total organic carbon analyzer (TOC-L, Shimadzu Co., Ltd., Kyoto, Japan).

2.4 Results and Discussion

2.4.1 CO_2 dynamics and budgets

The seasonal dynamics of the daily NEE, GPP and R_e throughout the rice-cropping season in Japanese rice paddy fields are shown in Fig. 2.4 (a). During the initial growth period (DAT 0-16), NEE showed values close to zero because GPP was nearly equivalent to R_e. GPP increased from DAT 17 and then exceeded R_e, causing NEE to decrease. This was attributed to increasing photosynthesis with plant growth. From DAT 52 to DAT 75 which included the heading period, NEE and GPP often showed respective values of below -30 g CO_2 m^{-2} d^{-1} and above 48 g CO_2 m^{-2} d^{-1}. During this period the weather was mostly sunny with little rain. These facts suggest that CO_2 photosynthesis by rice plants was actively conducted with plant growth under sunny days that were appropriate conditions for rice plants to photosynthesize. After DAT 76, NEE increased and maintained positive values from

DAT 109 to DAT 115. The increase in NEE resulted from a decreases in GPP. In addition, the increase in R_e from DAT 105 to DAT113 also contributed to the increased NEE. The increase in R_e was probably due to enhanced CO_2 emission from soil owing to final drainage at this time.

The seasonal changes in the daily NEE, GPP and R_e in the Thailand rice paddy fields are presented in Fig. 2.4 (b). The daily NEE between DAT 0-30 was always positive even though NEE gradually decreased, because R_e always exceeded GPP. These high values of R_e were probably from the result of large CO_2 emission due to high CO_2 respiration of rice plants and soil microorganisms under high air temperature (Fig. 2.5 d, Table 2.2), and due to large CO_2 emission from flooded water via diffusion and bubble ebullition under the high temperature conditions (Alberto et al., 2015; Komiya et al., 2015; Wassmann et al., 1997). Carbon dioxide in paddy soil was possibly produced from decomposition of abundant organic substances (weeds and weedy rice) that were plowed into the soil before the transplanting (Table 2.1) (Alberto et al., 2015). From DAT 31 to DAT 58, the increased GPP with plant growth exceeded R_e, leading to negative values of NEE. The NEE values from DAT 59 to DAT 96 were usually less than -15 g CO_2 m^{-2} d^{-1}. This was attributed to the increased photosynthesis of rice plants with plant growth. The NEE slightly increased from DAT 96 to DAT 120 with decreases in GPP. After the harvest date (DAT 121), NEE values became positive due to rapid decreases in GPP because rice plants were removed.

The Japanese rice paddy fields between 0-29 days acted as CO_2 sinks whereas the Thailand fields were CO_2 sources (Table 2.3). During this period, GPP in both countries was almost the same, but R_e in Thailand was about twice as high as that in Japan (Table 2.3). Mean air temperature (T_a) in Thailand was 6.8 degrees higher than that in Japan (Table 2.3). Therefore, these results suggest that the higher temperature in Thailand contributed to larger CO_2 emission by ecosystem respiration and by CO_2 ebullition than in Japan. From DAT 30 to DAT 59, even though the rice paddy fields in both countries acted as CO_2 sinks, NEE in Japan was only half of that in Thailand. In this period, GPP in Japan was 293.3 g CO_2 m^{-2} higher than that in Thailand even though the difference in R_e between both countries was only 65.6 g CO_2 m^{-2} due to the increasing temperature in Japan. The large difference in GPP might be due to a difference in photosynthesis ability between the Japan and Thailand rice cultivars. The CO_2

sink in the rice paddy fields in each country was greatest between DAT 60 and DAT 89 because this period included the heading season when CO_2 photosynthesis activated (Fig. 2.4 a, b). From DAT 90 to DAT 115, NEE in the Thailand rice paddy fields was more than three times larger than in Japan owing to the rapid decrease in GPP in Japanese rice paddy fields. The decrease in GPP for one month before the harvest date agreed well with Saito et al. (2005) who reported seasonal dynamics of NEE, GPP and R_e in rice paddy fields, cultivated with Koshihikari, in Tsukuba City, Ibaraki Prefecture in central Japan. In contrast to Japan, there are few similar reports of the slight decrease in GPP found in the Thailand paddy fields, and it is possible that this was due to the photosynthesis ability of Homcholasit during this period.

Although the cumulative GPP throughout the growth period in both countries was similar, the cumulative NEE in Thailand was only about half of that in Japan because the cumulative R_e in Thailand was higher than in Japan. This large CO_2 emission in Thailand was probably due to the more activate respiration of rice plants and microorganisms, and CO_2 ebullition, under the higher temperature conditions.

2.4.2 CH_4 dynamics and budgets

Daily CH_4 flux and soil CH_4 concentration in Japan gradually increased from the first day of flooding up to DAT 27 (Fig. 2.5 a, b). Increases in CH_4 flux were attributed to increases in soil CH_4 concentration due to activated methanogenesis under anaerobic soil conditions in the flooded soil. Methane fluxes between DAT 27 and DAT 41 in Japan were higher than during the earlier period (Fig. 2.5 a). Soil CH_4 concentration increased up to 6.6% v/v on DAT 41 (Fig. 2.5 b). Daily CH_4 flux in Japan was highest (0.24 g CH_4 m^{-2} d^{-1}) on DAT 44, soon after the start of the mid-summer drainage on DAT 43 (Fig. 2.5 a, e). The highest CH_4 flux was believed to be due to a CH_4 flush from the drained paddy soil which had stored abundant CH_4 during the flooded anaerobic period (Yagi et al., 1996). The daily CH_4 flux in Japan rapidly decreased between DAT 44 and DAT 50 during the mid-season drainage period (Fig. 2.5 a, e). Furthermore, soil CH_4 concentration obviously dropped to the low

value (2.7 % v/v) from the previous flooding period. These results suggested that soil CH_4 oxidation under aerobic soil conditions contributed to decreases in CH_4 flux and soil CH_4 concentration.

After re-flooding in the afternoon on DAT 49 in the Japanese paddy fields, the CH_4 flux increased and the soil redox potential decreased (Fig. 2.5 a, e). A distinct peak of CH_4 flux (0.19 g CH_4 m^{-2} d^{-1}) occurred on DAT 66 shortly before heading stage of "Koshihikari" (Fig. 2.5 a) which was cultivated in most of the measurement paddy fields. Hosono and Nouchi (1997) reported that the conductance for methane transport through rice plant (Koshihikari) was large before the heading stage. Soil CH_4 concentration on DAT 63 was 3.7 % (v/v) which was 5 orders of magnitude larger than the atmospheric CH_4 concentration (1.8-2.0 ppm) (Fig. 2.5 b). These results suggested that the large conductance of rice plants for methane transport and abundant soil CH_4 contributed to the large CH_4 emission. Methane flux increased again from DAT 81 and reached the maximum value (0.25 g CH_4 m^{-2} d^{-1}) on DAT 88 (Fig. 2.5 a). This probably resulted from a rapid increase in soil CH_4 concentration from DAT 76 to DAT 93 (Fig. 2.5 b). Total carbon in soil solution suddenly decreased from the middle stage to the later growth stages (Fig. 2.5 c) as Lu et al. (2002) reported seasonal changes in dissolved organic carbon in rhizosphere. Lu et al. (2002) also showed that microorganism biomass carbon was large under reduced conditions. These facts suggest that abundant methanogenesis produced CH_4 due to consuming the enriched carbon, which resulted in sudden increases in soil CH_4 concentration and in sudden decreases in dissolved total carbon. Methane flux decreased from DAT 88 to DAT 104 whereas soil CH_4 concentration maintained higher values over 17 % (v/v) (Fig. 2.5 a, b). This appeared to be primarily due to decreases in the conductance for methane transport through rice plants with aging (Hosono and Nouchi, 1997). The final drainage treatment on DAT 105 triggered high CH_4 emission (Fig. 2.5 a) due to CH_4 flush from soil (Yagi et al., 1996). After DAT 105, CH_4 flux decreased with increases in soil redox potential (Fig. 2.5 a, e). Soil redox potential exceeded 0 mV on DAT 106 and reached 400 mV on DAT 108 (Fig. 2.5 e). These results suggest that aerobic soil conditions (> 0 mV) led to activated CH_4 consumption by methanotrophs, resulting in decreases in CH_4 emission.

In Thailand, daily CH_4 flux increased from DAT 42 to DAT 45 and maintained values higher than 0.27 g CH_4 m^{-2} d^{-1} between DAT 43 and DAT 58 (Fig. 2.5 a). Pronounced variations in CH_4 flux

during this period are similar to those in previous reports (Neue et al., 1994; Watanabe et al., 1993). Large CH_4 emission seemed to be partly due to increases in soil CH_4 concentration during this period (Fig. 2.5 b). After DAT 68, CH_4 flux increased and reached a maximum value (0.46 g CH_4 m^{-2} d^{-1}) around the heading stage (Fig. 2.5 a, b). The paddy soil contained abundant CH_4 (> 27 % v/v) during this period. Aulakh et al. (2002) found that conductance for CH_4 transport in the rice cultivar "KDML105", which is a parental variety of Homcholasit, was greater at the heading stage. These results suggest that increases in CH_4 transport through rice plants and abundant CH_4 in soil contributed to larger CH_4 emission. In addition, large CH_4 emissions via bubble ebullition, which probably enhanced CH_4 emission from the rice paddy fields, were also observed during this period (see Chapter 5).

Daily $\log_{10}$-CH_4 fluxes in both countries were significantly correlated with GPP (Fig. 2.6). Daily $\log_{10}$-CH_4 fluxes in Japan were most strongly correlated with one-day-delayed GPP ($r=0.808$; $p<0.001$; Fig. 2.6). The photosynthesized carbon is primarily transported to the rhizosphere, transformed to CH_4, and then released into the atmosphere as CH_4 gas within 1 hour to 7 days (Minoda and Kimura, 1994; Minoda et al., 1996). These findings suggest that photosynthesized CO_2 contributed to next day-CH_4 emission in the Japanese rice paddy fields. In contrast, daily $\log_{10}$-CH_4 fluxes in Thailand were most strongly correlated with GPP on the same day ($r=0.381$; $p<0.01$; Fig. 2.6), suggesting that the photosynthesized carbon was emitted as CH_4 gas soon after it was transformed into CH_4 gas in the rhizosphere. The differences in the transition time from CO_2 to CH_4 in each country might be due to the different rice cultivars.

Daily $\log_{10}$-CH_4 fluxes in both countries were also significantly correlated with daily mean air temperature throughout the growth period (Fig. 2.7). Increases in CH_4 flux with increasing air temperature were primarily derived from increasing CH_4 conductance through rice plants and enhanced soil CH_4 production with increasing soil temperature (Hosono and Nouchi, 1997; Yao and Conrad, 2000). Although the rate of increasing CH_4 flux with respect to air temperature was very similar in both countries (Fig. 2.7): 0.089 (Japan) and 0.080 (Thailand), the y-intercept in Thailand was 0.62 higher than that in Japan (Fig. 2.7). This suggests that the CH_4 transport rates through rice

plants with respect to temperature were similar in both countries, but conductance for CH_4 transport of Homcholasit in Thailand was larger than that of Koshihikari and Nikomaru in Japan. Differences in methanogenesis between Thailand and Japan might also affect the y-intercept of CH_4 flux.

Daily CH_4 fluxes and soil CH_4 concentrations between DAT 36-90 in Thailand were always higher than those in Japan (Fig. 2.5 a, b). In addition, conductance for CH_4 transport in the Thailand rice cultivar was probably high relative to Japanese rice cultivars, as discussed above. These results suggest that a larger conductance for CH_4 transport and higher soil CH_4 concentration in Thailand contributed to the larger CH_4 emission in Thailand than in Japan.

Large differences in soil CH_4 concentration between DAT 36-90 seemed to be independent of the amount of carbon in the paddy soil because the amounts of dissolved total carbon were similar in both countries (Fig. 2.5 b, c). In addition, mean air temperature (30.4 ^oC) in Thailand was very similar to that (29.3 ^oC) in Japan (Fig. 2.5 d), suggesting that it did not contribute largely to the enhanced soil CH_4 concentration in Thailand. Based on these findings and suggestions, it is speculated that different methanogenesis might contribute to CH_4 production in each country's paddy soils, as discussed above.

During this period (DAT 36-90), water management was also different in the two countries. The continuous flooding treatment in Thailand always led to anaerobic conditions with soil redox potential below -180 mV, which was appropriate for methanogenic activity (Yu and Patrick, 2003). In contrast, the mid-summer drainage treatment in Japan produced aerobic conditions in the paddy soil where methanotrophs could consume CH_4 more actively, and which resulted in decreases in CH_4 flux and soil CH_4 concentration (Fig. 2.5 b). These findings suggest that the different water management partly contributed to the differences in CH_4 flux and soil CH_4 concentration in the two countries.

The cumulative CH_4 emissions in both countries are shown in Table 2.4. Cumulative CH_4 emission for the growth period in Japan was 10.1 g CH_4 m^{-2}, which was similar to the 12.4 g CH_4 m^{-2} reported by Miyata et al. (2005) who investigated cumulative CH_4 emission using the flux-gradient method in Japanese rice paddy fields growing the same cultivar "Koshihikari". Meanwhile, the cumulative CH_4 emission (18.6 g CH_4 m^{-2}) in Thailand between DAT 36-90, when CH_4 fluxes were measured, was more than two times larger than in Japan during the same measurement period. The

cumulative CH_4 emission for the entire growth period in Thailand was estimated by the regression equation using the daily mean air temperature (Fig. 2.7, dotted line), giving the estimated cumulative CH_4 emission of 36.0 g CH_4 m^{-2}, which was more than three times the measured total flux for the entire period in Japan. The Thailand estimate is comparable to the cumulative CH_4 emissions of between 22.3 and 78.6g CH_4 m^{-2} that Jermsawatdipong et al. (1994) reported for the growth period in Thailand rice paddy fields where the continuous flooding and organic matter applications were similar to my Thailand site. The differences in cumulative CH_4 emission between two countries can probably be attributed to differences in conductance for CH_4 transport of rice plants, in CH_4 production by different methanogenesis and in the water management, as discussed above.

2.4.3 Net greenhouse gas budget

The CH_4, CO_2 and net GHG budgets in the rice paddy fields in both countries are shown in Table 2.5. The net GHG budget was calculated as the sum of the CO_2 and CH_4 budgets, with 1g CH_4 assumed to be equivalent to 34 g CO_2 over a period of 100 years (IPCC, 2013). The net GHG budgets showed that Japanese rice paddy fields served as sinks for GHG whereas Thailand rice paddy fields were sources of GHG. The GHG sink in Japan was due to small CH_4 and CO_2 emissions (Table 2.3, 2.4, 2.5). In contrast, the GHG source in Thailand was derived from large CH_4 and CO_2 emissions (Table 2.3, 2.4, 2.5).

2.5 Conclusions

This study investigated the seasonal CH_4 and CO_2 flux dynamics and net GHG budget during one growth period in the temperate (Japan) and tropical (Thailand) rice paddy fields. In Japan, NEE decreased during the first half period of the growing period with plant growth, and increased from the middle period to the harvest date due to plant aging. The NEE in Thailand also decreased from the initial period to the middle period, but NEE remained above zero between DAT 0 and DAT 30, unlike

in Japan. This was a result of the larger R_e due to more active respiration of rice plants and microorganisms and due to CO_2 ebullition under the higher temperature conditions in Thailand. Additionally, NEE in Thailand increased only slightly from the middle stage to the harvesting stage in contrast to the larger increase in Japan, suggesting a difference in the photosynthetic activity between the rice cultivars in the different countries. The rice paddy fields in both countries acted as a CO_2 sink throughout the growth period. The strength of CO_2 sink in Thailand was only about half of that in Japan, mainly due to the larger CO_2 emission in Thailand than in Japan.

The CH_4 flux in Japan was enhanced during flooding periods, but decreased during the mid-summer and final drainage periods except for a CH_4 flush soon after the drainage treatments. This finding suggest that the CH_4 flux dynamic in Japan depended on water management. In Thailand, the CH_4 fluxes remained high (> 0.17 g CH_4 m^{-2} d^{-1}) under the permanent flooding. In addition, the seasonal dynamics of GPP and air temperature contributed to the CH_4 emission dynamics in each country. Throughout the growth period, CH_4 emission in Thailand was larger than Japan due to the large CH_4 transport capacity and enriched CH_4 concentration in the Thai paddy soil. The large difference in soil CH_4 concentration between the two countries is possibly attributable to differences in methanogenesis and water management.

The net GHG budgets in both countries revealed that Japanese rice paddy fields acted as GHG sinks, whereas Thailand rice paddy fields acted as GHG sources. This finding was mainly derived from the differences in air temperature, in CH_4 transport capacity due to different rice cultivars, in CH_4 production due to different methanogenesis and in water management between both countries.

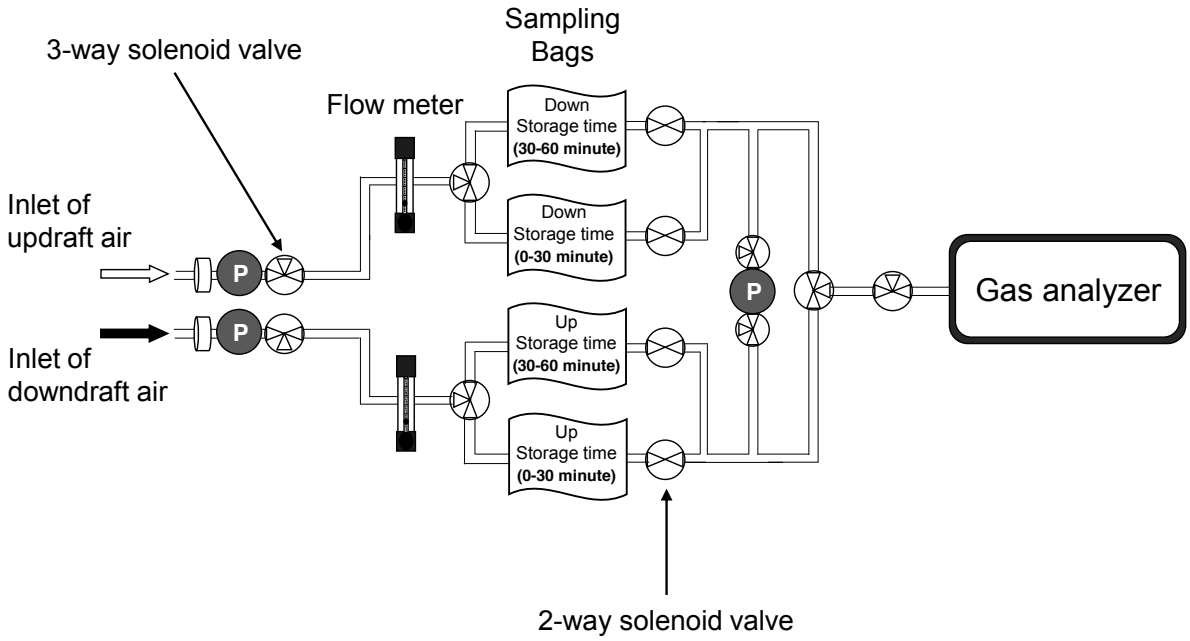

Fig. 2.1 Schematic diagram of the HREA system in Thailand (Komiya, 2012 diagram modified).

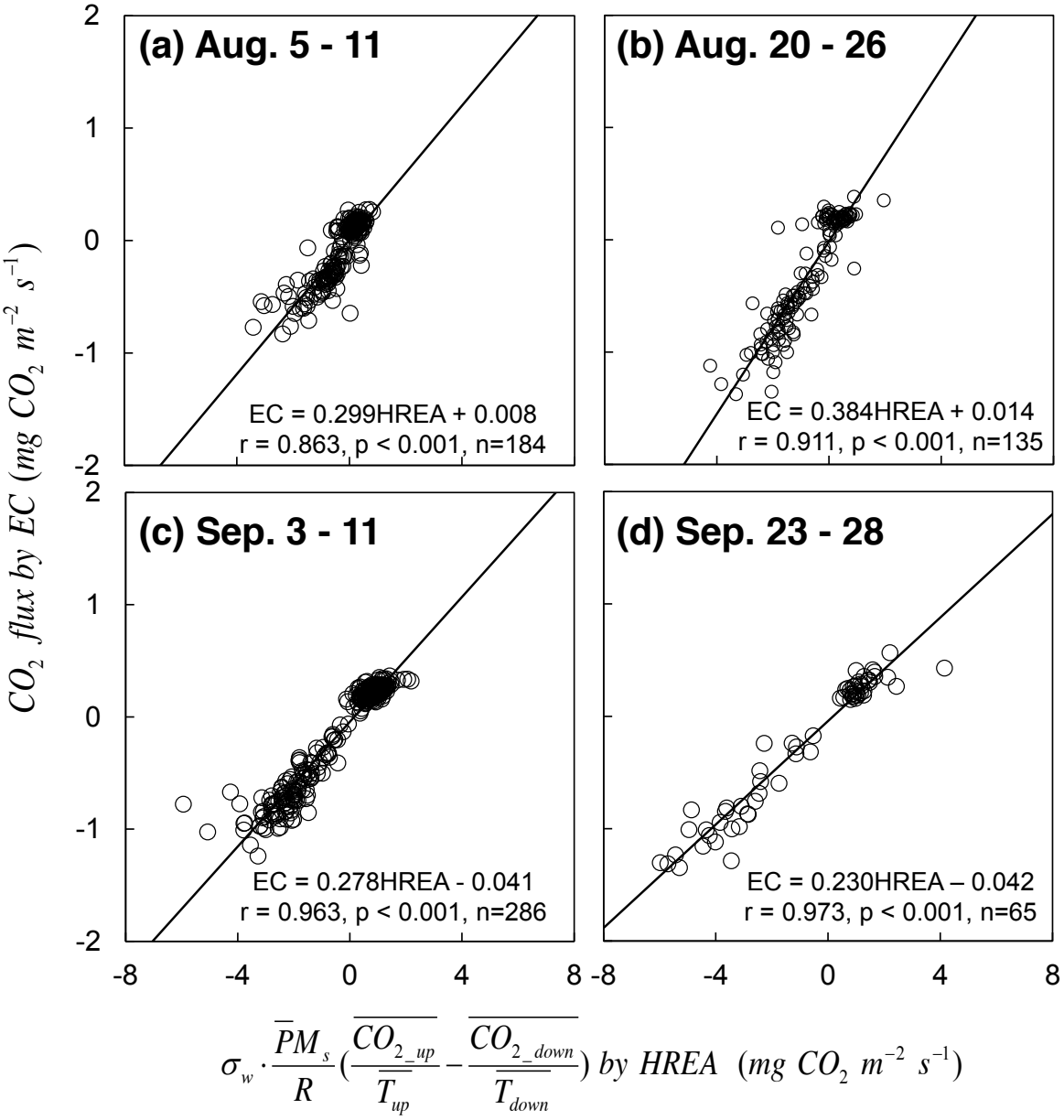

Fig. 2.2 Examples of the relationship between half-hourly CO_2 flux measured by the EC method and $\sigma_w \cdot \frac{\overline{P}M_s}{R}(\frac{\overline{CO_{2\_up}}}{\overline{T_{up}}} - \frac{\overline{CO_{2\_down}}}{\overline{T_{down}}})$ obtained by the HREA method in Thailand; (a) August 5-11, (b) August 20-26, (c) September 3-11, (d) September 23-28.

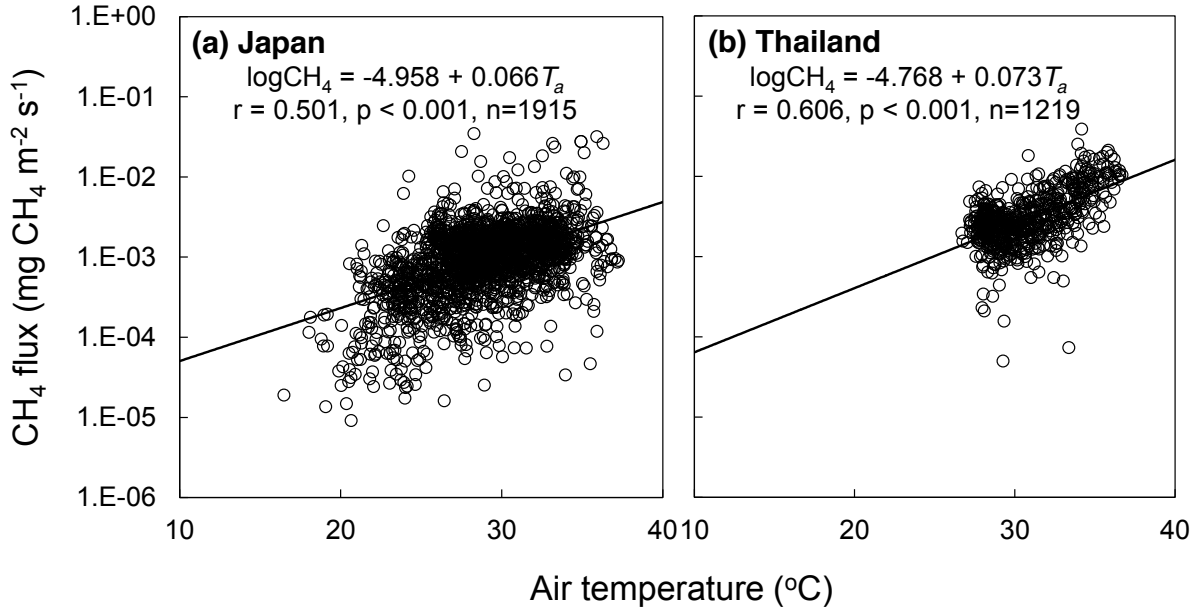

Fig. 2.3 Relationship between half-hourly CH_4 flux and air temperature in Japan (a) and Thailand (b).

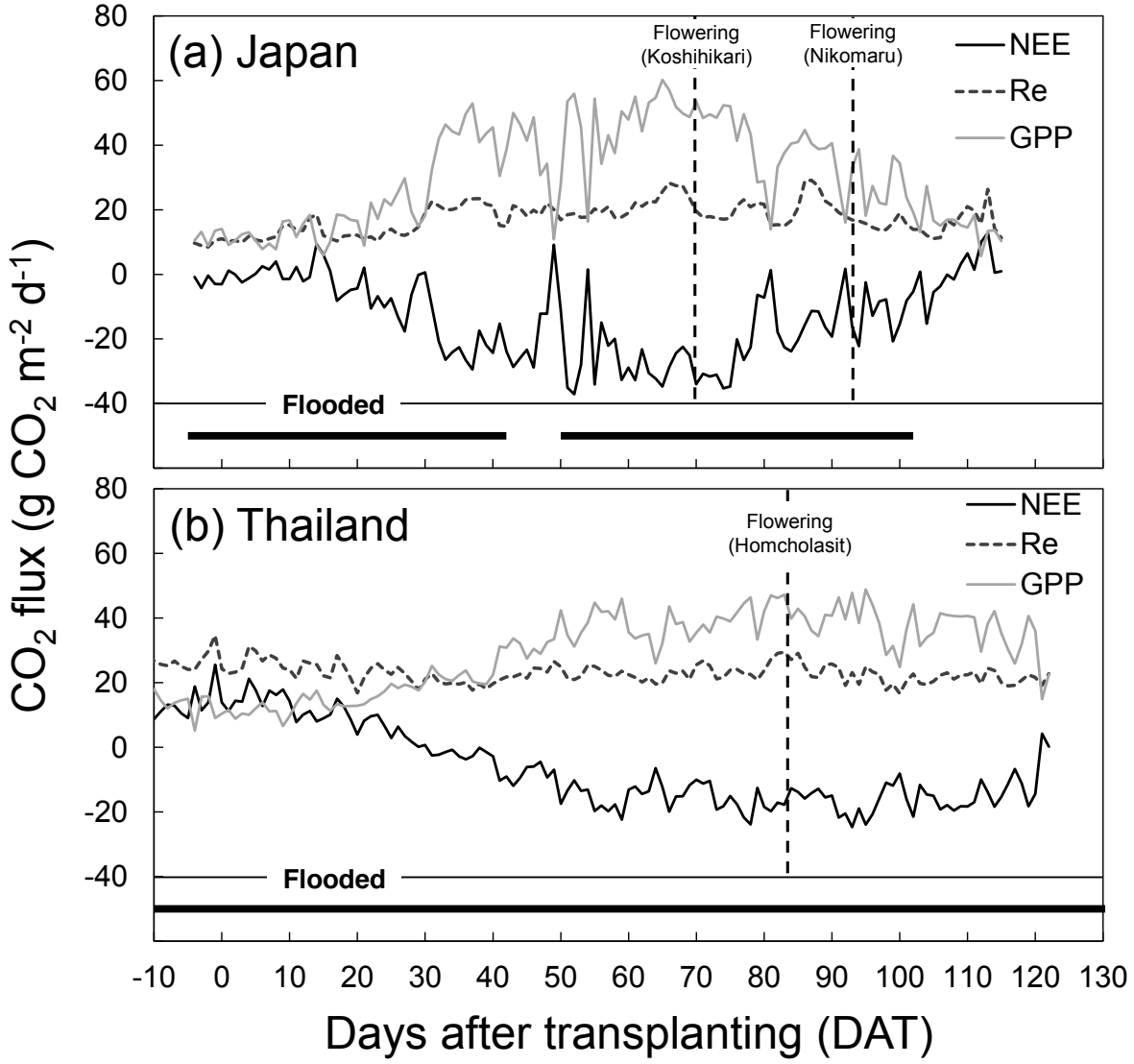

Fig. 2.4 Seasonal dynamics of NEE, R_e and GPP in rice paddy fields in Japan (a) and Thailand (b). The solid line at the bottom of each figure denotes the flooding periods.

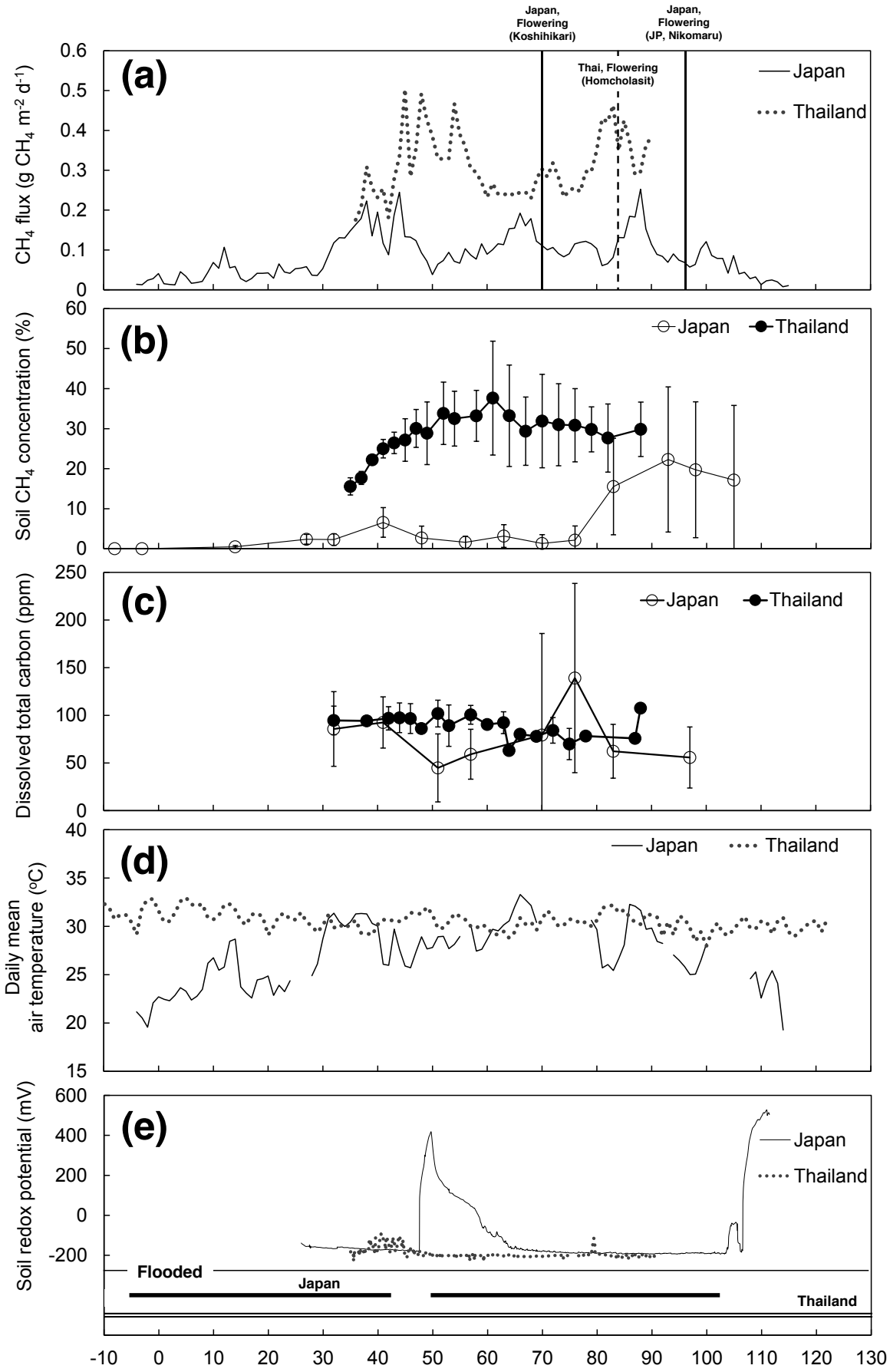
Japan, Flowering (Koshihikari)
Japan, Flowering (JP, Nikomaru)
Thai, Flowering (Homcholasit)
(a)
CH4 flux (g CH4 m-2 d-1)
Japan
Thailand
(b)
Soil CH4 concentration (%)
(c)
Dissolved total carbon (ppm)
(d)
Daily mean air temperature (oC)
(e)
Soil redox potential (mV)
Flooded
Japan
Thailand

Fig. 2.5 Seasonal variations in CH_4 flux (a), soil CH_4 concentration (b), dissolved total carbon (c), daily mean air temperature (d) and soil redox potential (e) over the rice-cropping season in Japan and Thailand. Day 0 indicates the transplanting date in each country.

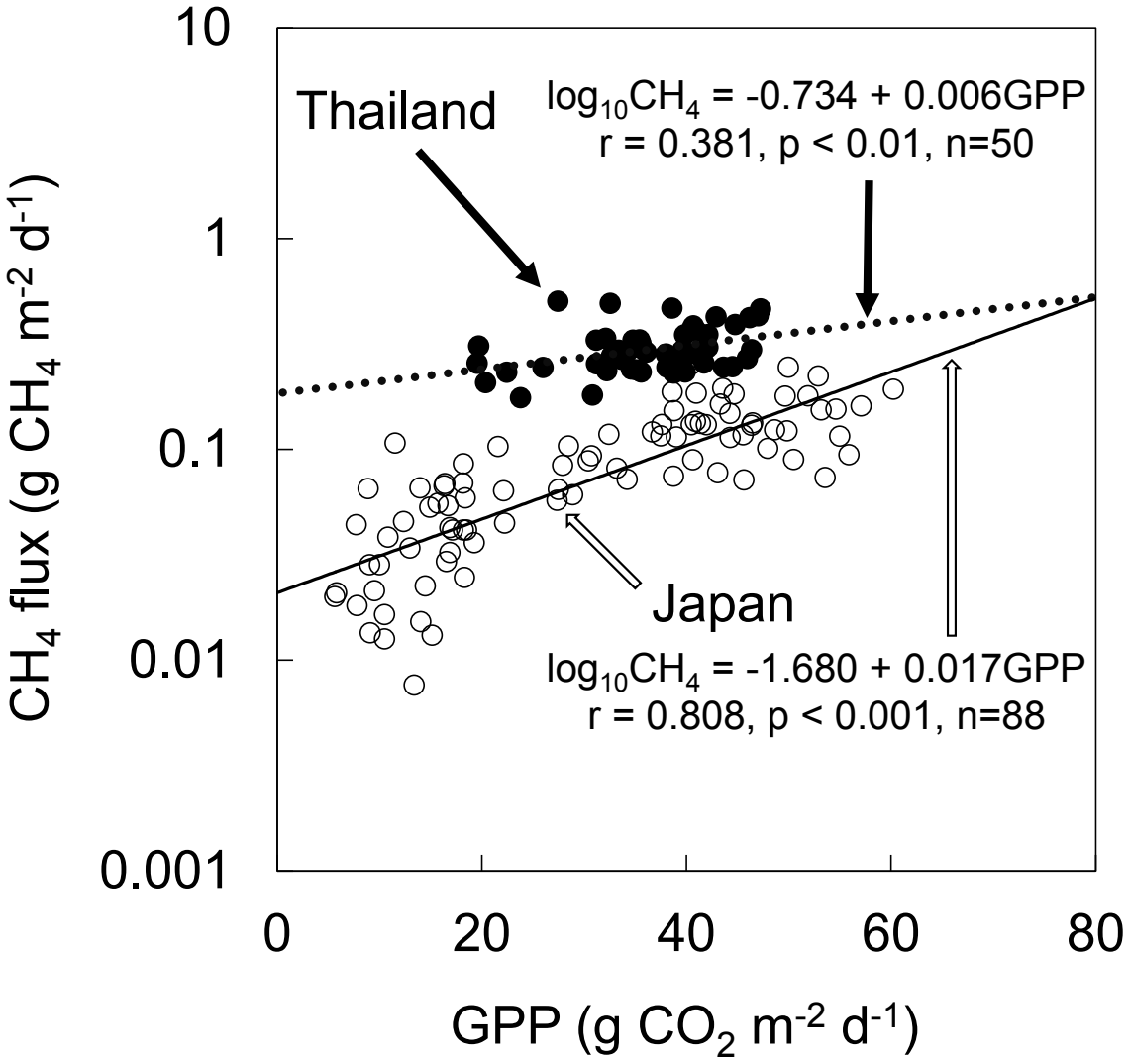

Fig. 2.6 Relationship between the daily CH_4 flux and GPP in Japan (open circles) and Thailand (solid circles).

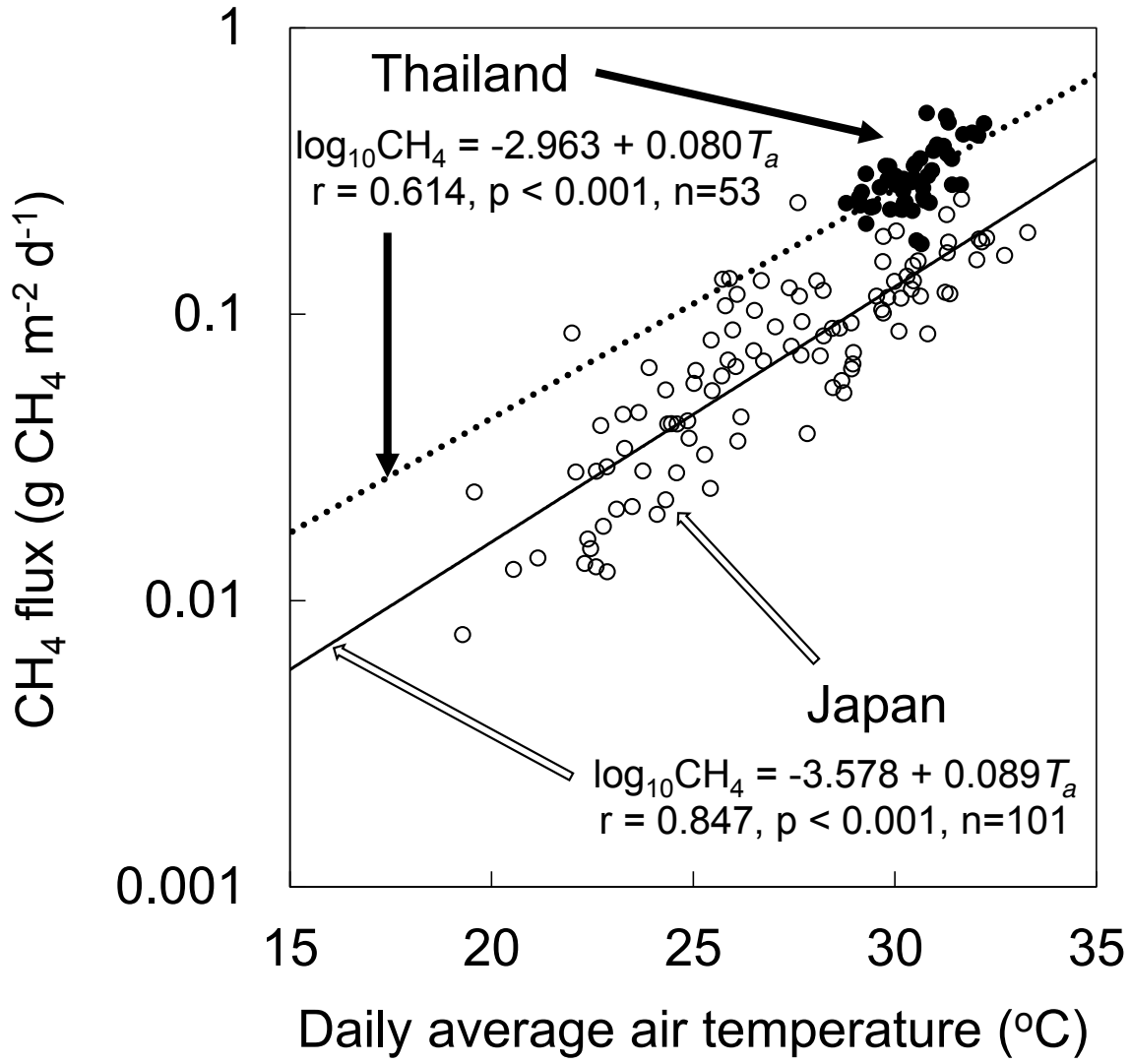

Fig. 2.7 Relationship between daily CH_4 fluxes and the daily average air temperatures (T_a) in Japan (open circles) and Thailand (solid circles).

Table 2.1 Times of field management operations after rice transplanting in both countries. The transplanting in Japan and Thailand was conducted on June 5, 2013 and on June 30, 2014, respectively.

Management practice	Day after transplanting (DAT)		
	Japan		Thailand
	rice cultivar		
	Koshihikari	Nikomaru	Homcholasit
Flooding	-5		-13
Plowing	-4		-13, -4
Transplanting	0		0
Fertilizing	0		20, 45
Mid-term drainage	43 – 49		na
Flowering	70	93	84
Final drainage	105		na
Harvest	116	137	120

Table 2.2 Fertilizer application rates in Japan and Thailand.

Fertilizer	Application rate (kg ha^{-1})		
	Japan (2013)	Thailand (2014)	
	Base	Base	Addition
N	56.5	25	31.3
P_2O_5	64.5	71.9	0
K_2O	56.5	0	0
MgO	12.1	0	0

Table 2.3 CO_2 budgets and daily average air temperatures for four rice growth periods in Japan and Thailand.

Country	DAT	NEE (g CO_2 m^{-2})	R_e (g CO_2 m^{-2})	GPP (g CO_2 m^{-2})	T_a (°C)
Japan	0-29	-78.5	372.6	451.1	24.3
	30-59	-617.2	592.2	1209.3	28.9
	60-89	-701.7	646.7	1348.4	29.9
	90-115	-135.6	421.0	556.6	25.5
	0-115	-1532.9	2032.5	3565.4	27.2
Thailand	0-29	317.3	727.4	410.1	31.1
	30-59	-258.2	657.7	916.0	30.5
	60-89	-451.3	711.2	1162.5	30.5
	90-115	-438.0	562.8	1000.8	29.9
	0-115	-830.2	2659.2	3489.4	30.5

Table 2.4 CH_4 budgets for growth periods DAT36-90 and DAT 0-115 in Japan and Thailand.

DAT (Days)	CH_4 budget (g CH_4 m^{-2})	
	Japan	Thailand
36 - 90	6.8	17.1
0 - 115	10.1	36.0

Table 2.5 CH_4, CO_2 and net GHG budgets during the cultivation season in Japan and Thailand.

Cultivation season	CO_2 budget (g CO_2 m^{-2})	CH_4 budget (g CO_2-eq. m^{-2})	Net GHG budget (g CO_2-eq. m^{-2})
Japan	-1532.9	343.5	-1189.4
Thailand	-891.9	1269.6	377.7

Chapter 3

Measuring CH_4 flux in a rice paddy field in Thailand using relaxed eddy accumulation (REA) method

3.1 Abstract

Rice paddy fields are a major anthropogenic source for methane (CH_4), one of the dominant greenhouse gases (GHGs). Recently, micrometeorological techniques have been developed for measuring GHG flux at the field scale. We evaluated a relaxed eddy accumulation (REA) method to measure methane (CH_4) flux in a rice paddy field during the flowering stage in Thailand. Methane flux at the paddy water surface was also measured using closed chambers installed in spaces between plants where no rice plant was growing. The CH_4 fluxes with the REA and closed chamber methods ranged between 1.9 and 43.6 mg m^{-2} h^{-1}, which agreed well with values previously reported in Southeast Asia. The exchange rates of CH_4 between the atmosphere and the rice canopy tended to increase during the daytime, and seemed to be regulated by the diurnal variations in horizontal wind speed and soil temperature. In addition, temporal changes in CH_4 fluxes at the water surface might have been affected by soil temperature. The CH_4 fluxes measured with the REA method were higher than those with the closed chamber method. It appears that the REA method was able to measure CH_4 fluxes above rice plant canopy and the water surface whereas the closed chamber method only measured fluxes above the water surface.

3.2 Introduction

Rice is a staple food in Southeast Asian countries, which account for around 31 % of global rice paddy areas (Redfern et al., 2012). Thailand in Southeast Asia has the fifth largest paddy area in the world, and is a major exporter of rice (Baldwin et al., 2012). Most rice is grown in rice paddy fields,

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* This chapter is a translation of the published paper: Komiya S, Noborio, K., Shoji, Y., Yazaki, T., Toojinda, T., 2014. Measuring CH_4 flux in a rice paddy field in Thailand using relaxed eddy accumulation (REA) method (in Japanese with English abstract). J. Jpn. Soc. Soil Phys. 128, 23–31.

and CH_4 emission from rice paddy fields is 29% of world anthropogenic CH_4 emissions (IPCC, 2001). In rice fields, most of the CH_4 emission occurs during the irrigated rice-cropping season (Buendia et al., 1997). Rice paddy fields are generally flooded during the rice growing period, leading to anaerobic conditions in paddy soil. The anaerobic conditions enhance methanogenic activity, resulting in CH_4 production and emission. Soil CH_4, produced in paddy soil, is mainly released into the atmosphere through three pathways: (1) via rice plants, (2) molecular diffusion between floodwater and the atmosphere and (3) via bubble ebullition (Schütz et al. 1989; Yagi, 2004). Methane emission via the rice plant has been reported to account for 48-85% of total CH_4 emission in a rice paddy (Wassmann and Aulakh, 2000). Also, plowing rice straw into paddy soil, can contribute to CH_4 emission via bubble ebullition, with reports of 35-62% of the total CH_4 emission (Wassmann et al., 1996), suggesting it could be an important emission pathway (Green, 2013). Methane emission from rice paddies varies due to physicochemical properties of the soil, field management methods and temporal changes in meteorological conditions (Yagi, 2004). In order to obtain a clear picture of CH_4 emission in rice paddy fields, continuous measurements of CH_4 flux are needed (Yagi et al., 1996).

Methane fluxes in rice paddy fields have been measured around the world since the 1980's (Cicerone and Shetter, 1981; Seiler et al., 1984; Yagi et al., 1990, 1996; Wassmann et al., 2000; Towprayoon et al., 2005; Xie et al., 2010). Although gas fluxes are generally measured using chamber and micrometeorological methods, the chamber method has been mainly utilized in measuring CH_4 fluxes in rice paddy fields around the world, including Thailand (Cicerone and Shetter, 1981; Seiler et al., 1984; Yagi et al., 1990, 1996; Wassmann et al., 2000; Towprayoon et al., 2005; Xie et al., 2010). However, the area measured by the chamber method is limited to within the bottom area of the chamber, so that the flux measured by chambers is not spatially representative (Simpson et al., 1995; Miyata et al., 2000). In addition, installing a chamber changes air flow, air pressure, air temperature, radiation and gas concentration, thus possibly affecting the flux value (Simpson et al., 1995; Hirano, 2001).

In contrast, micrometeorological (flux-gradient, eddy covariance, relaxed eddy accumulation) methods can make continuous measurements, while hardly disturbing the natural conditions at the

measurement point. Additionally, micrometeorological methods can measure the representative flux at the field scale because the obtained flux represents the average value for relatively large upwind area (Hirano, 2001). Due to these advantages, micrometeorological measurements have recently been popular for studies in rice paddy fields (Kanemasu et al., 1995; Miyata et al., 2000; Werle and Kormann, 2001; Kim et al., 2005; Takimoto et al., 2010).

The flux-gradient method needs to measure vertical profiles of wind velocity and gas concentration to measure CH_4 flux (Denmead, 1991; Miyata et al., 2000; Takimoto et al., 2010). In contrast, the eddy covariance method measures the wind velocity and the gas concentration at only one height, and can measure gas exchange directly due to atmospheric turbulence. Thus, the eddy covariance method is regarded as the most reliable method (Harazono et al., 1996). However, the eddy covariance method has not been widely used to measure CH_4 flux because of the extremely high cost of the highly-responsive CH_4 gas analyzer that needs to measure the CH_4 concentration at 10 Hz intervals (Miyata and Harazono, 2001).

Businger and Oncley developed the relaxed eddy accumulation (REA) method which measures wind velocity and gas concentration at one height, similar to the eddy covariance method, but it does not need a highly-responsive CH_4 gas analyzer. The REA method obtains the flux from the concentration differences between updraft and downdraft air over a fixed time. The updraft air is sampled when the vertical wind is positive, whereas the downdraft air is sampled when the vertical wind is negative. Beverland et al. (1996) reported that CH_4 fluxes in wetlands measured with the REA method agreed well with those measured by the eddy covariance method.

In this study, CH_4 fluxes from whole rice paddies were measured using the REA method and those from the floodwater were measured using closed chambers installed in unplanted areas in the same field. The relationships between CH_4 fluxes via either rice plants or floodwater and environmental conditions were assessed.

3.3 Materials and Methods

3.3.1 Experimental field and field management

The field study was carried out in the experimental paddy fields (14°02'14''N, 99°58'05''E) at Kamphaeng Saen campus, Kasetsart University located in Kamphaeng Saen district, Nakhon Pathom Province, Thailand. The site is located in central Thailand, in one of the country's major rice cultivation areas (FAO, 2002), and lies in the tropical savanna climate zone based on Köppen classification. According to the meteorological observatory located 2900 m south of the paddy field, the annual mean temperature and rainfall in 2009 were 27.6°C and 1.184 m, respectively (TMD, 2009). The experimental field is flat, and the paddy soil is classified as a clay loam (sand: 43 %, silt: 41 %, clay: 16 %).

The paddy fields were plowed five days before transplanting the young rice seedlings. Rice straw was incorporated into the paddy soil during plowing. The field was flooded four days after transplantation, and the floodwater depth was maintained between 0.05 - 0.1 m until final drainage. The field management for the rice paddies is shown in Table 1. The rice cultivation period was the rainy season, and the rice cultivar was an indica cultivar "Sinlek", developed by the Rice Science Center of Kasetsart University. Individual seedlings were transplanted at a hill spacing of 0.25 m × 0.25 m on July 2, 2009. Basal fertilizer was not applied, and top dressing fertilizer was applied 19 and 49 days after transplanting. Details of the top dressing fertilizer applications are shown in Table2. The rice was harvested on October 6, 2009, and the unhulled rice yield was 1565 kg ha^{-1}. The yield was less than half of the average yield (3938 kg ha^{-1}) of "Pathum Thani1" that is the representative rice cultivar in the Kamphaeng Saen district (Siangliw, personal communication) because "Sinlek" was developed as a highly functional variety rather than a high-yielding variety.

Measurements of CH_4 flux and environmental conditions in the paddy fields were conducted from September 5 to September 12 in 2009. This period covered the flowering and heading stage of the rice, and the plant height was about 1.2 m.

3.3.2 CH_4 flux

3.3.2.1 REA method

The average CH_4 fluxes from the field, through rice aerenchyma and flooded water, were measured using the REA method. Figure 3.1 is a schematic diagram of an REA measurement system. Vertical wind speed (w, m s^{-1}) at 2 m height from soil surface was measured using a three dimensional sonic anemometer-thermometer (SAT540, KAIJO Co., Tokyo, Japan) and a data logger (CR1000, Campbell Scientific, Inc., Logan, UT, USA) at 10 Hz intervals. The positive and negative values of w were classified into updraft and downdraft air, respectively. The updraft and downdraft air were stored in respective updraft and downdraft air tanks (2L), by controlling the switching of solenoid valves by the data logger (CR1000). Methane concentration in each air tank was measured every 20 minutes using a photoacoustic gas monitor (1412, INNOVA AirTech Instruments, Ballerup, Denmark), and then a 1-hour mean concentration of CH_4 was determined. The CR1000 controlled the photoacoustic gas monitor and stored the data from the gas monitor. Methane flux by the REA method (J_{REA}, mg m^{-2} h^{-1}) was calculated by Eq. (3.1) (McInnes and Heilman, 2005).

$$J_{REA} = B\sigma_w\left(\overline{C_u} - \overline{C_d}\right)\times 3600 \qquad (3.1)$$

where J_{REA} is the gas flux (mg m^{-2} h^{-1}), B is the experimental value (= 0.4 ~ 0.7) (Ammann and Meixner, 2002), σ_w is the standard deviation of the vertical wind velocity (m s^{-1}), and C_u and C_d (mg m^{-3}) are 1-hour mean values of CH_4 concentration in the up and down tank, respectively .

The value of B is usually determined by comparing the sensible heat flux by eddy covariance and REA methods (Hamotani et al., 2001). Previous research reported that B varied between 0.4 and 0.7 with a mean value of 0.56 (Ammann and Meixner, 2002; McInnes and Heilman, 2005). Furthermore, the median of B is between 0.55 and 0.57 in paddy fields and wetlands (Tsai et al., 2012). Therefore, the B was determined as 0.56.

The prevailing wind direction during the experimental period was west-southwest, therefore the rice cultivation was conducted in the paddy field west-southwest of the measuring point. The field size was 50 m × 50 m (Fig. 3.2). Using footprint analysis, Harazono et al. (1998) reported that the upwind

area within 50 m contributed 64 % of the total flux when the distance between zero plane displacement and wind measurement height was 1.7 m and the atmospheric stability was neutral. In this study, the upwind area within 50 m contributed to most of the flux because the distance between the wind measurement height (1.9 m) and the zero displacement (0.7 m), assumed as plant height × 0.64 (Campbell, 1986), was 1.2 m. In addition, in order to avoid the influence of the shed (2 m wide ×2 m long × 2 m high) housing the REA measurement system that was located 2 m north of the wind measurement point, the CH_4 flux calculation wasn't carried out when the wind direction was from north-northeast to north-northwest. Also, the CH_4 flux was not calculated during rainfall periods.

Shoji (2009) reported that CH_4 concentration measured by the same type of photoacoustic gas monitor as used in this study depended on the water vapor concentration, which consequently resulted in a less-accurate CH_4 flux measurement. Therefore, the calibration of the photoacoustic gas monitor was performed by multiple regression analysis by measuring the CH_4 concentration in accumulated air in the air tanks using both a gas chromatograph with FID (6890N, Agilent Technologies Inc., Santa Clara, CA, USA) and the photoacoustic gas monitor. The obtained calibration equation was as follows,

$$C_{cali} = 4.2 \times 10^{-2} \times C_{INNOVA} - 10^{-2} \times e_{sat} - 10^{-5} \times WV_{INNOVA} + 1.7 \quad (3.2)$$

where C_{cali} is the CH_4 concentration obtained from the calibration equation (mg m^{-3}), C_{INNOVA} is the CH_4 concentration measured with the gas monitor (mg m^{-3}), e_{sat} is the saturated vapor pressure in the atmosphere (hPa), and WV_{INNOVA} is the water vapor concentration measured with the gas monitor (mg m^{-3}). The relationship between the CH_4 concentration, measured by the gas chromatography, and the calibrated CH_4 concentration (C_{cali}) is shown in Fig. 3. The number of samples was n = 147, and the root mean square error (RMSE) of C_{cali} was 0.04 mg m^{-3}. The applicable range by Eq. (3.2) was between 1.1 and 1.5 mg m^{-3}.

3.3.2.2 Chamber method

The chamber method was used to measure only the methane flux through the water surface. The closed chambers were handmade using bottomless cylinders made of tin plate (diameter: 28.8 cm,

height: 23.5 cm). A sampling port and temperature sensor were mounted on the upper lid. Also, a pressure-regulating bag and an electric fan were mounted on the inner part of the upper lid.

On September 5, 2009, two chambers were installed between rice plants at the eastern edge of the paddy field to the south west of the REA system, and another chamber was installed between rice plants at the western edge of the adjacent paddy field to the south east of the REA system. The base part of each chamber was inserted 3.5 cm deep into the paddy soil. The internal volume of each chamber was obtained by measuring four point heights from water surface to the upper lid at the time of every chamber measurement. In addition, the chamber in the field to the southeast of the REA system was moved beside the other two chambers on September 11 because the water depth in the eastern paddy field rose. Details of the installation positions of the chambers are shown in Fig. 3.2. The headspace air in each chamber was collected using a 40 mL syringe at 0, 10, 20 and 30 min after closing the upper lid of the chamber. Each collected gas sample was injected into a pre-vacuumed 20-ml vial, and then the vials with gas samples were stored in a cooler-box with refrigerant. The samples were then stored in a refrigerator, before being transported in a cool box to Japan where they were analyzed using a gas chromatograph with FID. Gas samples were collected about every seven hours between September 5 and 12, 2009.

Gas flux by the closed chamber method was determined by the following equation (de Mello and Hines, 1994).

$$J_{ch} = \frac{V}{A}\left[\frac{dC(t)}{dt}\right] \tag{3.3}$$

where J_{ch} is the gas flux (mg m^{-2} h^{-1}), V is the chamber volume (m^3), A is the water-surface area covered by the chamber (m^2), t is elapsed time (h) and $C(t)$ is temporal changes in gas concentration (mg m^{-3}). When gas flux was considered to be affected by artificial disturbance, the gas flux was excluded.

The temporal change of gas concentration in the chamber was assumed to follow the following equation (de Mello and Hines, 1994).

$$\left[\frac{dC(t)}{dt}\right] = k(C_{\max} - C(t)) \tag{3.4}$$

where C_{max} is the maximum gas concentration (mg m^{-3}), and k is an experimental constant. When the initial gas concentration is assumed to be C_0, the analytical solution of Eq. (3.4) is obtained by the following equation (de Mello and Hines, 1994).

$$C(t) = C_{\max} - (C_{\max} - C_0)\exp(-kt) \tag{3.5}$$

The C_{max} and k are determined by adapting the analytical solution to the measured gas concentration using the Microsoft Excel Solver function.

3.3.3 Environment conditions

Air temperature and relative humidity at 2 m height above the soil surface were measured at 10 sec intervals using a temperature and humidity sensor (HMP45A, Vaisala). Soil temperature at 0.05 m depth was measured by a type T thermocouple, at the same time interval. The 5-min average data were recorded every 5 min using a data logger (CR23X, Campbell Scientific, Inc.). Atmospheric pressure was measured and recorded every 30 minutes using a barometer (RS-12P, ESPEC Corp., Japan).

3.4 Results and Discussion

During the heading stage, methane flux in the rice paddy fields by the REA and the chamber methods varied from 1.9 mg m^{-2} h^{-1} to 43.6 mg m^{-2} h^{-1} (Fig. 3.4 a). This variation range is similar to previously reported values of 3.4 - 55.6 mg m^{-2} h^{-1} measured in rice paddies during the heading stage in Southeast Asian countries by other researchers (Table 3.3).

During the measurement period, the horizontal wind speed increased from around 6 a.m., and reached maximum from around 12 p.m. to 4 p.m., and then decreased over the night (Fig. 3.4 b). CH_4 flux by the REA method increased from around 6 a.m. to around 12 p.m., and reached the maximum from around 12 p.m. to around 4 p.m. (Fig. 3.4 a). These results suggested the diurnal variations of

horizontal wind speed affected the CH_4 flux by the REA method (Fig. 3.4 a, b). Since CH_4 concentration in the rice canopy is usually higher than that in the atmosphere (Miyata et al., 2000), CH_4 exchange between rice canopies and atmosphere appeared to be enhanced due to wind penetrating inside the rice canopy when horizontal wind speed was high (Harazono et al., 1996). Moreover, the higher daytime wind velocity would have produced more turbulent eddies, which would have caused the increased standard deviation σ_w of the vertical wind speed. Therefore, based on Eq. (3.1), this would also have contributed to high CH_4 flux in the daytime relative to in the evening.

Increases in soil temperature also enhanced CH_4 fluxes in the daytime (Fig. 3.4 a, c). Increasing soil temperature enhances CH_4 production rate by methanogenesis in paddy soil (Westermann, 1993). Thus, CH4 flux in the daytime was higher than that in the nighttime (Wang et al., 1997). Methane, released into the atmosphere via paddy water, is mainly released due to bubble ebullitions (Wassmann et al., 1993, 1996). CH_4 concentration in the bubbles at this site was extremely high (31.4 % v/v) which were similar to those (1-59 % v/v) reported by Uzaki et al. (1991). The experiment paddy soil would have had suitable conditions to produce CH_4 bubbles because bubbles are more likely to be formed in paddy soil where crop residues such as rice straw have been plowed (Watanabe and Kimura, 1995). In fact, it was possible to visually observe the bubble ebullition from the flooded soil surface from 7 am to 3 pm when soil temperature increased. Bubble volume appeared to rise as the soil temperature rose during the day, which would have increased in bubble buoyancy (Kellner et al., 2006). Furthermore, it is likely that increasing bubble buoyancy enhanced the release of bubbles, leading to an increase in CH_4 flux through paddy water (Kellner et al., 2006).

The volume of the bubbles is also increased by decreases in atmospheric pressure (Fechner-Levy and Hemond, 1996; Kellner et al, 2006; Tokida et al, 2007). Tokida et al. (2007) reported that the sudden increase in CH_4 emission due to bubble ebullition with the large reduction of the air pressure (16 hPa). In this study, CH_4 flux increased and reached maximum with falling atmospheric pressure from 9 a.m. to 3 p.m. (Fig. 3.4 a, d), but the decrease in air pressure was not below 4 hPa. Therefore, although the reduced pressure possibly contributed to the increase in the CH_4 flux, further research is needed to determine the degree of contribution to CH_4 flux.

Throughout the measurement period, methane fluxes in rice fields by the REA method were larger than the mean flux values by the chambers that were installed in the unplanted areas (Fig. 3.5). When CH_4 flux by the REA method was above the 1:1 line, a significant linear relationship was observed between CH_4 flux by the REA and the chamber methods (slope = 1.06, $r = 0.976$, $p < 0.001$, $n = 10$), and the intercept was not 0 ($p < 0.001$). Methane flux by the REA method was about 6.4 mg m^{-2} h^{-1} greater than the mean CH_4 flux by the chamber method. This suggests that the CH_4 flux detected by the chamber method was only CH_4 emitted via paddy water, whereas the CH_4 flux detected by the REA method included CH_4 emitted via rice aerenchyma and paddy water.

However, the average value of CH_4 flux by the chamber method exceeded that by the REA method in the evening on September 7 and 11 (Fig. 3.5). One of the three chambers measured much higher fluxes that seemed to be due to rapid CH_4 release by bubble ebullitions, resulting in the higher averaged CH_4 fluxes by the chamber method than the REA method. In contrast, the REA method cannot always detect rapid emissions in CH_4 from localized areas because it measures the average CH_4 concentration in the atmosphere derived from the whole windward side.

3.5 Conclusions

In this study, CH_4 fluxes in Thailand rice paddies were measured using the REA method and the chamber method. The values of CH_4 flux by both methods (1.9 - 43.6 mg m^{-2} h^{-1}) were similar to previously reported values in Southeast Asia (3.4 - 55.6 mg m^{-2} h^{-1}). CH_4 flux, horizontal wind speed and soil temperature increased from the morning to the daytime, and then decreased from the daytime to the nighttime. This suggested that the diurnal variations of CH_4 fluxes were affected by horizontal wind speed and soil temperature as has been reported in previous studies. Throughout the measurement period, the CH_4 flux from the rice paddies by the REA method was about 6.4 mg m^{-2} h^{-1} greater than the mean CH_4 flux by the chambers that were installed in unplanted areas. This indicates that CH_4 flux from the unplanted soil was derived only from floodwater, whereas the CH_4 flux measured by the REA method was derived from both floodwater and rice aerenchyma.

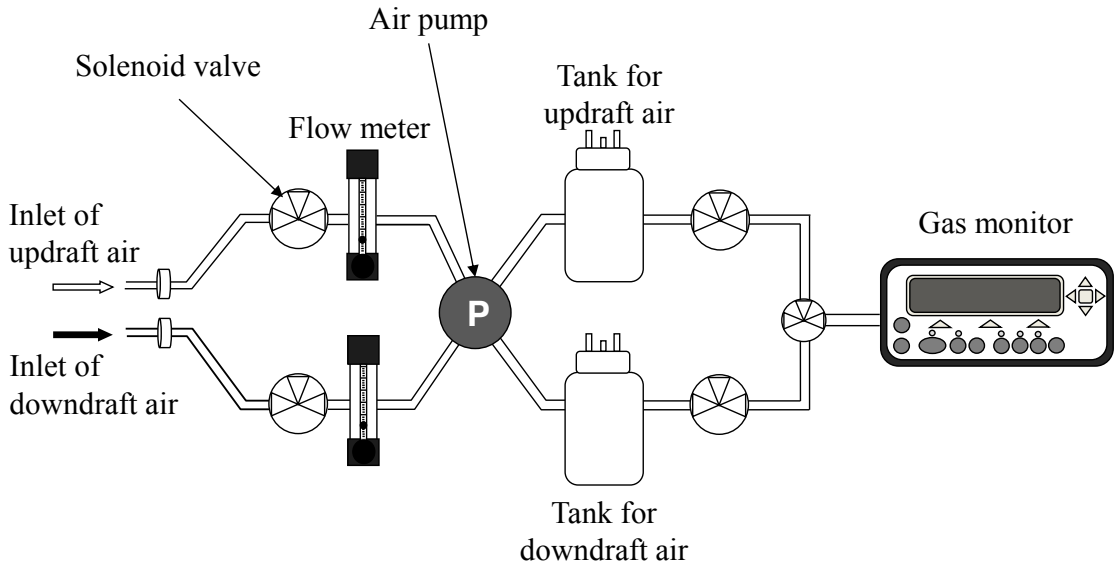

Fig. 3.1 Schematic diagram of the REA system (Shoji, 2009 diagram modified).

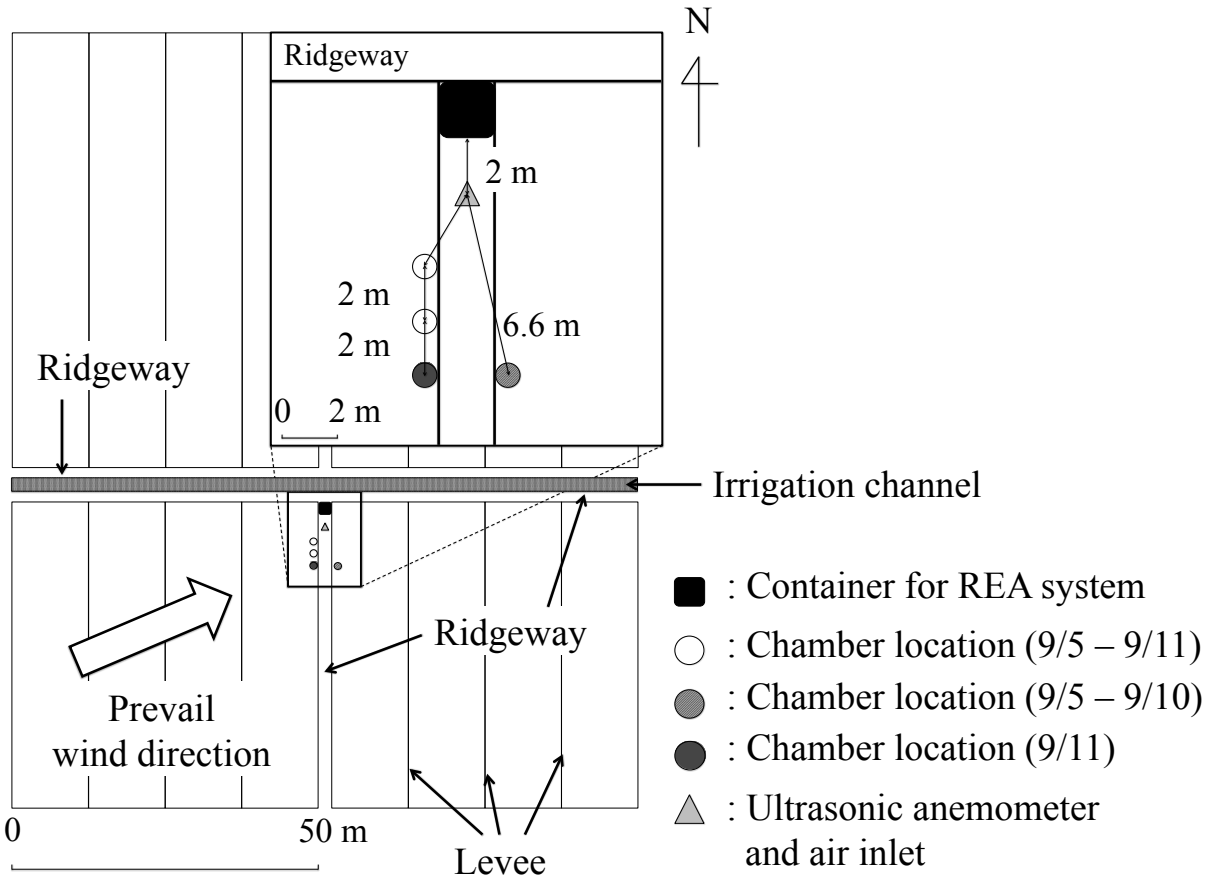

Fig. 3.2 Site diagram of the study field, showing the locations of the container for the REA system, closed chambers, ultrasonic anemometer, air inlet and the prevailing wind direction.

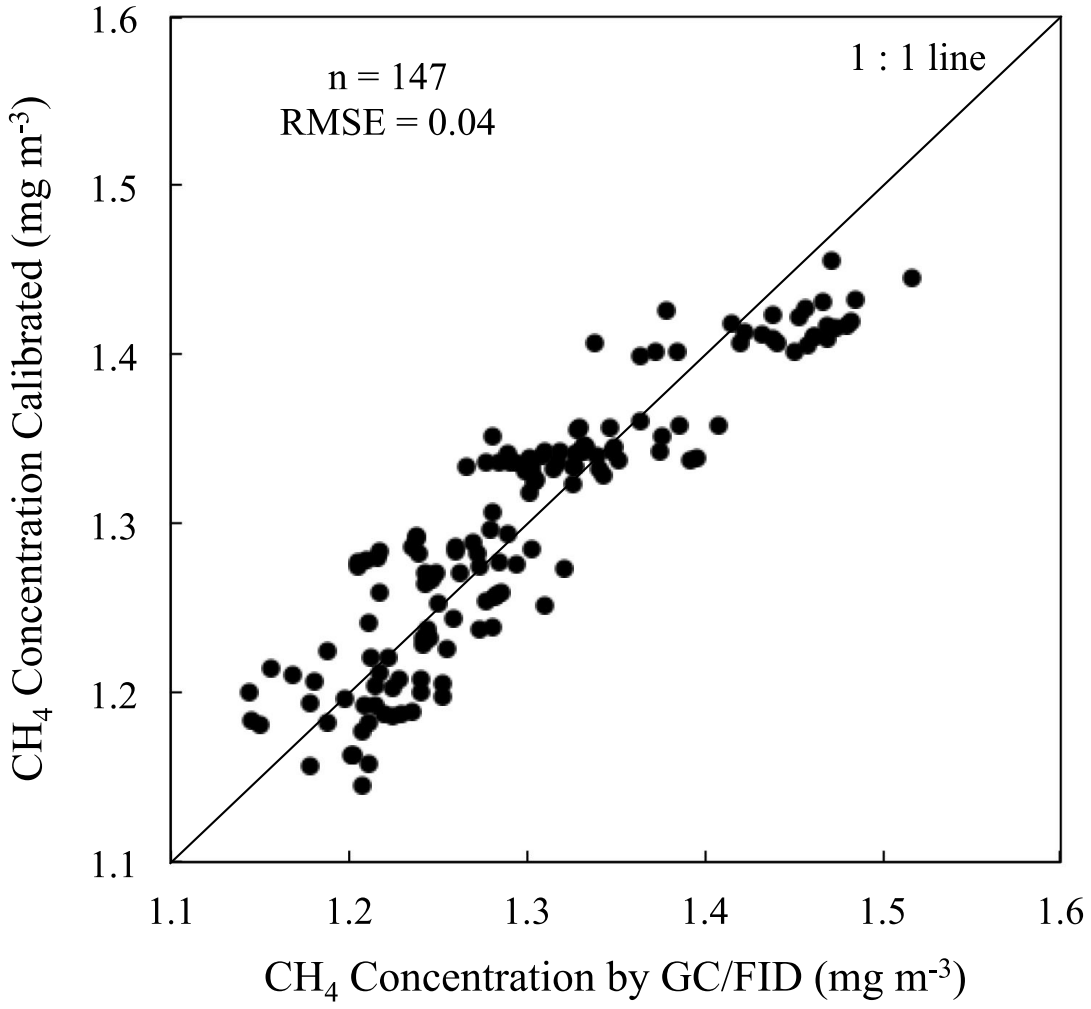

Fig. 3.3 Relationship between calibrated CH_4 concentration and CH_4 concentration by GC/FID.

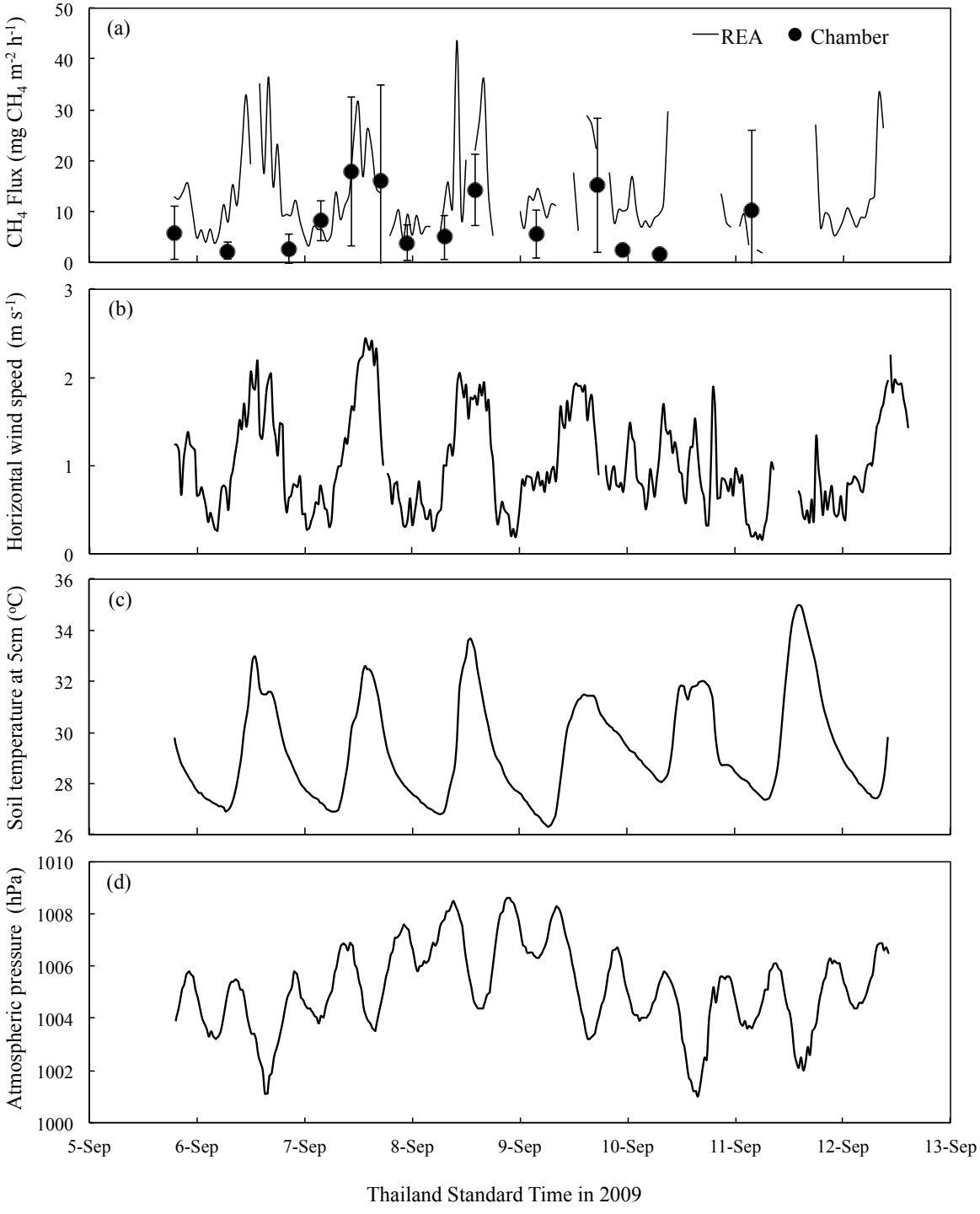

Fig. 3.4 Temporal changes in (a) CH_4 flux by REA and chamber methods, (b) horizontal wind velocity, (c) soil temperature at 5 cm deep, and (d) atmospheric pressure.

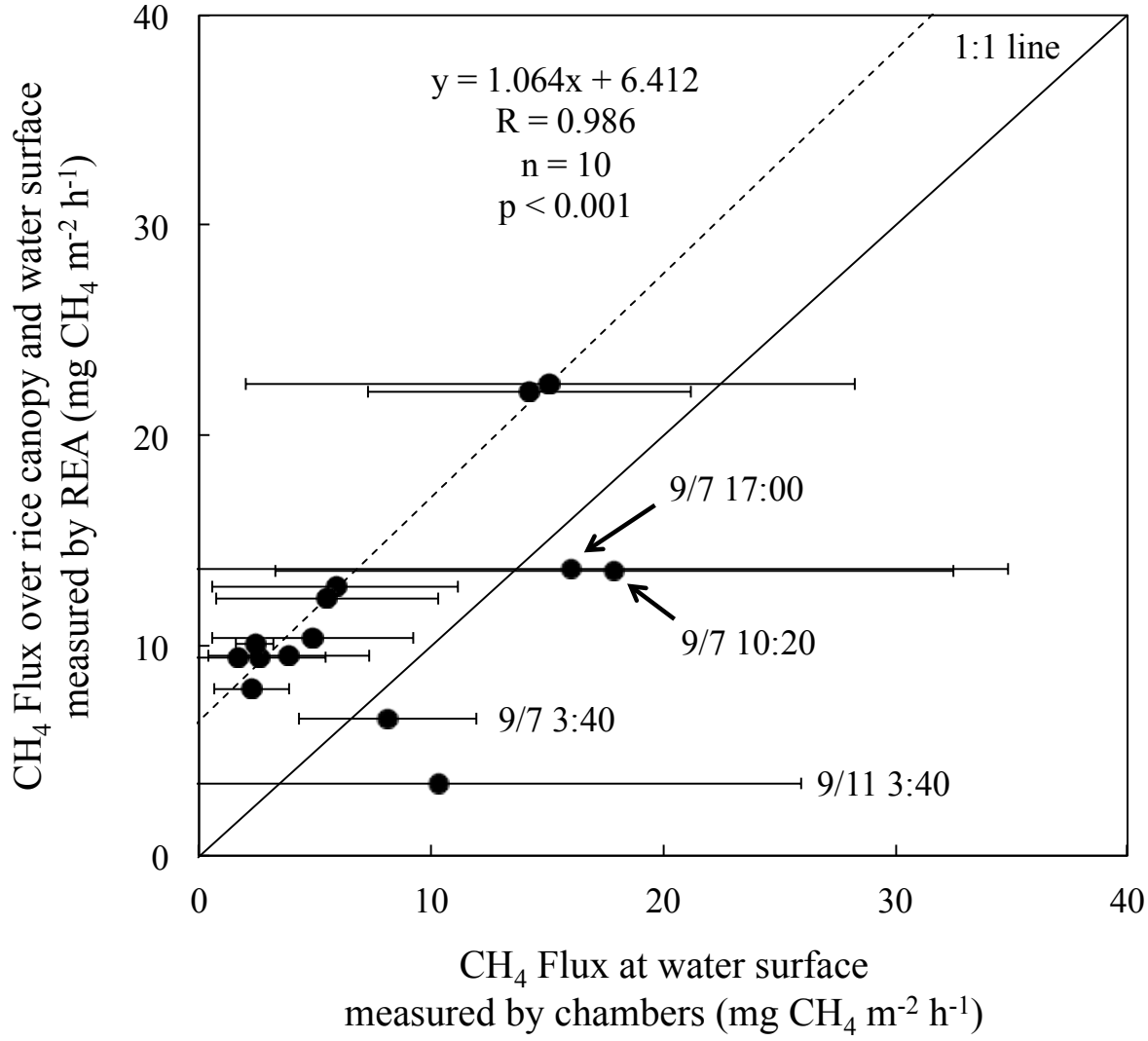

Fig. 3.5 Comparison of CH_4 fluxes over rice canopy and the water surface measured by REA and at the water surface measured by chamber methods. Bars indicate one standard deviation (n=3).

Table 3.1 Field management for the experimental rice paddy field.

Management practice	Date
Plowing	June 26
Applying rice straw	June 26
Transplanting	July 1
Flooding	July 5
First top dressing	July 20
Second top dressing	August 19
Flowering	September 9
Drainage	September 26
Harvest	October 20

Table 3.2 Amounts of topdressing fertilizer applied to the study field.

Fertilizer	Application rate (kg ha^{-1})	
	First	Second
N	9.2	10
P	0	7.5
K	0	5

Table 3.3 Comparison of CH_4 fluxes in rice paddy fields in Southeast Asia during heading and flowering stages.

Location	CH_4 flux (mg CH_4 m^{-2} h^{-1})	Season	Irrigation condition	Application of organic matter	Measuring method	References
Indonesia	19.5 - 44.8	Dry and Rainy	Flooded	Rice straw	Chamber	Nugroho et al. (1996)
Philippines	9.7 - 37.4	Dry	Flooded and drainage	Organic matter	Micrometeorology	Simpson et al. (1995)
Thailand	6.7 - 23.4	Rainy	Flooded	Rice straw or rice straw compost	Chamber	Jermsawatdipong et al. (1994)
Thailand	3.4 - 55.6	Rainy	Flooded	No data	Chamber	Towprayoon et al. (2005)
This study	1.9 - 43.6	Rainy	Flooded	Rice straw	Micrometeorology	This study

Chapter 4

Contribution of ebullition to methane and carbon dioxide emission from water between plant rows in a tropical rice paddy field

4.1 Abstract

Although bubble ebullition through water in rice paddy fields dominates direct methane (CH_4) emissions from paddy soil to the atmosphere in tropical regions, the temporal changes and regulating factors of this ebullition is poorly understood. Bubbles in a submerged paddy soil also contain high concentrations of carbon dioxide (CO_2), implying that CO_2 ebullition may occur in addition to CH_4 ebullition. We investigated the dynamics of CH_4 and CO_2 ebullition in tropical rice paddy fields using an automated closed chamber installed between rice plants. Abrupt increases in CH_4 concentrations occurred by bubble ebullition. The CO_2 concentration in the chamber air suddenly increased at the same time, which indicated that CO_2 ebullition was also occurring. The CH_4 and CO_2 emissions by bubble ebullition were correlated with falling atmospheric pressure and increasing soil surface temperature. The relative contribution of CH_4 and CO_2 ebullitions to the daily total emissions were 95–97 % and 13–35 %, respectively.

4.2 Introduction

Understanding the dynamics of methane (CH_4) and carbon dioxide (CO_2) fluxes in rice paddy fields is crucial for improving the accuracy of estimating CH_4 and CO_2 emissions from global rice paddy fields. In particular, flooded rice paddies are considered to be a major source of anthropogenic CH_4. Methane emissions from rice paddies in tropical Asian countries account for 90 % of global annual CH_4 emissions from rice paddies (Yan et al. 2009; IPCC 2013).

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Methane produced in an anaerobic-flooded paddy soil is mainly transported to the atmosphere through the aerenchyma of rice plants (Nouchi et al. 1990; Butterbachbahl et al. 1997; Wassmann and Aulakh 2000). Such emissions through the aerenchyma are estimated to account for 48-85 % of net CH_4 emissions throughout the rice-cropping season (Wassmann and Aulakh 2000). In addition, CO_2 exchange in paddy fields mainly results from photosynthesis and respiration of rice plants, as well as soil microbial respiration.

Also, some of the CH_4 and CO_2 produced in rice field soil is directly emitted to the atmosphere through paddy water. In one study, when rice straw was applied to a paddy field, CH_4 emissions via bubble ebullition from the soil accounted for 35-62 % of total CH_4 emissions (Wassmann et al. 1996). However, research on the direct CH_4 and CO_2 exchanges between paddy soil and the atmosphere, via paddy water, is limited and so further studies are required on these emissions, as has been noted by other researchers (Usui et al. 2003; Green et al. 2013).

Methane in paddy soil is transported to the atmosphere through paddy water by two pathways: (1) diffusion between soil and atmosphere, and (2) bubble ebullition (Schütz et al. 1989). Methane emission by bubble ebullition is considered to be greater than that by diffusion from paddy water (Wassmann et al. 1996). The bubbles usually contain a high concentration of CH_4 ranging between 1 - 82 % (v/v) (Uzaki et al. 1991; Rothfuss and Conrad 1998), and comprise most of the total CH_4 pool in flooded paddy soil (Tokida et al. 2013). Bubble production and ebullition are enhanced by applied organic materials during the initial plant growth period (Denier Van Der Gon and Neue 1995; Watanabe and Kimura 1995; Wassmann et al. 1996) and by organic substances originating from rice roots during latter growth stages (Watanabe and Kimura 1995; Wassmann et al. 1996; Tokida et al. 2013). Although the variation of CH_4 bubble ebullition during the cultivation period has been studied previously, the factors controlling the diurnal changes in CH_4 ebullition remain unclear (Neue 1997).

Methane ebullition from submerged peatlands, which are similar to flooded paddy soil in that they contain many bubbles, is controlled by atmospheric pressure, soil temperature and water table level (Fechner- Levy and Hemond 1996; Kellner et al. 2006; Tokida et al. 2005, 2007). Falling atmospheric pressure has been shown to be the most important contributor to CH_4 bubbling in

peatland (Tokida et al. 2005, 2007). A study in rice paddy fields in Thailand also suggested that CH_4 ebullitions occurred when atmospheric pressure dropped, but further research is needed to clarify this (Komiya et al., 2014).

In contrast, CO_2 exchange through paddy water is the result of photosynthesis of aquatic plants and respiration of both the plants and soil microorganisms (Koizumi et al. 2001). Emission due to soil respiration is suppressed by paddy water during flood irrigation (Koizumi et al. 2001; Nishimura et al. 2014), but the CO_2 concentration in soil bubbles is between 2.2 – 13.0% (v/v) (Rothfuss and Conrad 1998; Cheng et al. 2005), which suggests that bubble ebullition will release both CH_4 and CO_2 from paddy soil into the atmosphere.

Therefore, in this paper we examined the dynamics of both CH_4 and CO_2 ebullition in tropical rice paddy fields in Thailand using an automatically closing chamber method.

4.3 Materials and Methods

Gas field measurements were conducted on September 20th and 21st 2014 in a rice field of Kasetsart University, Kamphaeng Saen campus (14° 00' 33"N, 99° 59' 03"E) located in Nakhon Pathom Province, Thailand. The soil had a clay texture (65.7 % clay, 23.30 % silt and 11.0 % sand) with a dry bulk density of 1.69 g m^{-3}. The soil was sampled on September 17 and had a pH of 6.0 (1:1 for soil:water), 4.32 % organic matter, 1.81 % total carbon, and 1.85 % total nitrogen. Seedlings of the rice variety “Homcholasit” were transplanted on June 30 at 18 × 30 cm spacing with 4-5 seedlings per hill, after the soil had been plowed on June 17 and 26 when weeds and rice plants that had grown during the fallow period were plowed into the soil. The rice plants headed on September 22 and were harvested on October 28. The paddy field was continuously flooded from June 17 until harvest, with. flooding water depth maintained at 2 - 20 cm. During the gas measurement period, the water depth slowly decreased from 5.5 to 4 cm because there was no precipitation or irrigation.

The CH_4 and CO_2 fluxes were measured using the automatic closed chamber method. A customized-bottomless polycarbonate chamber (50 × 20 cm at the base and 40 cm height, Green Blue

Corp., Tokyo, Japan) was placed between the rows of rice plants on August 8; the base part was inserted 4.5 cm deep into the paddy soil (Fig. 4.1). The lid of the chamber was automatically closed for 10 min every 1 h by a pneumatic piston, with the lid kept open for the rest of the time. A small electric fan was installed on the upper sidewall inside the chamber, and was kept running throughout the experiment to uniformly mix the air within the chamber. The chamber headspace air was circulated at 500 ml min^{-1} (using a diaphragm pump; TD-4X2N, Brailsford Co., Rye, NY, USA) between the chamber and a 250 mL buffer tank placed in a shed located approximately 4 m away from the chamber to minimize the high frequency noise. A loop line was installed between the buffer tank and a wavelength-scanned cavity ring-down spectroscopy CH_4/CO_2 analyzer (G2201-i, Picarro Inc., Santa Clara, CA, USA). Air in the buffer tank was withdrawn to the analyzer at a flow rate of ~ 25 ml min^{-1} using another diaphragm pump (UN84.4 ANDC-B, KNF Neuberger Inc., NJ, USA) and then returned to the loop line. Concentrations of CH_4 and CO_2 were analyzed at approximately 3.6 s intervals by the gas analyzer. The sampled air was dried before entering the gas analyzer using a reflux method with a membrane dryer (SWG-A01-06, Asahi Glass Engineering Co., Chiba, Japan) so that the water vapor concentration in the air was kept < 0.1 %. Based on the internal volumes of the buffer tank and connecting tube and the flow rate the air inside the chamber was calculated to first reach the gas analyzer 2 min after closing the chamber lid. The measurements of CH_4 and CO_2 concentrations in the chamber air stopped when the chamber lid opened meaning that a measurement cycle of gas flux measurements lasted 8 min every hour.

Temporal changes in CH_4 concentration in the chamber during a measurement cycle were categorized into either a sudden increase (Figs. 4.2a, 4.2c, 4.2e) or a slow-constant increase (Figs. 4.2c and 4.2e). Emission by bubble ebullition events was defined as a sudden increase in concentration ($\Delta C/\Delta t$) of $\geq$ 0.29 ppm min^{-1}, whereas emission by diffusion was defined as a slow-constant increase($\Delta C/\Delta t$) of < 0.29 ppm min^{-1}.

Changes in CO_2 concentration in the chamber showed either an episodic increase accompanied by CH_4 ebullition events (Figs. 4.2b, 4.2f), a steady increase (Fig. 4.2d), or a decrease by plant uptake

(Fig. 4.2f). CO_2 emission by bubble ebullition was defined as episodic CO_2 concentration increases accompanied by CH_4 ebullition, whereas emission by diffusion was defined as a constant CO_2 increase. The CO_2 uptake by photosynthetically active aquatic plants was defined by a decrease in CO_2 concentration (Fig. 4.2f) observed during the daytime on both days.

Since CH_4 and CO_2 concentrations in the chamber often changed episodically with time due to bubble ebullition events (Figs. 4.2a, 4.2b, 4.2c, 4.2e, 4.2f), CH_4 and CO_2 fluxes were calculated for each single flux event and then summed proportionately for the time of each event to give a total flux for each 8 min measurement period. The start of each flux event was determined as the intersection between tangent lines at the inflection point of the time series of CH_4 or CO_2 concentrations (Fig. 4.2). The end of each event was the time just before the start of the next flux event or the end of the 8 min measurement period (Fig. 4.2). The gas flux F (mg m^{-2} h^{-1}) was calculated using temporal changes in gas concentrations as (de Mello and Hines 1994):

$$F = \frac{V}{A}\left[\frac{dC(t)}{dt}\right]_{t=0} \tag{4.1}$$

where V is the headspace volume within the chamber (m^3), A is the water-surface area covered by the chamber (m^2), t is elapsed time (h), and $C(t)$ is temporal changes in gas concentration (mg m^{-3}) expressed as:

$$C(t) = C_{\max} - (C_{\max} - C_0)\exp(-kt) \tag{4.2}$$

where C_{max} is the maximum gas concentration (mg m^{-3}), C_0 is the initial gas concentration (mg m^{-3}) and k is a rate constant. The values of C_{max}, C_0 and k were iteratively obtained using the data of observed gas concentration versus time. Substituting Eq. 4.2 at t=0 into Eq. 1 means the gas flux F (mg m^{-2} h^{-1}) can be calculated as (de Mello and Hines 1994):

$$F = \frac{V}{A}k(C_{\max} - C_0) \tag{4.3}$$

Atmospheric pressure and air temperature were measured with a barometer (MPXAZ6115A and MPXV7007DP, Freescale Inc., TX, USA) and a thermometer (HMP45A, Vaisala Inc., Helsinki, Finland), respectively. Water depth in the rice field was measured with a water level sensor (eTapeTM Continuous Fluid Level Sensor, Milone Technologies Inc., NJ, USA). Soil surface temperature was measured with a type T thermocouple.

Bubbles in soil were collected directly with a syringe by disturbing the topsoil at 3 p.m. local time on September 20. The CH_4 and CO_2 concentrations in the bubbles were measured using the CH_4/CO_2 gas analyzer after the sampled air was diluted 101 times with high-purity nitrogen gas.

4.4 Results and Discussion

4.4.1 CH_4 emission

Episodic and rapid increases in CH_4 concentration were identified in 21 out of the 46 measurements (Figs. 4.2a, 4.2c and 4.2e). These sudden increases in CH_4 concentration are likely to be from bubbles released from the soil to the atmosphere because the CH_4 concentration in topsoil bubbles was as high as 63.73 % v/v. In the other 25 measurements, the CH_4 concentration in the chamber air increased gradually with time ($\Delta CH_4/\Delta t < 0.29$ ppm min^{-1}) during the closure period, indicating that CH_4 was released from the water surface to the atmosphere by molecular diffusion. The CH_4 fluxes at the water surface fluctuated between 0.7 and 218.7 mg m^{-2} h^{-1} on the observation days, which are similar to previously reported values of -0.6 – 192.0 mg m^{-2} h^{-1} (Byrnes et al. 1995).

The large CH_4 emissions via bubble ebullition mainly occurred between 10:00 am and 5:00 pm local time (Fig. 4.3a). During this period, atmospheric pressure markedly decreased and reached a minimum value (Fig. 4.3b). A night-time CH_4 ebullition event also occurred at 2:50 am local time on September 21 (Figs. 4.2c, 4.3a, 4.3b), once again when air pressure decreased. There was a significant negative linear correlation between atmospheric pressure and $\log_{10}$-CH_4 emission by bubble ebullition (Fig. 4.4a; $r=-0.77$, $p<0.001$). These results suggesting that decreases in atmospheric pressure triggered the CH_4 ebullitions in the tropical rice paddy field are supported by the findings of at Tokida et al. (2005, 2007) who reported that decreases in atmospheric pressure triggered CH_4 ebullitions in peatlands.

In peatlands, air pressure reduction expands bubble volume and thereby enhances bubble buoyancy which causes the bubbles to rise to the water surface (Fechner-Levy and Hemond 1996).

Reduced air pressure also increases the CH_4 concentration of gas bubbles by degassing dissolved CH_4 in soil solution (Fechner-Levy and Hemond 1996; Baird et al. 2004; Tokida et al. 2009). These factors probably caused the higher CH_4 emissions via ebullition that were found in the current study. Moreover, the higher CH_4 ebullition emissions in the daytime, compared with nighttime, is probably due to larger decreases in daytime atmospheric pressure which would increase the volume of the bubbles and the CH_4 concentration.

Rising soil temperature also increases the buoyancy and CH_4 concentration of bubbles as barometric pressure decreases (Kellner et al. 2006; Tokida et al. 2009). In the current study, soil surface temperature increased from around 6:30 am and reached a maximum value at 3:00-3:30 pm on each day (Fig. 4.3b). This period approximately corresponded to that when CH_4 ebullition events frequently occurred. The positive and significant correlation between soil surface temperature and $\log_{10}$-CH_4 emission via bubble ebullition ($r=0.66$; $p<0.005$; Fig. 4.4b), indicates that the increase in soil surface temperature contributed to CH_4 ebullitions in the daytime. Ebullition events occurred at 8:50 am on both days and at 9:50 am on September 21, even though atmospheric pressure did not fall between 6:30 am and 10:00 am on either day. These ebullitions indicate that the rising soil temperature principally triggered the release of bubbles at those times. Rising soil temperature also has a role in enhancing methanogenic activities, leading to increases in CH_4 production in soil (Yao and Conrad 2000). Therefore such increased biological activities might have also increased the CH_4 concentration in the bubbles.

CH_4 emission via bubble ebullition (546–617 mg m^{-2} d^{-1}) contributed 95–96 % of total daily CH_4 emission (567–647 mg m^{-2} d^{-1}) through flooded water (Table 4.1). These CH_4 ebullitions mainly occurred in the daytime and were associated with falling atmospheric pressure and increasing soil temperature, as discussed above (Figs. 4.3a, 4.3b). In contrast, CH_4 emission by diffusion (21–30 mg m^{-2} d^{-1}) accounted for only 3.7–4.7 % of total daily CH_4 emission from flooded water (Table 4.1). The CH_4 emissions by diffusion were mostly observed at nighttime when soil temperature decreased (Figs. 4.3a, 4.3b). Therefore, these results clearly show that CH_4 emission in rice paddy fields is predominantly by daytime ebullition from flooded water with much lower CH_4 emissions at nighttime

by diffusion.

4.4.2 CO_2 emission

Episodic increases in CO_2 concentration were found in 14 of the 21 measurements when CH_4 ebullition events occurred. During these 14 chamber closure periods, the CO_2 concentration in the chamber air increased abruptly (Figs. 4.2b, 4.2f) at about the same time as CH_4 concentration increased (Figs. 4.2a, 4.2e). These similar patterns indicate that CO_2 was released to the atmosphere in the bubbles along with the CH_4. In the other 7 measurements, there was a steady increase in CO_2 concentration but no episodic increase, as shown in Fig. 4.2d, while CH_4 concentration abruptly increased (Fig. 4.2c). This suggests these bubbles did not contain much CO_2.

CO_2 uptake via the photosynthetic activities of the aquatic plants was also observed in these measurements. In the other 25 measurements, there was a transfer of CO_2 from flooded water to the atmosphere by diffusion, likely due to the gradient in CO_2 concentration at the interface between the flooded water and the atmosphere, and also due to respiration of the aquatic plants (Koizumi et al. 2001). The values of CO_2 fluxes ranged between -120.4 and 196.2 mg m^{-2} h^{-1} which are within the previously reported range of -285.1 to 459.4 mg m^{-2} h^{-1} (Liu et al. 2013).

On September 20, most of the CO_2 fluxes were outgoing emissions due to bubble ebullitions. The highest CO_2 emission (196.2 mg m^{-2} h^{-1}) occurred at 2:50 pm (Figs. 4.2d, 4.3a), coinciding with a high CO_2 concentration in the bubbles of up to 11.74 % (v/v). However, at 1:50 pm there was a negative (incoming) CO_2 flux, even though there was a CO_2 ebullition event. This overall negative flux must have been due to the fact that CO_2 uptake by photosynthesis of the aquatic plants exceeded emissions by bubble ebullition, as shown in Fig. 4.2f for CO_2 transfer.

During the daytime on September 21, the CO_2 fluxes mainly showed negative values even though CO_2 ebullition events were observed. Therefore, this indicates that CO_2 assimilation by the aquatic plants dominated CO_2 fluxes on that day.

The $\log_{10}$-CO_2 emissions by bubble ebullitions, omitting measurements with evidence of

absorption by plant photosynthesis, were significantly correlated to changes in atmospheric pressure ($r=-0.72$; $p<0.05$; Fig. 4.4c) and soil surface temperature ($r=0.72$; $p<0.05$; Fig. 4.4d). This indicates that these two environmental factors control CO_2 ebullition in addition to CH_4 ebullition. As previously discussed, these two triggered expanding bubble volume and degassing of gas dissolved in soil solution (Fechner-Levy and Hemond 1996; Kellner et al. 2006). In addition, the soil surface temperature was between 27 and 40 ^oC during the measuring period which was optimal for respiratory soil microbes in the submerged paddy soil (Yao and Conrad 2000). Therefore, all these factors probably enhanced CO_2 bubble ebullitions.

CO_2 emission by bubble ebullition, accounted for only 13–35 % of total CO_2 emissions, compared with 65-87% from CO_2 diffusion (Table 4.2), indicating that CO_2 ebullition did not dominate CO_2 emissions from flooded water unlike CH_4 ebullition. This is probably due to the fact that CO_2 uptake by aquatic plants would have exceeded CO_2 emission by bubble ebullition. Moreover, the very low concentration of CO_2 in the bubbles also contributed to lower CO_2 emission by bubble ebullition. The CO_2 emissions by diffusion mostly occurred at nighttime just like for CH_4. The nighttime CO_2 emissions by diffusion were mostly attributed to the gradient in CO_2 concentrations between the atmosphere and the flooded water, and also to CO_2 respiration by small aquatic plants (Koizumi et al. 2001).

4.5 Conclusions

Our study found that daytime CH_4 ebullition events in tropical rice paddy fields occurred due to falling atmospheric pressure and increasing soil surface temperature. At nighttime, the drop in atmospheric pressure predominately triggered the CH_4 ebullition because soil temperature was low compared with that in the daytime. The fact that CH_4 and CO_2 concentrations in the chamber air increased abruptly when bubbles were released suggests that bubble ebullition events caused not only CH_4 emission but also CO_2 emission. The CO_2 ebullition events were also controlled by decreases in air pressure and increases in soil temperature. Therefore, diurnal changes in atmospheric pressure and

soil temperature play major roles in regulating CH_4 and CO_2 ebullitions in tropical rice paddy fields.

We also found that CH_4 emission was predominantly due to daytime ebullition, whereas only a small proportion of CO_2 emissions were due to daytime ebullition. The low CO_2 ebullition throughout the day was due to CO_2 photosynthesis and respiration by aquatic plants, meaning that CO_2 emission was mainly by diffusion between flooded water and the atmosphere.

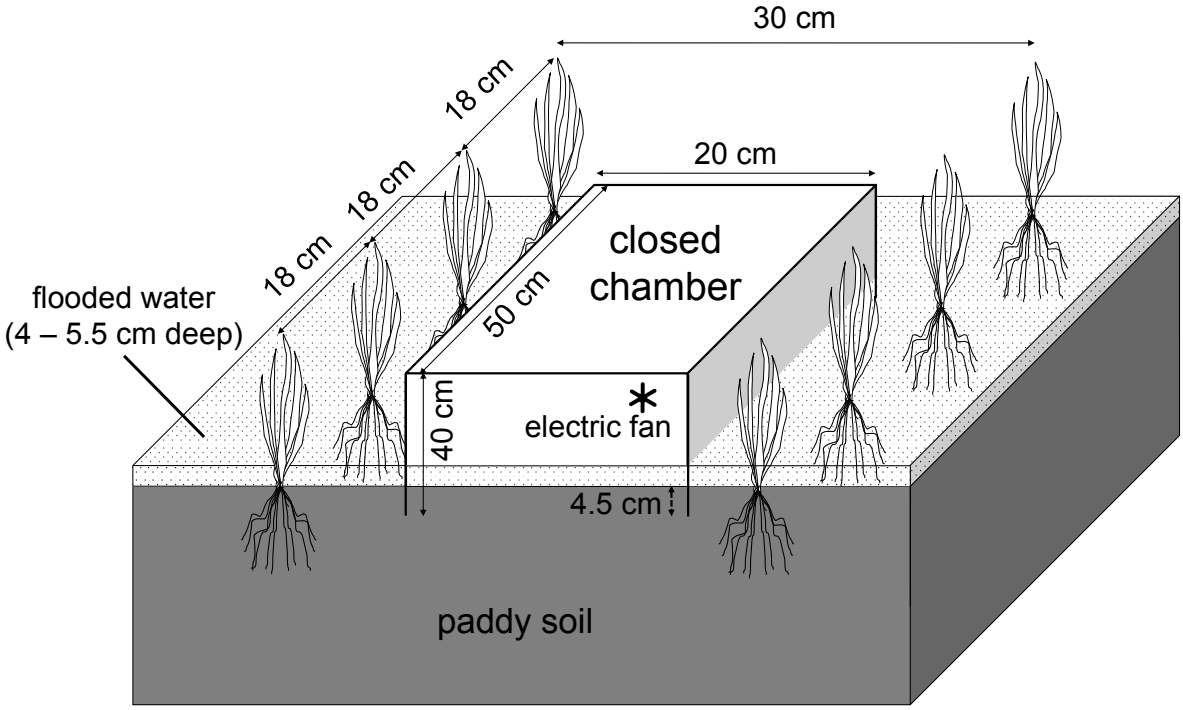

Fig. 4.1 Schematic diagram of an automatic closed chamber placed between the rows of rice plants.

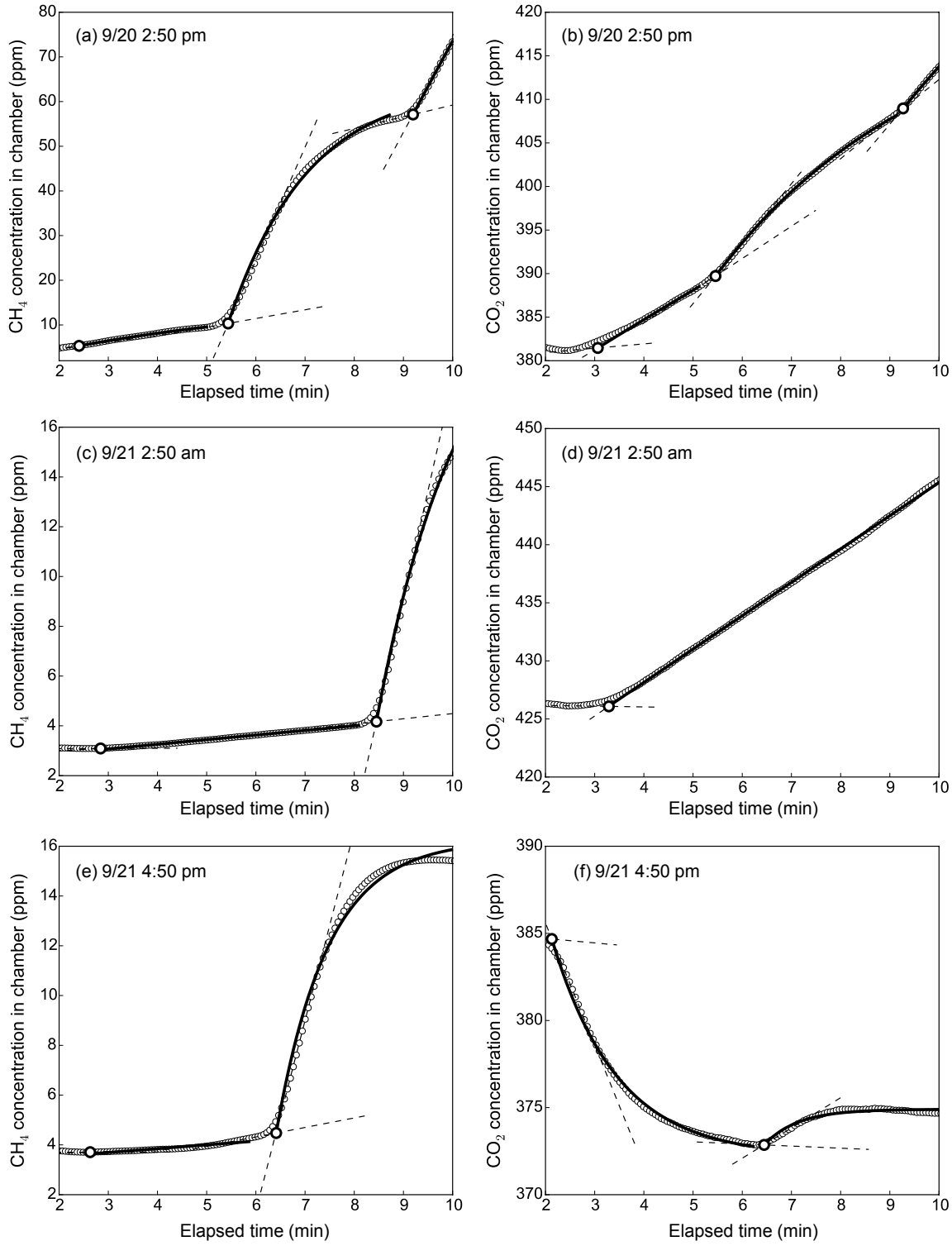

Fig. 4.2 Examples of the changes in CH_4, CO_2 concentrations (7-point running average) in the closed chamber measured at 2:50 pm on September 20 (a), (b), at 2:50 am on September 21 (c), (d) and at 4:50 pm on September 21 (e), (f). The solid line denotes the best fitting line for each emission/uptake. The

white circle with black edge indicates the event starting point. The dashed lines denote the tangent lines at the local maximum or minimum points for CH_4, CO_2 emission/uptake rates, before respective increase or decrease events.

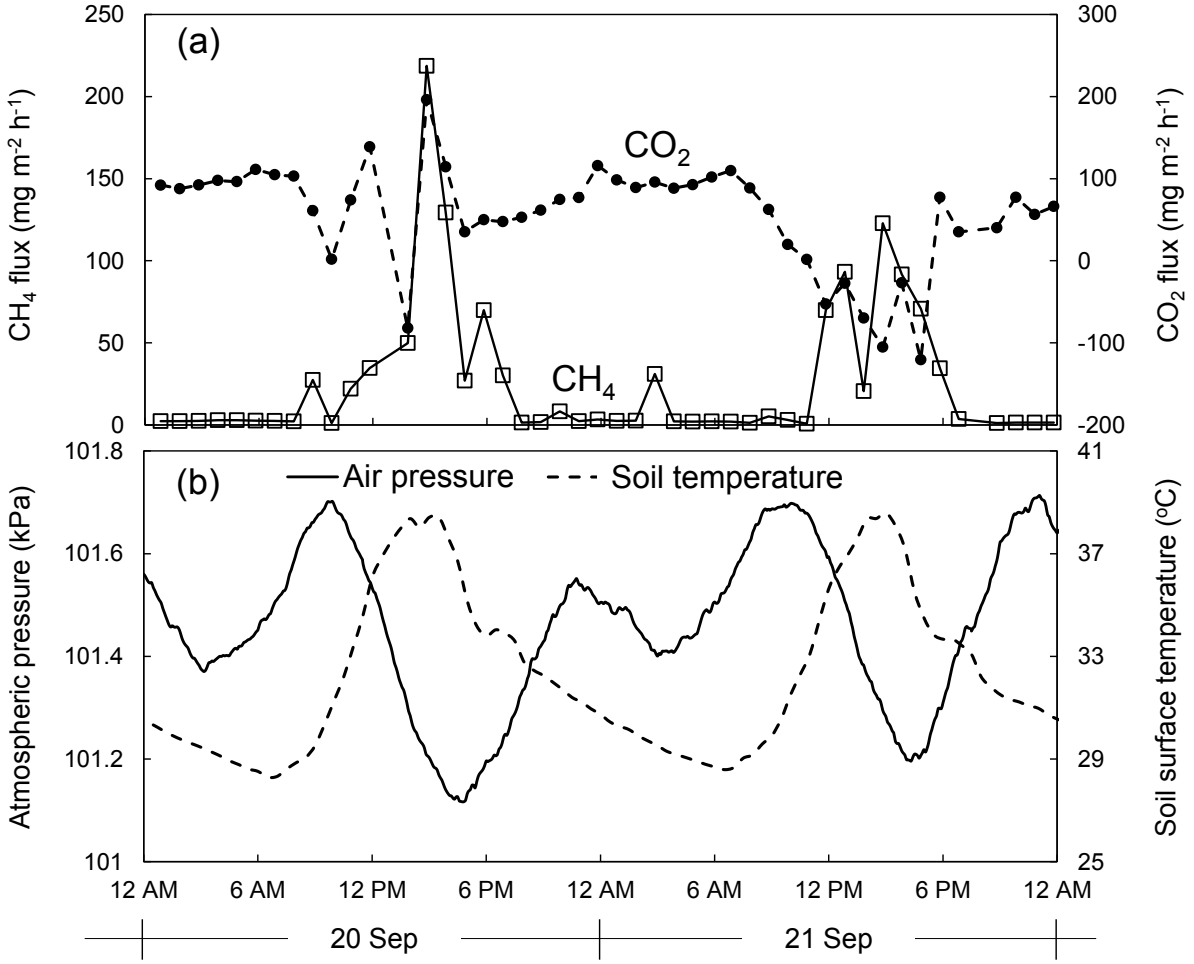

Fig. 4.3 Temporal changes on September 20 and 21 in (a) CH_4 and CO_2 fluxes measured with the automatic closed chamber method, and (b) atmospheric pressure and soil surface temperature.

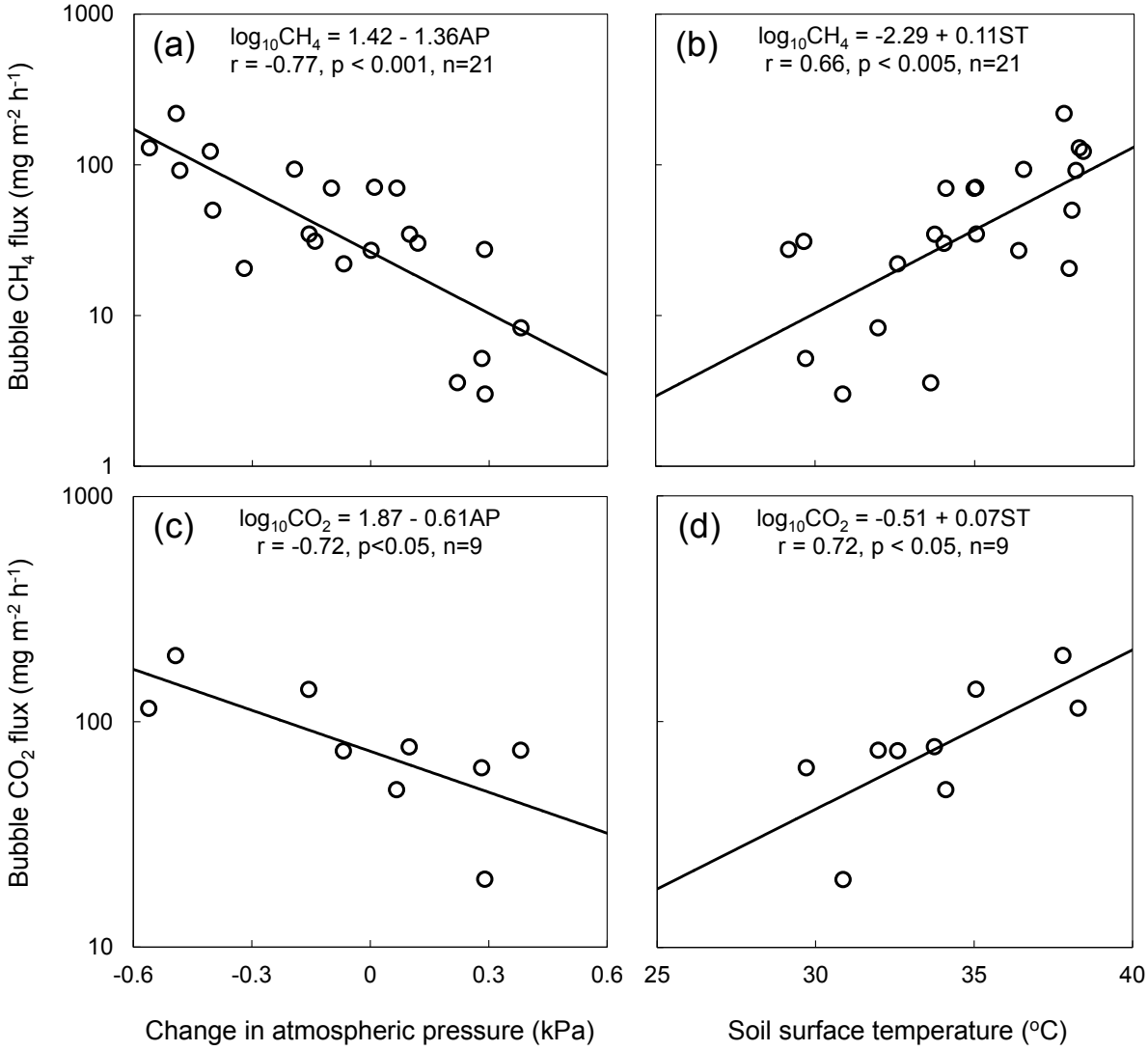

Fig. 4.4 Relationship between CH_4 emission by bubble ebullition and change of atmospheric pressure (a) or soil surface temperature (b). Relationship between CO_2 emission by bubble ebullition and change of atmospheric pressure (c) or soil surface temperature (d). The change in atmospheric pressure was determined as the difference between the local maximum or minimum value and the value closest to the time when the CH_4 or CO_2 ebullition occurred.

Table. 4.1 Cumulative CH_4 emissions and relative contribution of bubble ebullition and diffusion processes to total emissions.

Date	CH_4 ebullition ($mg\ m^{-2}\ d^{-1}$)	via CH_4 ebullition (%)	CH_4 diffusion ($mg\ m^{-2}\ d^{-1}$)	via CH_4 diffusion (%)	Total CH_4 emission ($mg\ m^{-2}\ d^{-1}$)
20 Sep	617.4	95.3	30.3	4.7	647.7
21 Sep	546.2	96.3	20.9	3.7	567.1

Table. 4.2 Cumulative CO_2 emissions and relative contributions of bubble ebullition and diffusion processes to total emissions.

Date	CO_2 ebullition (mg m^{-2} d^{-1})	via CO_2 ebullition (%)	CO_2 diffusion (mg m^{-2} d^{-1})	via CO_2 diffusion (%)	Total CO_2 emission (mg m^{-2} d^{-1})
20 Sep	648.2	35.0	1203.8	65.0	1852.0
21 Sep	159.7	13.3	1040.4	86.7	1200.1

Chapter 5

Methane dynamics through plants and water surface in tropical rice paddy fields

5.1 Abstract

CH_4 in paddy soil during irrigated growth periods is mainly released through rice plants and floodwater, but separate CH_4 emission dynamics via plant or water, has not been clearly evaluated. In order to elucidate CH_4 emission dynamics in rice paddies in more detail, we separately investigated the main three processes of CH_4 production, oxidation and transportation at the soil-plant-atmosphere and soil-water-atmosphere interfaces around the heading stage in tropical rice paddy fields using natural abundance carbon stable isotope ratios ($\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2). The soil gases in the rhizosphere were enriched with $^{13}CH_4$ and $^{12}CO_2$ relative to those in the non-rhizosphere, suggesting that CH_4 oxidation occurred in the rhizosphere due to oxygen supply through root aerenchyma. The rate of CH_4 production by acetoclastic methanogens in the rhizosphere surpassed that in the non-rhizosphere because of organic materials derived from rice roots. The $\delta^{13}C$-CH_4 in the aerenchyma almost corresponded to that at 15 cm deep in the rhizospheric soil, indicating that soil CH_4 entered the root aerenchyma with little isotopic fractionation. The diurnal changes of $\delta^{13}C$-CH_4, emitted via the plant, were similar to those of CH_4 oxidation in the rhizosphere. The diurnal variations of CH_4 emission rates via the plant seemed to be regulated by those in the conductance of lacunal CH_4 diffusion near the soil surface. Bubble CH_4 in the non-rhizosphere was seemed to be released through floodwater from 9cm deep or deeper without large isotopic fractionation. The isotopic signatures of CH_4 also revealed that the CH_4 diffusion process, defined as a steady increase in CH_4 concentration, involved not only CH_4 diffusion but also steady ebullition of micro CH_4 bubbles. Bubble ebullition events were frequently observed in the daytime, whereas the diffusion processes dominated CH_4 emission in the nighttime.

5.2 Introduction

Increasing concentration of atmospheric methane (CH_4) contributes to global climate change (IPCC, 2013). CH_4 emissions from anthropogenic sources account for 54-72% of the total global CH_4 emission (Bridgham et al., 2013). Rice paddy fields are one of the largest anthropogenic CH_4 sources (Bridgham et al., 2013). The estimated CH_4 emission from global rice paddies ranges between 25 - 300 Tg CH_4 yr^{-1}, which still has a large margin of error (Bridgham et al., 2013). Yan et al. (2009) reported that 90% of CH_4 emission from the world's rice paddies is derived from tropical Asia. In order to constrain the uncertainty, further field observations of CH_4 emission dynamics and the regulating factors in tropical rice paddies are needed (Melton et al., 2013; Bridgham et al., 2013).

During irrigated rice cropping seasons, CH_4 is mainly produced from fermentation of acetate and reduction of carbon dioxide with hydrogen (H_2/CO_2) by methanogens which are activated by anaerobic submerged soil condition (Takai, 1970; Whiticar et al., 1986; Conrad, 2005). Some of the soil CH_4 is oxidized by methanotrophic bacteria in the aerobic surface soil and rice rhizosphere soil where oxygen is supplied from atmosphere via the rice aerenchyma system (Schütz et al. 1989). The unoxidized CH_4 in paddy soil is mainly released into atmosphere through either the rice plants, bubble ebullition or molecular diffusion between paddy water and atmosphere (Schütz et al. 1989; Chanton, 2005). Since CH_4 emission dynamics are primarily controlled by CH_4 production, oxidation and transportation (Schütz et al. 1989), studies on the main three processes are required so as to clarify CH_4 emission dynamics in rice paddy fields.

Natural abundance stable carbon isotope methods are useful for understanding the processes of CH_4 production, oxidation and transportation in rice paddy fields (Tyler et al., 1997; Conrad, 2005; Chanton, 2005). The $\delta^{13}C$ values of CH_4, CO_2 and acetate make it possible to estimate the relative contribution of acetate- and H_2/CO_2-dependent methanogenesis to total CH_4 production, and the proportion of CH_4 consumption by methanotrophs (Tyler et al., 1997; Krüger et al., 2002; Conrad, 2005). The $\delta^{13}C$ of emitted CH_4 also enables evaluation of the transportation modes from paddy soil to

atmosphere (Chanton, 2005; Tokida et al., 2014).

Recently, studies using natural carbon stable isotopes have reported on CH_4 production, oxidation and transportation in rice paddy fields (Tyler et al., 1994, 1997; Bilek et al., 1999; Krüger et al., 2002; Krüger and Frenzel, 2003; Nakagawa et al., 2002; Rao et al., 2008; Zhang et al., 2011, 2012, 2013). The previous researchers mainly investigated the linkages between soil CH_4 and emitted CH_4, mixed by the plant- and water-mediated pathways because the plant-mediated transportation usually dominated the overall CH_4 emission (90%) and the water-mediated transportation was considered to be negligible (Schütz et al. 1989; Butterbach-Bahl et al., 1997). However, Wassmann et al. (1996) reported that CH_4 ebullition through flooded water accounted for 35-62 % of total emissions when rice straw was applied to tropical rice paddy fields. The high contribution of CH_4 emission via water makes it difficult to comprehend the entire CH_4 cycling in rice paddies accurately. Therefore, studies are required on the separate CH_4 emission dynamics (production, oxidation and transportation) at the soil-plant-atmosphere and soil-water-atmosphere interfaces (Bridgham et al., 2013).

In this study, we investigated the CH_4 emission dynamics at both the soil-plant-atmosphere and soil-water-atmosphere interfaces in tropical rice paddy fields in Thailand using carbon stable isotopes.

5.3 Materials and Methods

5.3.1 Field measurements

Field experiments were carried out between September 17 and 26 in 2014 in a farmer's rice paddy field at Kasetsart University (14° 00' 33"N, 99° 59' 03"E), Kamphaeng Saen campus in Nakhon Pathom Province, Thailand. The paddy soil was classified as clay soil (65.7 % clay; 23.30 % silt; 11.0 % sand). The topsoil, sampled on September 17, had a soil pH of 5.98 (1:1, soil:water), 4.32 % organic matter, 1.81 % total carbon and 1.85 % total nitrogen. Weeds and weedy rice were plowed into the paddy field soil on June 17 and 26, and then 4-5 seedlings of the rice variety "Homcholasit" were transplanted per hill at 18 × 30 cm space on June 30. The heading of the rice plants began on

September 22. Continuous flooding was conducted between June 17 and October 28 (harvest day) at 2-20 cm water depth. From the start of the gas measurement period on September 17 to the midday on September 24, the floodwater depth decreased from 7.8 to 2.5 cm. Then the water depth rose to 10.6 cm due to heavy rain (21.9 mm day^{-1}) on September 24, followed by another declined to 8.3 cm by the midnight on September 26.

The emissions of CH_4 and $\delta^{13}C\text{-}CH_4$ through rice plants and paddy water were measured using two automatic closed chambers. On August 20, one polycarbonate chamber for the plant-mediated transportation (24 × 24 cm at the base and 140 cm tall, Green Blue Corp., Tokyo, Japan) was placed over a rice hill with the lid left open. From September 13, the water surface at the bottom of the plant-chamber was covered by cushioning material to prevent capture of methane emissions via paddy water, in order that (as much as possible) the chamber only captured CH_4 transported through the rice plants. The other polycarbonate chamber (50 × 20 cm at the base and 40 cm height, Green Blue Corp., Tokyo, Japan) was inserted between rice plants on August 8 to measure the CH_4 exchanges via paddy water. From September 17 to 24, the top lid of each chamber was automatically closed for 10 min every hour, and the CH_4 fluxes and emitted $\delta^{13}C\text{-}CH_4$ at each chamber were measured. The headspace air in each chamber was mixed during lid closure using a small electric fan which was incorporated into each chamber. The fans also ran during non-measurement periods when the lids were open in order to prevent the gas residence at the bottom of the tall chambers. During the lid closure period, the headspace air in each chamber was circulated through a wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) analyzer (G2201-i, Picarro Inc., Santa Clara, CA, USA) which monitored the change in CH_4 concentration and $\delta^{13}C\text{-}CH_4$ in each chamber at around 3.6 s intervals. The initial air after closing the chambers reached the WS-CRDS analyzer in 2 min. Each chamber measurement was finished when the lid of the chamber opened, so that one measurement cycle for each chamber ran for 8min. The measurement system between each chamber and the CH_4/CO_2 analyzer was the same as that described by Komiya et al. (2015).

Methane flux was calculated using exponential or linear regression methods (de Mello and Hines 1994; Davidson et al. 1998) following Komiya et al. (2015). The $\delta^{13}C\text{-}CH_4$ (δ_s) in the released CH_4

was calculated as

$$\delta_s = [(C_{end} \times \delta_{end}) - (C_{ini} \times \delta_{ini})] / (C_{end} - C_{ini}) \quad (5.1)$$

where C_{ini} and δ_{ini} are the 1-min averages of the concentration (ppm) and $\delta^{13}C$ value in the chamber air immediately before the start of measurement, and C_{end} and δ_{end} are the 1-min averages of the concentration (ppm) and $\delta^{13}C$ value in the chamber air at the end of measurement.

The gases in the paddy soil and water were collected using diffusive equilibration samplers. The diffusive equilibration samplers consisted of a PVC pipe (id = 38 mm; od = 39 mm; length = 400 mm) with several drilled holes of 7 mm dia., and a 0.5 mm thick silicon sheet which entirely covered the pipe (Fig. 5.1, Katano, 2015), similar to Kato et al. (2013). The soil/water contact side of the silicon sheet was protected by wrapping that side of the sheet in a plastic mesh. Both ends of the sampler were sealed with silicon rubber stoppers, and one of the rubber stoppers was connected to a nylon tube which was extended above ground in order to collect gas samples. The soil gas samplers were buried horizontally at 3, 9 and 15 cm depths under both a rice hill and an unplanted space between rice plants on July 30. The water gas sampler was submerged flat in the flooded water on July 30. The gas samples under the planted soil were taken by plastic syringes at noon local time on September 18, 20 and 26. The gases in the unplanted soil and surface water were collected at noon local time on September 17, 20 and 26. After sampling the gases, the end of nylon tube above ground was sealed by a three-way stopcock to prevent gas exchange between the sampler and atmosphere during non-measurement periods. We measured the concentration and $\delta^{13}C$ of CH_4, CO_2 in the soil/water gas samples, which were diluted 101x with high-purity nitrogen gas, using the WS-CRDS analyzer.

The $\delta^{13}C$-CH_4 measurement was calibrated using two CH_4 working standard gases: $\delta^{13}C$-CH_4 = -43.3‰ (5, 13 and 1000 ppm CH_4, 1000 ppm CO_2, N_2 balance) and $\delta^{13}C$-CH_4 = -66‰ (1000 ppm CH_4, N_2 balance). The $\delta^{13}C$-CO_2 measured by the WS-CRDS analyzer was also calibrated by two CO_2 working standard gases: $\delta^{13}C$-CO_2 = -9.468±0.039‰ (403 ppm CO_2, N_2/O_2 balance) and $\delta^{13}C$-CO_2 = -34.732±0.028‰ (9790 ppm CO_2, N_2 balance). Before the calibration, the high CO_2 gas concentration (9790 ppm) was diluted to 3647.25 ppm with high-purity nitrogen gas because the original concentration was too high concentration for the WS-CRDS analyzer.

Atmospheric pressure was measured with a barometer (MPXAZ6115A and MPXV7007DP, Freescale Inc., TX, USA), and air temperature was measured with a temperature sensor (HMP45A, Vaisala Inc., Helsinki, Finland). Soil temperatures were measured at 0, 3, 9 and 15 cm below the soil surface with type T thermocouples. Water depth above the soil surface was measured with a water level sensor (eTapeTM Continuous Fluid Level Sensor, Milone Technologies Inc., NJ, USA).

5.3.2 CH_4 production and oxidation analysis

Assuming that total CH_4 is produced from acetate and H_2/CO_2 substrates, the proportion of acetate fermentation (f_{ac}) and H_2/CO_2 reduction ($1\text{-}f_{ac}$) to net CH_4 production is obtained using the following mass balance equation (Tyler et al., 1997; Krüger et al., 2002; Conrad, 2005),

$$\delta^{13}CH_4 = f_{ac} \times \delta^{13}CH_{4(acetate)} + (1 - f_{ac}) \times \delta^{13}CH_{4(H2/CO2)} \quad (5.2)$$

where $\delta^{13}CH_{4(acetate)}$ and $\delta^{13}CH_{4(H2/CO2)}$ are the $\delta^{13}C$ values of acetate-derived and H_2/CO_2-derived CH_4, respectively. $\delta^{13}CH_4$ is the δ^{13}C value of total CH_4. The range of $\delta^{13}CH_{4(acetate)}$ has been frequently reported between -37 to -43‰ in Japanese and Italian rice paddy soils (Sugimoto and Wada, 1993; Krüger et al., 2002). Therefore, the value of $\delta^{13}CH_{4(acetate)}$ was determined as the average, -40‰.

The value of $\delta^{13}CH_{4(H2/CO2)}$ is calculated through the following definitional equation for carbon isotope fractionation factor ($\alpha_{CO2/CH4}$),

$$\alpha_{CO2/CH4} = (\delta^{13}CO_2 + 1000) / (\delta^{13}CH_{4(H2/CO2)} + 1000) \quad (5.3)$$

solved for $\delta^{13}CH_{4(H2/CO2)}$,

$$\delta^{13}CH_{4(H2/CO2)} = (\delta^{13}CO_2 + 1000) / \alpha_{CO2/CH4} - 1000 \quad (5.4)$$

where $\delta^{13}CO_2$ is the $\delta^{13}C$ value of the CO_2. The $\alpha_{CO2/CH4}$ in submerged paddy soil decreased from 1.083 to 1.076 as temperature rises from 10 to 37 ^oC (Fey et al., 2004). Therefore, as the mean soil temperature at 3-15 cm depth was 30.4 ^oC on the gas sampling days, the value of $\alpha_{CO2/CH4}$ was set to be 1.078 at 30 ^oC (Fey et al., 2004).

The fraction of CH_4 oxidation (F_{ox}) is estimated by the following equation (Tyler et al., 1997),

$$F_{ox} = (\delta^{13}CH_{4(initial)} - \delta^{13}CH_{4(oxidized)}) / [(1/\alpha_{ox} - 1) \times (\delta^{13}CH_{4(oxidized)} + 1000)] \quad (5.5)$$

where $\delta^{13}CH_{4(initial)}$ is the δ^{13}C value of initial and unoxidized CH_4 produced in soil, and $\delta^{13}CH_{4(oxidized)}$ is the δ^{13}C value of CH_4 oxidized by methanotrophs. α_{ox} is the isotopic fractionation during the CH_4 oxidation process. α_{ox} is nonlinearly related to temperature in landfill soil, which is similar to anaerobic paddy soil (Chanton et al., 2008). The value of α_{ox} was determined as 1.025 at 30 ^{o}C following Chanton et al. (2008), because the mean soil temperature was 30.4 ^{o}C, as mentioned above.

5.4 Results and Discussion

5.4.1 CH_4 oxidation, production

The mean CH_4 concentrations at each depth in the planted rhizospheric soil were lower than those in the unplanted non-rhizospheric soil (Fig. 5.2a), but the CO_2 concentrations in the planted soil were higher than that in the unplanted soil (Fig. 5.2b). The gases in the planted rhizosphere had enriched $^{13}CH_4$ and $^{12}CO_2$ relative to those in the unplanted non-rhizosphere (Fig. 5.2). Rhizospheric CH_4 is partly oxidized to CO_2 because oxygen is available for the methane-oxidizing bacteria in the rhizosphere due to transportation from atmosphere via rice aerenchyma (Schütz et al. 1989; Hayashi et al., 2015). Moreover, methanotrophic bacteria preferentially consume $^{12}CH_4$ and produce $^{12}CO_2$, leaving residual ^{13}C-enriched CH_4 (Coleman et al., 1981; Happell et al., 1994). These findings suggest that CH_4 oxidation occurred in the rhizosphere during the measurement period in our study. In addition, root respiratory CO_2 might have partly contributed to enhancing the concentration of $^{12}CO_2$ (Zhu and Cheng, 2011).

The minimum CH_4 concentration (7.0% v/v) and maximum δ^{13}C-CH_4 (-45‰) occurred at 15 cm deep in the rhizosphere soil (Fig. 5.2a). The largest difference in δ^{13}C-CH_4 between planted and unplanted soil (7.4‰) also occurred at 15cm depth. Furthermore, the planted soil gas at 15 cm deep also contained the largest CO_2 concentration (25.7% v/v) and the smallest δ^{13}C-CO_2 (-15.3‰) (Fig. 5.2b). These findings indicate that the methanotrophic bacteria had the highest activity at 15 cm depth

in the planted soil.

The estimated proportion of CH_4 oxidation using Eq. (5.5) also showed the highest level of CH_4 consumption at 15 cm depth (Table 5.1). The f_{ox} values at each depth were defined as the fraction of CH_4 oxidiation that occurred in the planted rhizosphere assuming that CH_4 produced in the unplanted non-rhizosphere soil was exposed to the oxidized rhizosphere at each depth. The $\delta^{13}C$ values of soil CH_4 in unplanted and planted soil were substituted for $\delta^{13}CH_{4(initial)}$ and $\delta^{13}CH_{4(oxidized)}$ at each depth, respectively.

Oxygen release via aerenchyma occurs from the apical part of rice roots because the barriers to radial oxygen loss (ROL) are developed in the basal zones of roots in order to transfer oxygen to the root tip (Armstrong 1979, Armstrong et al., 2000; Nishiuchi et al., 2012). The rice cultivar used in the study typically has roots extending to 15-40 cm depth, with a high root density at 0-15 cm depth during tillering - flowering stage (Meechai, personal communication), indicating that there would have been more root tips around 15 cm depth as compared to at 3, 9 cm depths. This higher density of root tips probably resulted in a higher supply of oxygen at 15 cm depth, which promoted CH_4 oxidation by methanotrophic bacteria.

The flooded water had the highest value of $\delta^{13}C$-CH_4 (-37.9‰), but it had the second lowest values of $\delta^{13}C$-CO_2 (-13.9‰) (Fig. 5.2). When CH_4 transfers from soil to flooded water, $^{12}CH_4$ is preferentially transformed to $^{12}CO_2$ at the oxidized soil-floodwater interface by the methane-oxidizing bacteria (Happell et al., 1994; Chanton, 2005). In addition, the lighter $^{12}CH_4$ isotope in the floodwater is diffusively released into the atmosphere faster than the heavier $^{13}CH_4$ isotope at the water-air interface, leaving more $^{13}CH_4$ in the floodwater (Chanton, 2005). These facts probably contributed to the enhanced concentrations of $^{13}CH_4$ and $^{12}CO_2$ in the surface water.

The proportions of the acetate-derived CH_4 production at 3, 9, 15 cm depths in both the planted and unplanted soils are given in Table 5.1. The f_{ac} values were then estimated using the $\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2 in the soil gas at each depth (Table 5.1). The f_{ac} values in the soils ranged from 30 to 86% (Table 5.1), which is similar to previously estimated values for rice paddy fields in Thailand of between 45% to 83% (Nakagawa et al., 2002; Chawanakul et al., 2009).

CH_4 production by acetoclastic methanogenesis in the planted rhizosphere soil exceeded that in the unplanted non-rhizosphere soil (Table 5.1). Paddy soils at the heading stage contain abundant acetate substrate in the rhizosphere derived from root exudates and root decay (Schütz et al. 1989; Hayashi et al., 2015), which probably enhanced the activity of acetoclastic methanogens in the rhizosphere soil (Chawanakul et al., 2009).

The f_{ac} values increased with depth in both the planted and unplanted soil (Table 5.1). This indicates that there was more acetate in the deeper zones in both soils. In the planted soil, this would have been supplied from rice root exudation in the rhizosphere, while in the unplanted soil, it was likely derived from soil organic matter or rice straw that remained in the deeper zone due to lower acetoclastic methanogenesis at the lower temperature in deeper soil.

5.4.2 CH_4 dynamics via plants

The mean $\delta^{13}C\text{-}CH_4$ emitted via rice plants ranged from -57.8 to -59.0‰ on September 18, 20 and 26 (Table 5.2). CH_4 emission from aerenchyma to the atmosphere causes an isotopic fractionation (11 - 16‰) because of the preferential transportation of the lighter $^{12}CH_4$ isotope (Chanton et al., 1997; Tyler et al., 1997; Krüger et al., 2002; Zhang et al., 2014), which enables estimation of the $\delta^{13}C\text{-}CH_4$ values in the aerenchyma (= rhizosphere). The calculated $\delta^{13}C\text{-}CH_4$ values in the rhizosphere (-41.8 to -48.0‰) were similar to the values of $\delta^{13}C\text{-}CH_4$ at 15 cm depth (-44.1 to -48.6‰) in the planted rhizosphere soil (Table 5.2). Little is known about isotopic discrimination in the roots (Krüger et al., 2002). However, if negligible isotopic discrimination is assumed during CH_4 entry, our results indicate that soil CH_4 preferentially entered through the root surface at 15 cm deep and was then transferred via the plant into the atmosphere.

CH_4 in soil water and bubbles mainly enters the root aerenchyma due to the concentration gradient between soil water/air and aerenchyma (Nouchi et al., 1990; Tokida et al., 2013). CH_4 surrounding roots is diffusively transferred into the root aerenchyma, which generates isotopic fractionation owing to the preferential transport of $^{12}CH_4$ (Nouchi et al., 1990; Chanton et al., 1997;

Tokida et al., 2013). The passage of CH_4 is easier in the apical area than in the basal area where the barrier to ROL is developed (Armstrong 1979, Armstrong et al., 2000; Nishiuchi et al., 2012). These indicate that little isotopic discrimination occurred at 15 cm depth where root tips were concentrated.

Water uptake due to plant transpiration also possibly allows dissolved CH_4 to pass through the root surface and be emitted via the plant to the atmosphere (Nisbet et al., 2009). In our study, CH_4 concentration at 15 cm depth was markedly low (7.0% v/v) (Fig. 5.2a), indicating that methane abundance as bubbles was the smallest and so the rice roots probably could not interact easily with CH_4 bubbles. No isotopic fractionation of water occurs during the process of root water absorption (White et al., 1985; Dawson and Ehleringer, 1991). These facts suggest that the dissolved CH_4 in the soil water was also transported into the rice aerenchyma without any isotopic discrimination.

Soil CH_4 could also have entered the root aerenchyma at 3 and 9 cm depths because the aerenchyma is develop not only at the apical zone but also at the basal zone (Armstrong 1979, Hosono and Nouchi, 1997; Armstrong et al., 2000; Nishiuchi et al., 2012). The concentrations of CH_4 at 3 and 9 cm depths was about three times higher than that at 15 cm depth, meaning a larger CH_4 concentration gradient between the soil at 3, 9 cm deep and the atmosphere (Fig. 5.2a). The CH_4 gradient between soil and atmosphere mainly drives CH_4 emission (Nouchi et al., 1990). These facts indicate that soil CH_4 at 3 and 9 cm depths appeared to enter the root aerenchyma and reach the atmosphere via the plant.

The $\delta^{13}C$-CH_4 values in the aerenchyma were about 6‰ greater than those at 3, 9 cm deep in the rhizosphere soil (Table 5.2). The CH_4 concentrations at those depths were more than three times higher (22.7%, 23.9% v/v) than that at 15 cm deep (7.0 % v/v) (Fig. 5.2a), suggesting the richer CH_4 bubbles at 3, 9 cm deep in paddy soil (Tokida et al., 2013). When bubbles come into contact with the rice roots, CH_4 diffuses across the root surface into the root aerenchyma, causing isotopic fractionation as mentioned above (Nouchi et al., 1990; Chanton et al., 1997; Tokida et al., 2013). The ROL barrier, developed in the basal root, obstructs not only oxygen leakages but also CH_4 entry. These elements probably contributed the large isotopic fractionation at 3, 9 cm depth.

The typical diurnal cycle of CH_4 and environmental elements on the two sunny days is presented

in Fig. 5.3. The maximum $\delta^{13}C\text{-}CH_4$ value occurred around midday with lower values at nighttime, which roughly coincided with the diurnal patterns of the CH_4 emission rates. Chanton et al. (1997) suggested that the relationship between emitted $\delta^{13}C\text{-}CH_4$ and CH_4 flux was related to the diurnal variation in transpiration. Our results also showed that soil CH_4 might be transported into the atmosphere by transpiration as discussed above. Thus, the diurnal patterns of transpiration partly appeared to affect the diurnal variation in CH_4 transportation.

In contrast to Chanton et al. (1997), Nouchi et al. (1990) found that CH_4 was mainly released from micropores in the leaf sheaths rather than leaf stomata, and that CH_4 emission via rice plants didn't depend on transpiration. This fact indicates that there are other stronger factors regulating diurnal variations of CH_4 transportation. The CH_4 fluxes during the entire measurement period were positively and significantly related to the rhizospheric $\delta^{13}C\text{-}CH_4$ which was estimated using fixed isotopic fractionation during transportation (-13.5‰) (Fig. 5.4a). Cho et al. (2012) recently showed that oxygen supply via aerenchyma increased in the daytime and declined in the nighttime, leading to the higher CH_4 oxidation in the daytime and lower CH_4 oxidation at nighttime. These results suggest that the diurnal variations of CH_4 oxidation in the rhizosphere caused the diurnal variations in the $\delta^{13}C\text{-}CH_4$ emitted via the plants.

Although the diel change in released $\delta^{13}C\text{-}CH_4$ can be explained by that of CH_4 oxidation, the enhanced CH_4 oxidation in the daytime indicates lower CH_4 abundance in the rhizosphere. Therefore, the diurnal changes of CH_4 emissions from the aerenchyma are probably controlled by the other elements. Hosono and Nouchi (1998) reported that CH_4 emission increased with increasing conductance of rice plants for CH_4 diffusion, due to the increase in soil temperature. CH_4 emission rates were positively related with soil temperature at 0, 3, 9, 15 cm depths (Fig. 5.5), which probably resulted in the enhanced release of lacunal CH_4 in the daytime.

The strongest relationship between CH_4 flux and soil temperature was initially expected to be at 3cm depth where there was the maximum CH_4 concentration gradient and at 15 cm depth where there was no isotopic fractionation. Nevertheless, the strongest correlation was at the soil surface, and declined with increasing soil depth (Fig. 5.5). Hosono and Nouchi (1998) also showed positive

stronger relationship at 1cm depth than at 5cm depth where the maximum soil CH_4 concentration occurred. These results suggest soil CH_4 entered the root and was transported to the aerenchyma near the soil surface, and then the transport of this lacunal CH_4 into the atmosphere increased with rising soil surface temperature.

5.4.2 CH_4 dynamics via water

The $\delta^{13}C$-CH_4 emitted via flooded water on the soil gas sampling days is shown in Table 5.3. The bubble ebullition and molecular diffusion processes were defined as the episodic increase of CH_4 concentration and the steady increase in CH_4 concentration, respectively (Komiya et al. 2015).

The values of $\delta^{13}C$-CH_4 released via bubble ebullition on September 17 and 20 were very similar to those at 9 cm soil depth (Table 5.3). Bubbles in soil pass through the soil surface (oxidation zone) rapidly and reach the atmosphere without isotopic fractionation, which results in almost the same isotopic composition of the emitted and bubble CH_4 (Martens et al., 1986; Chanton, 2005). Therefore, this suggests that the released bubbles on September 17, 20 originated from around 9cm depth. However, the $\delta^{13}C$-CH_4 emitted via bubble ebullition on September 26 was 4.2‰ lower than that at 9 cm in soil (Table 5.3). The $\delta^{13}C$-CH_4 in soil bubbles varies spatially (Happell et al., 1994). In addition, the gas collected in the permeable gas samplers was an average of dissolved CH_4 with depleted $^{12}CH_4$ and bubble CH_4 with enriched $^{12}CH_4$. Therefore, it suggests that the samplers could not directly catch the released bubbles that were more enriched in $^{12}CH_4$.

Bubble ebullition triggers not only high CH_4 emission but also high CO_2 emission (Komiya et al., 2015). Isotopic discrimination during CO_2 ebullition is considered to be very small just like for CH_4 ebullition, making it possible to estimate the contribution of acetate fermentation to bubble CH_4 using the values of $\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2 emitted via bubble ebullition. The fraction of the acetate-derived CH_4 in bubble CH_4 ranged between 0.42 – 0.73 (Table 5.4), which was similar to the values at 9 cm depth or lower in the unplanted soil (Table 5.1, 5.4). This indicates that the released bubbles were derived from the soil at 9 cm or deeper.

The isotopic signatures of the CH_4 emitted via diffusion on September 17, 20 and 26 were similar to those at 3 cm depth on each day (Table 5.3). The $\delta^{13}C\text{-}CH_4$ values in the paddy water were much greater than those in the paddy soil (Table 5.3), indicating the steady state in the floodwater (Happell et al., 1994; Chanton, 2005). Under steady conditions, the quantity and isotopic composition of CH_4 entering the floodwater from the soil and outgassing from the water surface should be balanced (Happell et al., 1994; Chanton, 2005). This probably contributed to the agreement between the released CH_4 and soil CH_4 at 3 cm deep near the surface.

Methane fluxes through paddy water increased and reached maximum values in the daytime (Fig. 5.3). During the high-emission periods, the isotopic signatures of emitted CH_4 were smaller (Fig. 5.3), which confirmed that the higher CH_4 emission in the daytime derived from CH_4 ebullitions because CH_4 bubbles contained rich $^{12}CH_4$ (Chanton, 2005). The daytime bubble ebullitions were probably regulated by increasing soil temperature and falling atmospheric pressure during the hotspot periods (Fig. 5.3) (Komiya et al. 2015). In contrast, the night measurements by the automatic chamber via floodwater almost always detected a slow increase in CH_4 concentration and greater $\delta^{13}C\text{-}CH_4$ emitted from the water-surface (Fig. 5.3). This suggests that the CH_4 diffusion process is dominant at nighttime.

The released $\delta^{13}C\text{-}CH_4$ via bubble ebullition ranged between -61.6 to -50.2‰ throughout the measuring period (Fig. 5.4b). The isotopic composition of the CH_4 emitted via the diffusion process ranged from -61.1 to -33.5‰ (Fig. 5.4b). In the diffusion process, the range between -50.1 and -33.5‰ was higher than that via bubble ebullition (Fig. 5.4b), which indicated that the heavier $\delta^{13}C\text{-}CH_4$ was released via molecular diffusion. The diffusive range of between -61.1 and -50.2‰ overlapped the bubble range. Bubble ebullition is mainly classified into episodic and steady ebullitions (Coulthard et al., 2009). These facts indicate that the steady increase in CH_4, emitted from floodwater, comprised not only the diffusion process but also steady bubble ebullition process which is unobservable from the change of CH_4 concentration.

5.5 Conclusions

We examined the CH_4 oxidation, production and transportation processes at both the soil-plant-atmosphere and soil-water-atmosphere interfaces using natural $\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2. The respective $\delta^{13}C$-CH_4 and $\delta^{13}C$-CO_2 values in the rhizosphere were heavier and lighter than in the non-rhizosphere, suggesting that CH_4 oxidation occurred in the rhizosphere owing to oxygen supply through the root aerenchyma. The highest CH_4 oxidation activity in the planted soil during the heading stage occurred at 15 cm depth where root tips appeared to gather. Also, CH_4 production by acetoclastic methanogens was more active in the planted soil than in the unplanted soil. These results indicate that the rice roots at the heading stage greatly affected the CH_4 oxidation and production processes in the paddy soil.

The planted CH_4 at 15 cm depth passed into the root aerenchyma with little isotopic discrimination, which was attributed to the lack of any ROL barriers in the roots at that depth. Soil CH_4 at 3 and 9 cm depths also seemed to travel through the root aerenchyma into the atmosphere, due to the larger CH_4 gradient between the soil and atmosphere, even though the ROL barriers interrupted CH_4 entry. In order to clarify the mechanism of CH_4 transportation between soil and root aerenchyma, further investigations are required to determine whether soil CH_4 passed through the root surface cell without isotopic fractionation and how the ROL barriers affect CH_4 entry.

The $\delta^{13}C$-CH_4 emitted via the plant correlated with that in the rhizosphere, indicating that the diel changes in CH_4 oxidation in the rhizosphere probably reflected those in the $\delta^{13}C$-CH_4 released via the plant. After soil CH_4 passed through the root aerenchyma to the stem aerenchyma around soil surface, the lacunal CH_4 appeared to be released with enhancing conductance of lacunal CH_4 diffusion due to the increase in soil surface temperature.

The isotopic signatures of CH_4 emitted via bubble ebullition were similar to those of CH_4 at 9 cm depth in the unplanted non-rhizospheric soil. Moreover, the proportions of acetated-derived CH_4 to emitted bubble CH_4 were similar to those in the unplanted soil at 9 and 15 cm depths. These results suggest that CH_4 emitted by bubble ebullition originated from 9 cm depth or deeper in the soil. In

addition, the measurements of $\delta^{13}C\text{-}CH_4$ emitted via water allowed us to find that there was steady CH_4 ebullition process contributing to the gradual increase in CH_4 concentration which was initially considered to be by molecular diffusion. Increasing soil temperature and falling atmospheric pressure in the daytime triggered CH_4 ebullition, leading to the ^{12}C-enriched CH_4, emitted through water. At nighttime, the CH_4 emitted via water showed depleted ^{12}C, which indicated that the diffusion process dominated at night.

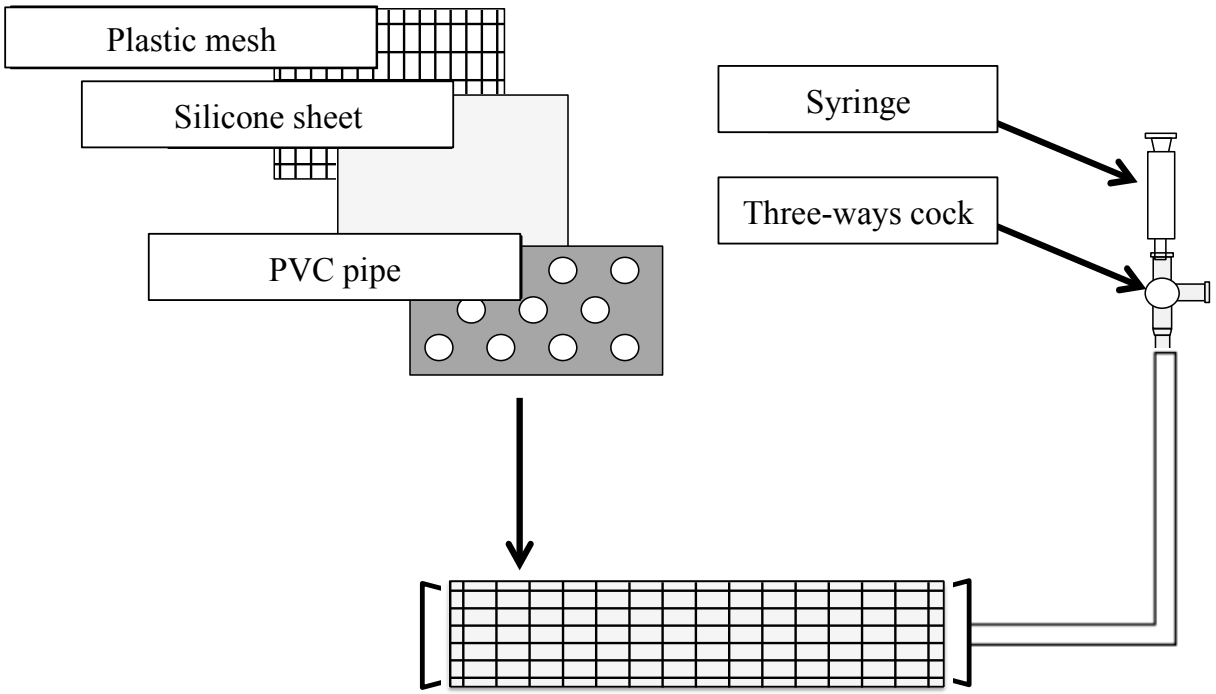

Fig. 5.1 The outline of soil gas sampler (Katano, 2015).

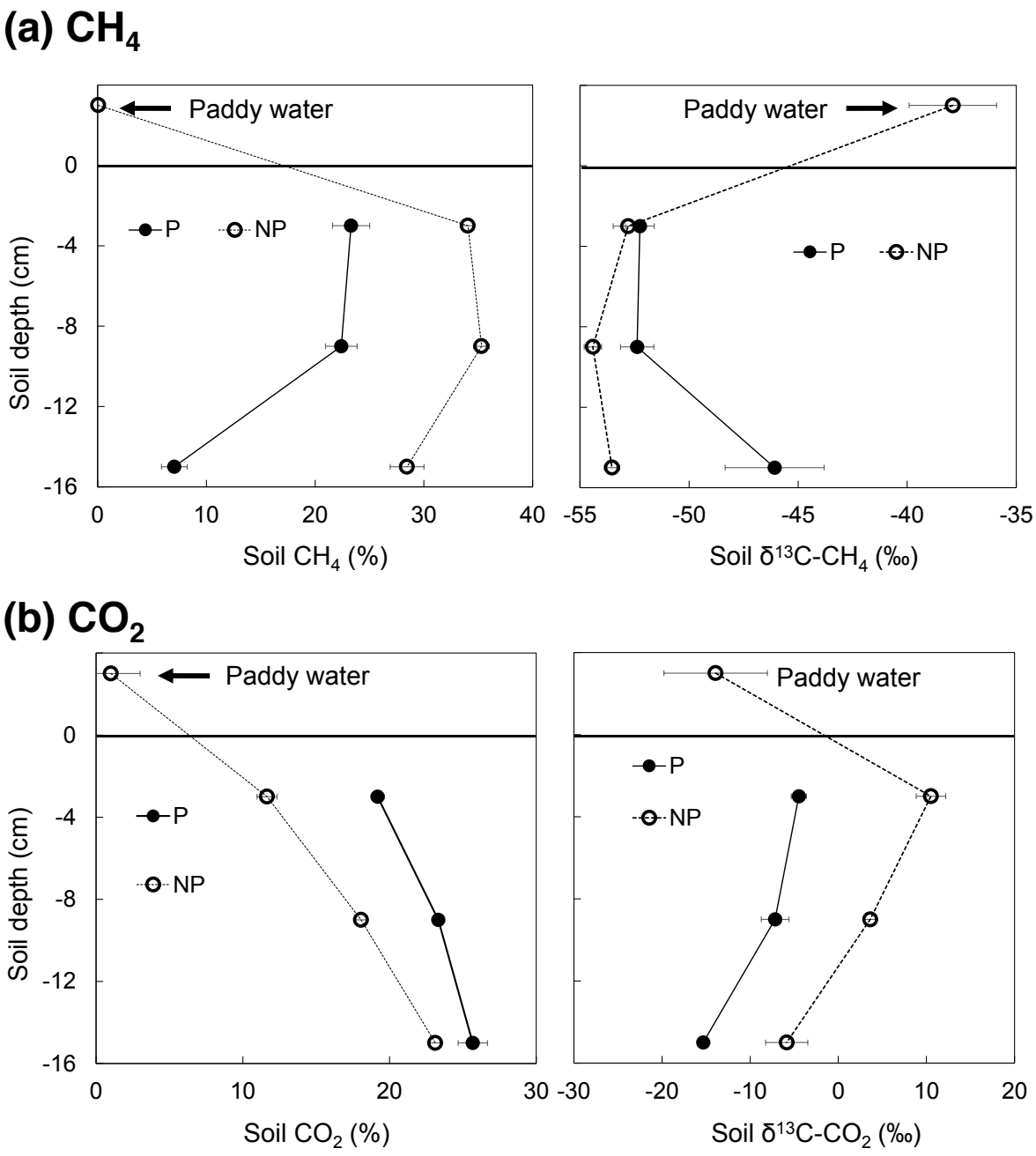

Fig. 5.2 Depth profiles of the concentrations and carbon isotopic signatures of CH_4 (a) and CO_2 (b) in the floodwater, the planted (P) and unplanted (NP) soil. The CH_4, CO_2 concentrations, $\delta^{13}C\text{-}CO_2$ and $\delta^{13}C\text{-}CH_4$ values were averaged for 3 gas sampling days. The bars show one standard deviation (n=3).

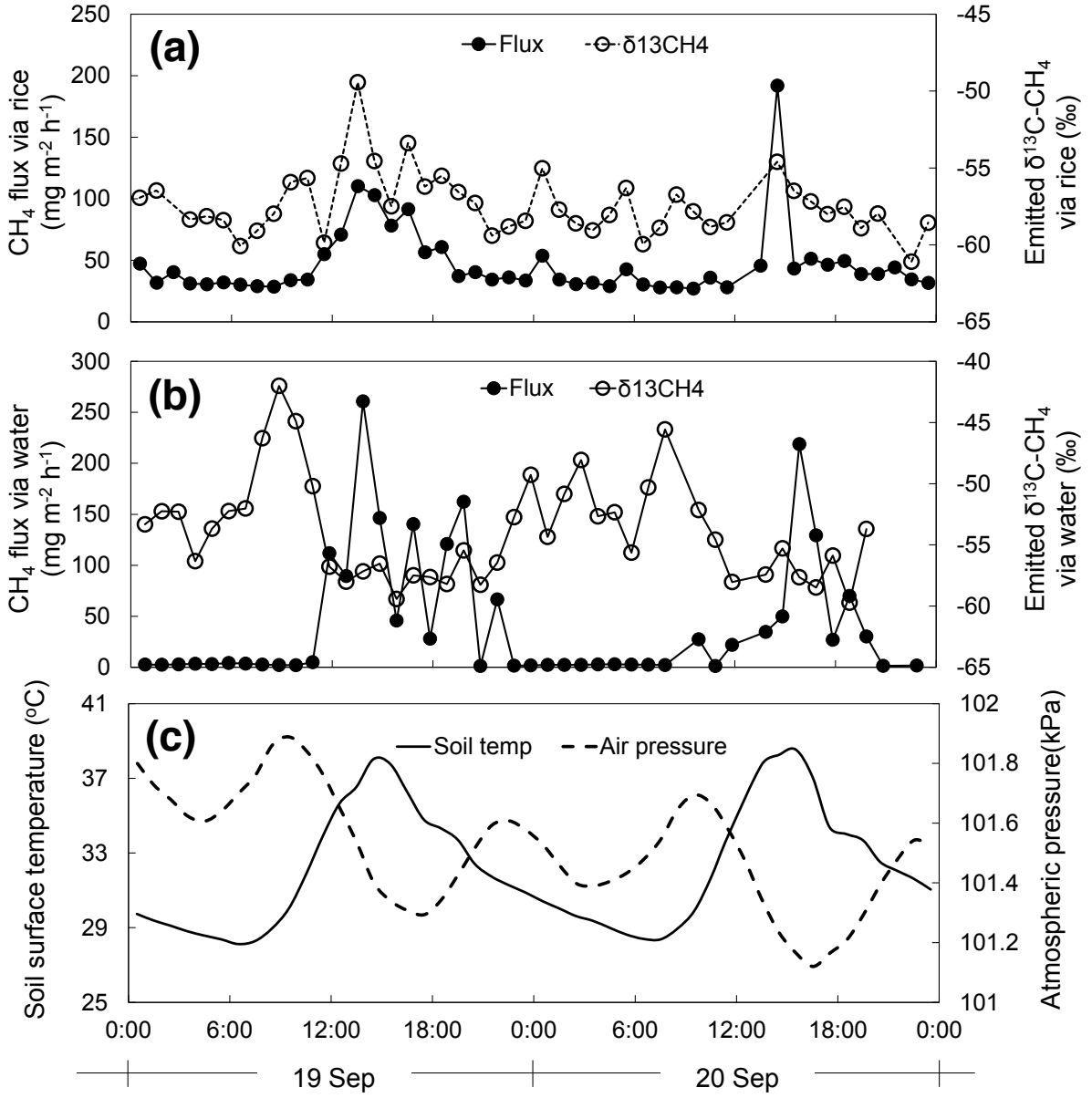

Fig. 5.3 Temporal changes over two sunny days in (a) CH_4 fluxes and $\delta^{13}C$-CH_4 emitted via the plant, (b) CH_4 fluxes and $\delta^{13}C$-CH_4 emitted via water, and (c) soil surface temperature and atmospheric pressure.

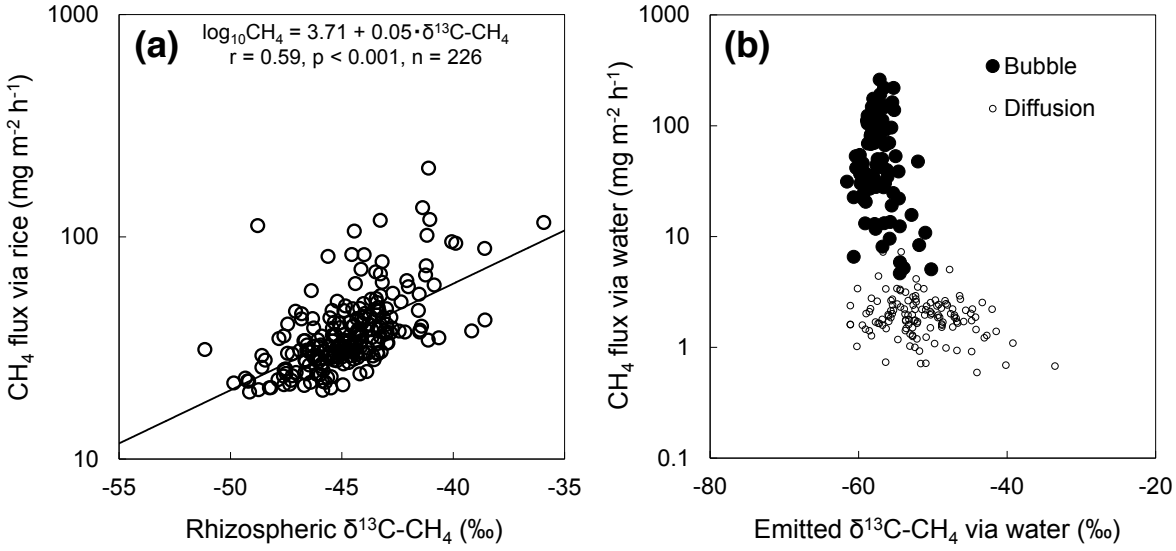

Fig. 5.4 Comparisons of CH_4 flux via plants and rhizospheric $\delta^{13}C$-CH_4 during the measurement period (a). Plot of CH_4 flux and $\delta^{13}C$-CH_4 emitted via floodwater during the measurement period (b). The rhizospheric $\delta^{13}C$-CH_4 values were estimated by adding the fixed isotopic fractionation of transportation (13.5‰) to the $\delta^{13}C$-CH_4 emitted via plants. The CH_4 emission via floodwater was categorized into bubble ebullition and diffusion processes according to the changes in CH_4 concentrations in the chambers as mentioned in section 4.3.

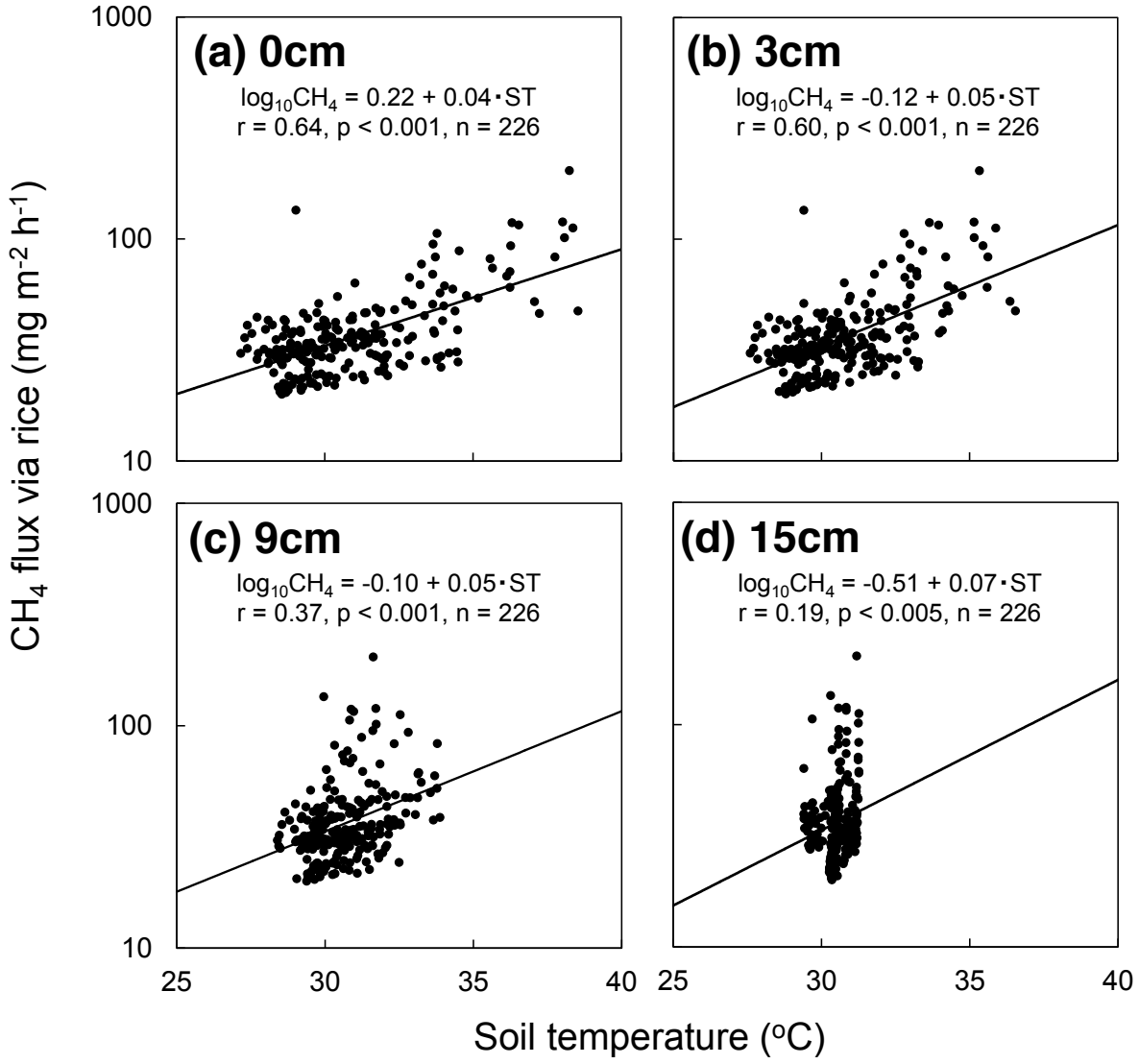

Fig. 5.5 Relationship between CH_4 flux via the plant and soil temperature at 0 (a), 3 (b), 9 (c) and 15 (d) cm depths during the measuring period.

Table 5.1 Fraction of acetate fermentation (f_{ac}) to net CH_4 production and CH_4 oxidation (F_{ox}) in planted rhizosphere and unplanted non-rhizosphere soil.

Depth	f_{ac}		F_{ox}
	Rhizosphere	Non-rhizosphere	
3 cm	0.62	0.30	0.02
9 cm	0.64	0.41	0.07
15 cm	0.86	0.60	0.25

Table 5.2 Isotopic signatures of CH_4 in planted rhizospheric soil gases, emitted via the rice plant and in the aerenchyma.

Date	Rhizospheric $\delta^{13}C$-CH_4 (‰)			Emitted $\delta^{13}C$-CH_4 via plant (‰)[1]	Aerenchyma (=Rhizosphere) $\delta^{13}C$-CH_4 (‰)[2]
	3 cm	9 cm	15 cm		
18-Sep	-51.9	-52.0	-45.6	-57.8 ± 0.7 (n=12)	-46.8 to -41.8
20-Sep	-51.8	-51.9	-44.1	-58.0 ± 0.7 (n=12)	-47.0 to -42.0
26-Sep	-53.0	-53.3	-48.6	-59.0 ± 2.2 (n=12)	-48.0 to -43.0

[1]Emitted $\delta^{13}C$-CH_4 values via the plant were averaged between 12 AM and 12 PM to enable comparison with the rhizospheric $\delta^{13}C$-CH_4 because the equilibrium time of the soil gas samplers was estimated at 12 hours in the laboratory. (Mean ± 1SD)

[2]The carbon isotopic signatures of CH_4 in the aerenchyma (=rhizosphere) were estimated by adding the isotopic fractionation of transportation (11 - 16 ‰) to $\delta^{13}C$-CH_4 emitted via the plant.

Table 5.3 Comparisons of $\delta^{13}C\text{-}CH_4$ in the unplanted non-rhizospheric soil gases and the gases emitted via bubble ebullition and diffusion.

Date	Non-rhizospheric $\delta^{13}C\text{-}CH_4$ (‰)			$\delta^{13}C\text{-}CH_4$ via bubble ebullition (‰)[1]	$\delta^{13}C\text{-}CH_4$ via diffusion (‰)[1]
	3 cm	9 cm	15 cm		
17-Sep	-52.6	-54.5	-53.9	-55.5 ± 3.2 (n=4)	-49.7 ± 4.6 (n=6)
20-Sep	-52.2	-54.0	-53.2	-56.3 ± 2.4 (n=2)	-51.3 ± 3.1 (n=9)
26-Sep	-53.5	-54.7	-53.5	-58.9 (n=1)	-54.6 ± 2.9 (n=11)

[1]Emitted $\delta^{13}C\text{-}CH_4$ values via bubble ebullition and diffusion were averaged from 12 AM to 12 PM to enable comparison with the non-rhizospheric $\delta^{13}C\text{-}CH_4$ as mentioned in Table 2. (Mean ± 1SD)

Table 5.4 Isotopic signatures of CH_4 and CO_2 emitted via bubble ebullition, and fraction of acetate fermentation (f_{ac}) to CH_4 production in emitted bubbles on September 17, 20 and 26.

Date	$\delta^{13}C$-CH_4 via bubble ebullition (‰)	$\delta^{13}C$-CO_2 via bubble ebullition (‰)	f_{ac}
9/17 4:50 PM	-56.8	-31.4	0.71
9/17 6:50 PM	-59.3	-5.9	0.42
9/20 10:50 AM	-54.6	-28.5	0.73
9/20 11:50 AM	-58.0	-18.5	0.60
9/20 2:50 PM	-55.3	-10.9	0.60
9/20 4:50 PM	-58.5	-22.5	0.62
9/20 5:50 PM	-55.9	-28.2	0.71
9/26 1:50 AM	-58.9	-24.1	0.63

Chapter 6

Summary and Conclusion

I conducted the field studies, shown in Chapter 2-5, with two main objectives. The first objective was to evaluate the seasonal CH_4 and CO_2 flux dynamics, and the net GHG budgets in rice paddy fields in temperate Japan and tropical Thailand. The controlling factors for GHG dynamics and budgets between the climate regions were also examined. The second objective was to examine the diurnal dynamics and mechanisms of CH_4 emission in detail in tropical rice paddy fields in Thailand. All the field studies were conducted at around the heading and flowering stages when there was large CH_4 emission. The following paragraphs briefly summarize and draw conclusions about the field studies.

In Chapter 2, I conducted the field study in rice paddies in temperate Japan and tropical Thailand so to achieve the first objective. I found that the seasonal dynamics in CO_2 fluxes in both countries were analogous throughout the growth period, but the CO_2 flux values in Thailand for DAT 0-30 were always positive unlike in Japan. This difference was primarily due to larger CO_2 emissions by ecosystem respiration in tropical Thailand than in temperate Japan because the CO_2 uptakes by plant photosynthesis in both countries were similar during this period. The seasonal CO_2 budgets revealed that the strength of the CO_2 sink in Thailand rice paddy fields was about half of that in Japanese rice paddy fields because of the large ecosystem respiration in Thailand compared to that in Japan. I confirmed that CH_4 fluxes in Japan increased during flooding periods and decreased during drainage periods. This suggests that the CH_4 flux trends in Japan depended on the water management. In Thailand, the pronounced CH_4 flux dynamics might have been derived from the plant growth and continuous flooding. The CH_4 budget in Thailand surpassed that in Japan, which was mainly due to the larger amount of CH_4 in Thailand paddy soil than in Japan. The large differences in soil CH_4 concentration possibly resulted from differences in methanogenesis and water management. The net

GHG budget, obtained from the sum of the CH_4 and CO_2 budgets, was negative in Japan, but positive in Thailand. This suggests that rice paddies in temperate Japan act as GHG sinks, whereas those in tropical Thailand are GHG sources.

In Chapters 3 to 5, I described the research in tropical Thailand that focused on the second objective. In Chapter 3, I examined CH_4 fluxes from rice canopies and floodwater during the flowering stage using the REA and closed chamber methods. I confirmed that CH_4 fluxes by REA and the closed chamber methods were reasonable by comparison with previously reported flux values in rice paddy fields in Southeast Asia. The diurnal changes in CH_4 fluxes over rice canopies were possibly controlled due to changes in horizontal wind speed and soil temperature. I also speculated that the CH_4 emissions via bubble ebullition through floodwater were affected by the reduction of atmospheric pressure and the increase in soil temperature. CH_4 fluxes over rice canopies using the REA method generally exceeded those from floodwater using the closed chamber method. This result suggests that the REA method measured CH_4 fluxes both through rice plants and flooded water whereas the closed chamber method only measured emissions through floodwater.

In Chapter 4, I investigated in detail the CH_4 ebullition dynamics from flooded water and the regulating factors in order to elucidate the speculation in Chapter 2 that CH_4 ebullition increased with increases in soil temperature and reductions in atmospheric pressure. Additionally, I examined CO_2 ebullition dynamics based on the hypothesis that bubbles, containing abundant CH_4 and CO_2, might cause not only large CH_4 emission but also CO_2 emission. The automatic closed chamber measurements revealed that bubble ebullition events triggered not only large CH_4 emission but also large CO_2 emission. CH_4 and CO_2 ebullition events were mainly controlled by reduction in atmospheric pressure and increase in soil surface temperature. The CH_4 ebullitions accounted for 95–97 % of the daily total CH_4 emission. Based on this result, I concluded that CH_4 ebullition dominated CH_4 emission from floodwater. In contrast to CH_4 ebullition, CO_2 ebullition comprised only 13–35 % of total daily CO_2 emission. The low contribution of CO_2 ebullition was probably due to CO_2 uptake by photosynthesis and respiration of aquatic plants.

In Chapter 5, I examined CH_4 emission dynamics at the soil–plant–atmosphere and soil–water–

atmosphere interfaces at around the heading stage in the tropical Thailand paddy fields using natural carbon stable isotope ratios ($\delta^{13}C\text{-}CH_4$ and $\delta^{13}C\text{-}CO_2$). The observed isotopic signatures of CH_4 and CO_2 in the planted rhizospheric and unplanted non-rhizospheric soils suggest that CH_4 oxidation occurred more actively in the planted soil than in the unplanted soil. This result indicates that CH_4 oxidation in the flooded soil depended on the oxygen supply from the atmosphere through the plant aerenchyma. The $\delta^{13}C\text{-}CH_4$ and $\delta^{13}C\text{-}CO_2$ in the rhizosphere also suggests that acetoclastic methanogens mainly produced CH_4 by consuming organic substances derived from rice plant roots. The $\delta^{13}C\text{-}CH_4$ in the plant aerenchyma and rhizosphere at 15 cm deep were similar, which suggests that soil CH_4 at 15 cm depth traveled through the root aerenchyma into the atmosphere without large isotopic fractionation. The diurnal changes in $\delta^{13}C\text{-}CH_4$ emitted via the plant suggest that CH_4 oxidation occurred during the daytime but not at nighttime. However, even though CH_4 oxidation occurred during the daytime, the CH_4 emission rates were higher during the day than at night. This was probably due to the increase in the conductance of lacunal CH_4 diffusion and soil CH_4 production due to higher daytime soil temperature. Based on the results of $\delta^{13}C\text{-}CH_4$ in the rhizosphere and via the plant, I conclude that CH_4 production, oxidation and transportation at the soil–plant–atmosphere interface were mainly regulated by the rice plant. The $\delta^{13}C\text{-}CH_4$ in bubbles released from the unplanted soil suggested that these bubbles came from 9 cm depth or deeper The $\delta^{13}C\text{-}CH_4$ emissions through the water surface suggested that steady ebullition events were part of the molecular diffusion process, defined as the constant increase in CH_4. On the basis of $\delta^{13}C\text{-}CH_4$ in the unplanted soil and via surface-water, I concluded that soil CH_4 in the unplanted soil was released into the atmosphere by the three pathways: (1) bubble ebullition, (2) steady bubble ebullition by micro-bubbles, and (3) molecular diffusion. I also showed that the dominant CH_4 emission pathways in the daytime and nighttime were bubble ebullition and diffusion, respectively.

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Appendix

Letter of Permission

2015 年 12 月 20 日

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転載許可申請書

下記により土壌の物理性に掲載されている内容の転載を許可願います。なお、本申請以外の用途では使用いたしません。

記

転載希望箇所
タイトル：　タイ王国の水田における CH_4 フラックスの緩和渦集積（REA）法による測定
著者名：小宮秀治郎・登尾浩助・庄子侑希・矢崎友嗣・Toojinda Theerayut
号、年：　128 号、2014 年
転載部分：謝辞を除く本稿全て、なお文章は全て英訳された

転載先
小宮 秀治郎 の博士学位論文（タイトル「Methane and carbon dioxide dynamics in temperate and tropical rice paddy fields」）内の Chapter 3 に転載

----------許可証----------

2015 年　12 月　23 日
学会長名　長　裕幸　印

申し出の転載申請を許可いたします。下記の条件に必ず従ってください。
■掲載書（または該当箇所のコピー（電子ファイル可））を一部、本学会事務局まで送付すること。
□特になし。