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Stoichiometry of CH₄ and CO₂ flux in a California rice paddy

Andrew M. S. McMillan,¹ Michael L. Goulden,¹ and Stanley C. Tyler¹

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[1] Rice paddies contribute significantly to the atmospheric burden of CH₄ but may also sequester atmospheric CO₂. Previous studies based on putative relationships between net CO₂ exchange and CH₄ emissions have concluded that globally significant amounts of carbon can be stored in rice paddy soils. However, the annual ratio of CH₄ emissions to net CO₂ exchange has not previously been measured. We simultaneously measured the net exchange of CO₂ (F_{CO_2}) by eddy covariance and the CH₄ emission rate (F_{CH_4}) using a combination of a flux gradient technique and weekly chamber sampling. During rice growth, F_{CH_4} was 1.9% to 2.4% of net carbon uptake (mole per mole). F_{CO_2} closely followed biomass accumulation. In contrast, F_{CH_4} increased during vegetative rice growth and decreased over the ripening and reproductive phases of rice growth, suggesting that the plants release substrate for methanogenesis early in the season. CH₄ emissions represented 4.8% to 5.6% of the net CO₂ uptake when summed over an entire year (including a 20-week period over which the field was unplanted and flooded). Assuming harvested rice is remineralized within 1 year, the remaining 0.67 t C ha⁻¹ that was sequestered by the paddy potentially offsets the radiative forcing of the emitted CH₄ by 26% to 31%. The ratio of F_{CH_4} to F_{CO_2} varied widely over the course of a year depending on management practices in a specific field. The results reported here emphasize the importance of year-round measurements to obtain a reliable estimate of CH₄/CO₂ exchange stoichiometry.

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1. Introduction

[2] Rice paddies have the potential to either increase or decrease the net balance of greenhouse gases in the atmosphere. The radiative effect of CH₄ released from rice paddies may be partially or wholly offset by the radiative effect of atmospheric CO₂ sequestration in paddy soils. An improved understanding of the complex relationship between the exchange of CH₄ and CO₂ is a critical part of efforts to determine whether paddies are a net source or sink of greenhouse gases and is the focus of the research reported here.

[3] Whiting and Chanton [1993] reported a linear relationship between net CO₂ exchange (the net ecosystem exchange or NEE) and CH₄ flux across 6 natural wetlands and a Louisiana rice paddy; 33 moles of CO₂ were fixed for every mole of CH₄ emitted. More recent measurements extended to an annual time period have shown that CO₂:CH₄ ratios range from 9 to 33 for subtropical wetlands and from 5 to 8 for boreal wetlands [Whiting and Chanton, 2001]. Whiting and Chanton measured NEE and CH₄ flux with flux chambers that were controlled for humidity, CO₂ and temperature and that were transparent to photosynthetically active radiation (PAR). The measurements by Whiting

and Chanton [1993] were taken at midday during the period of the season when NEE was greatest (midsummer), and provide a constraint for the stoichiometry of wetland ecosystems at optimal conditions for photosynthesis and CH₄ emission. However, more comprehensive sampling is required to reliably extrapolate over a year and calculate the annual stoichiometry of CH₄ and CO₂ exchange.

[4] Only a few published studies of F_{CO_2} and F_{CH_4} over an entire year (or years) would allow calculation of the annual stoichiometry in wetlands [e.g., Whiting and Chanton, 2001]. To the best of our knowledge, no such studies exist for rice paddies. Short-term measurements of F_{CH_4} and F_{CO_2} conducted in wetlands have provided estimates of stoichiometry on subannual timescales. High-latitude wetlands sequester atmospheric CO₂ over long timescales by peat accumulation [Gorham, 1991]. The accumulation of carbon in the soil is a combined effect of low temperatures and poor soil aeration acting to limit decomposition. As a result, CO₂ that was fixed by the wetland vegetation does not get returned to the atmosphere by respiratory processes to the same extent as it does in warmer, drier ecosystems. Fan *et al.* [1992] measured the exchange of CH₄ and CO₂ in the subarctic tundra using eddy covariance during 5 weeks in July and August and found a rate of CO₂ uptake of 1.1 mg CO₂ m⁻² d⁻¹, which was roughly 17 times the rate of CH₄ efflux on a mole to mole basis.

[5] The IPCC's Special Report on "Land Use, Land-Use Change and Forestry" [Intergovernmental Panel on Climate

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Change, 2000] suggests that agricultural practices in rice cultivation (residue management, fertilization, drainage management) could result in the accumulation of up to 200–800 kg C ha⁻¹ yr⁻¹. *Stallard* [1998] suggested that the burial of carbon in rice paddies might currently account for a sink of up to 1×10^{15} g of carbon. This estimate was arrived at by combining global estimates of F_{CH_4} from rice with a 1:14 ratio of F_{CH_4} to F_{CO_2} uptake derived from *Whiting and Chanton* [1993]. However, the stoichiometry reported by Whiting and Chanton was based on measurements only during times of peak CO₂ uptake and peak F_{CH_4} . We suspect that it does not provide a reliable basis on which to estimate carbon sequestration from F_{CH_4} data since it neglects heterotrophic respiration during nighttime and fallow periods. Further, roughly half the aboveground biomass is removed from paddies during harvest and the fate of this carbon is not accounted for in Stallard's calculation.

[6] The stoichiometric relationship between the exchange of CH₄ and CO₂ in rice paddies has two additional implications: (1) linking photosynthetic and respiratory processes in rice plants to F_{CH_4} can help determine management strategies that simultaneously maintain or increase yields and stabilize or reduce CH₄ emissions from rice; and (2) establishing relationships between NEP, NPP and CH₄ emissions would allow the remotely sensed proxies for NPP to be also used to estimate fluxes of CH₄ and/or NEP.

[7] Simultaneous measurements of F_{CH_4} and F_{CO_2} over annual time periods allow the determination of the CH₄:CO₂ stoichiometry and can be used to test whether the exchange of one of these gases can be used to estimate the flux of the other gas. Here we report on simultaneous measurements of F_{CH_4} and F_{CO_2} in a California rice paddy. We then determine the ratio of F_{CH_4} to F_{CO_2} on annual and shorter-term scales, and the extent to which carbon sequestration in rice fields can offset the radiative effect of CH₄ emissions.

2. Materials and Methods

2.1. Site Description

[8] Our site was located in the northern Sacramento Valley, 7 km northeast of Maxwell, California, in Colusa County (39°17' N, 122°11' W). The experiment was performed in a commercial rice field owned by L. C. Dennis Co. that has been under continuous rice agriculture for the past 30 years with no crop rotation. The rice variety was M-202, a high-yielding, semidwarf cultivar developed for California conditions and in common use in Colusa County.

2.2. Crop Management

[9] The 2001 crop was harvested on 27 September. Following harvest, the crop residue was chopped and incorporated into the soil, followed by field flooding on 10 October 2001. The field was drained on 28 February 2002, followed by seed bed preparation beginning 10 April. The field was flooded one week later and mineral fertilizer applied (165 kg N ha⁻¹ and 72 kg P ha⁻¹). Rice seed was aerially broadcast on 23 April at 190 kg ha⁻¹. The reproductive phase of plant growth (indicated by panicle initiation) started on 2 July. Ripening (indicated by 50% anthesis) commenced on 29 July. The 2002 crop was harvested on 21

September. Grain yields (at 14% moisture content) were 11.9 t ha⁻¹ and 11.7 t ha⁻¹ for 2001 and 2002 respectively.

2.3. Eddy-Covariance Measurements

[10] A 3-m tripod tower (Campbell Scientific, Logan, UT) was erected on a wooden platform that stood 1 m above the soil surface. A CSAT3 sonic anemometer (Campbell Scientific, Logan, UT) and a LI7500 open path non-dispersive infrared gas analyzer (LICOR, Lincoln, NE) were mounted on the tower and oriented toward East (normal to the two most prevailing winds, SW and N). The outputs from the LI7500 and CSAT3 were recorded using a CR23X datalogger (Campbell Scientific, Logan, UT) that was housed in an air-conditioned enclosure. The Licor 7500 was calibrated every 3 months with reference gases traceable to NIST standards for CO₂ and with a LI-610 dew point generator for water vapor (Licor, Lincoln NE). Only minor adjustments to the LI-7500 calibration constants were necessary for these calibrations.

[11] The 3-D wind vector was trigonometrically rotated so that the mean vertical wind over a 30-min interval was zero [McMillen, 1988]. We removed linear trends in the concentration of CO₂ before fluxes were calculated. Corrections for the effects of water vapor concentration and sensible heat flux on the density of air (and hence the mass/volume mixing ratios of CO₂ and H₂O) followed methods of *Webb et al.* [1980] and *Miller et al.* [2004]. Turbulent fluxes were calculated from the covariance of the vertical wind velocity and horizontal wind velocity (momentum flux), CO₂ (F_{CO_2}), H₂O (latent heat flux) and temperature (sensible heat flux). Nocturnal fluxes during calm periods ($u^* < 0.15$ m s⁻¹) were replaced with a modeled flux based on a 7-day linear relationship with air temperature or, in the absence of a strong relationship, an average value for noncalm periods [Goulden et al., 1996; Falge et al., 2001]. F_{CO_2} (often referred to as net ecosystem exchange or NEE) was assigned a negative value when there was a net uptake of CO₂ by the paddy.

2.4. Flux Gradient System

[12] A second micrometeorological system was used to measure the vertical profiles of CH₄ and CO₂ concentrations above the rice canopy (Figure 1). This system incorporated a sampling system to collect air from 4 heights (50 cm, 100 cm, 150 cm and 300 cm) into Tedlar gas sampling bags (Supelco, Bellefonte, PA) at a constant rate. The Tedlar bags were sealed in an airtight plastic box, which was gradually evacuated using a small diaphragm pump (KNF Neuberger, Trenton, NJ) over a 30-min period. Air from each bag was then drawn sequentially through a closed-path infrared gas analyzer (IRGA) (LICOR 6262, Lincoln, NE) to measure the CO₂ and H₂O mixing ratio. The flow from the bag was redirected for 30 s to a 5 mL sample loop attached to a Valco 6 port gas chromatography injection valve (VICI, Houston, TX). The sample loop was then isolated from the air flow and the downstream end equilibrated with atmospheric pressure for 10 s. The injection valve then connected the sample loop with a stream of N₂ carrier (25 mL min⁻¹) and the contents of the sample loop was passed to a 1829 mm × 3.175 mm Molecular Sieve 5-A, 80/100 mesh gas chromatography column (Alltech, Deerfield, IL) inside a Shimadzu Mini-II gas chromatograph

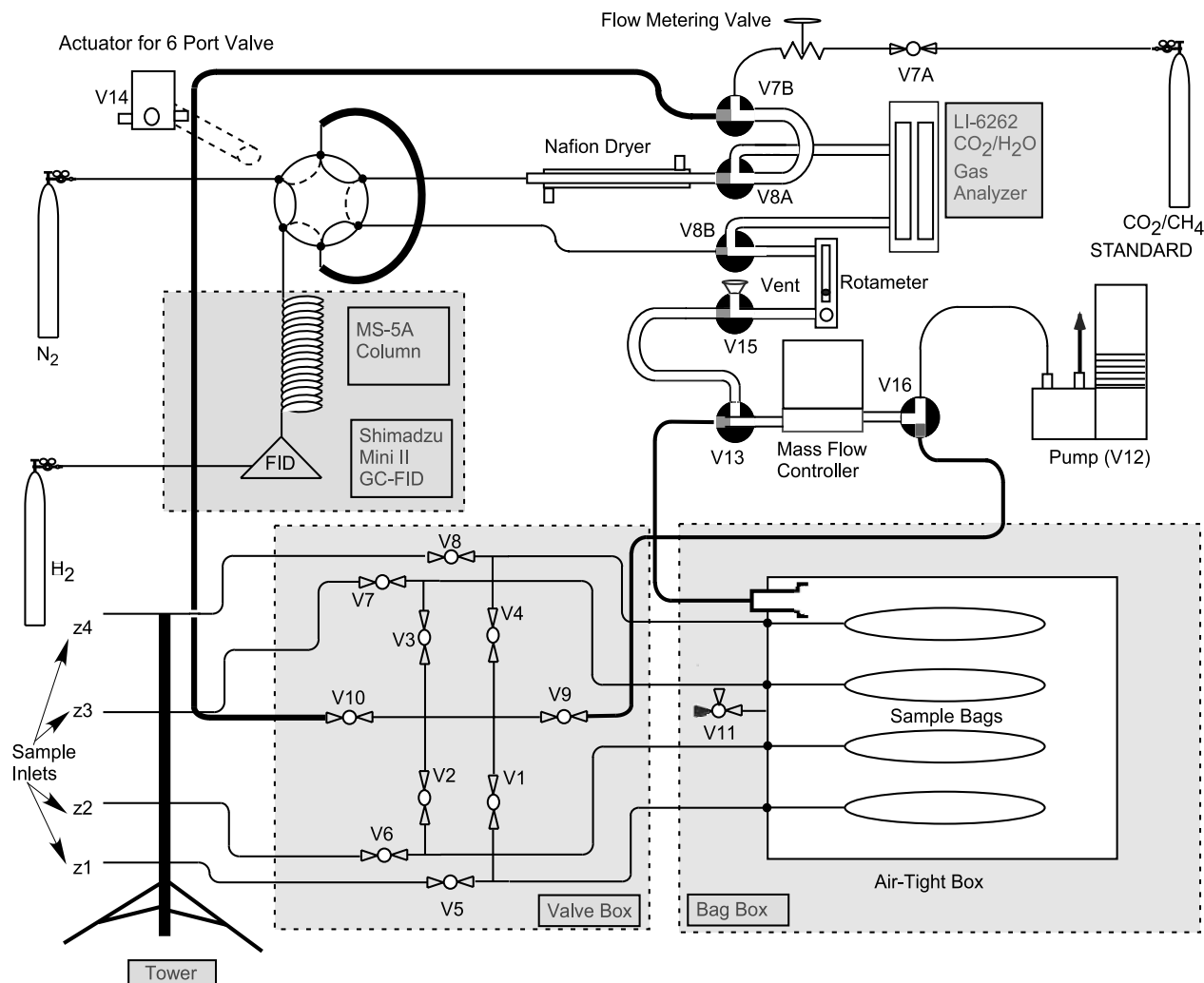


Figure 1. Schematic diagram of the flux gradient system. The pump performed three functions: (1) evacuating the airtight box while the bags inside were in line with the sample inlets of the tower (so that the bags fill over a 30-min period); (2) sequentially drawing the samples from the bags through the mass flow controller, IRGA cell, and GC loop for analysis; and (3) evacuating the remaining contents of the bags in preparation for the next sampling period. Inlet heights were at 1.0, 1.5, 2.0, and 3.0 m. The flow through the sample loop was 75 mL min^{-1} . Sample flow was controlled by switching of: two-way valves, V1 to V8; three-way valves, V7A, V7B, V8A, V8B, V13, V14 and V15; and the pump, V12. The flow of the standard gas to the sample loop was controlled by V7A and V7B. The box was evacuated with the pump and V16, and was vented with V11. V14 controlled the actuation of the GC sample valve. The tanks containing the carrier gas and the fuel for the FID are indicated by N₂ and H₂, respectively.

(Shimadzu Corp, Columbia, MD) equipped with a flame ionization detector (FID). The analog output of the FID was digitized and the chromatographic peaks were subsequently integrated using programs written in Matlab (Mathworks Inc., Natick, MA).

[13] The system switched from the sampling mode (described above) to an analysis mode after 30 min. Reference gases were analyzed at the beginning and end of each 30-min analysis sequence and also between the second and the third bags. Two analyses of CH₄ were obtained for each sample bag. A Campbell Scientific data logger (CR10X) was programmed to switch valves 1 to 16 in the desired order. High Purity N₂ carrier gas (99.999%, Oxygen Services Co, Anaheim, CA) was used

as the carrier for the GC-FID system. Ultra high purity H₂ (Oxygen Services Co) supplied the fuel for the FID. Because of the high consumption of air by the FID, zero air was generated in the field. Ambient air was pressurized to 800 kPa with an oil-free compressor (Gast Manufacturing Inc, Benton Harbor, MI) and then dried to a dew point of -60°C using a reciprocating molecular sieve air drier (HD Series, Perma Pure, Toms River, NJ). The dried air was then split three ways: (1) to a Nafion membrane drier that dried the air entering the sample loop of the GC; (2) to the actuator of the Valco 6 port valve; (3) to a zero air generator with a capacity of 1.1 L min^{-1} (Balston, Parker-Hannifin, Tewksbury, MA). This latter stream supplied the FID with zero air at a rate of 350 mL min^{-1} .

[14] The reference gas was a mixture of 1.744 ppm CH₄ and 354.8 ppm CO₂ in zero air (Scott-Marrin Inc., Riverside, CA), which was calibrated against primary reference gases certified by NOAA-CMDL. The integrity of the sample collection and analysis system was verified by filling the sample bags with standard and allowing the analysis to proceed as if real air samples had been collected. The values for CO₂ measured in the bags filled with reference gas and the reference gas itself agreed to within 0.4 ppmv while those for CH₄ agreed to within 4.4 ppbv.

2.5. Measurement of CH₄ Using Static Chambers

[15] Measurements of CH₄ emissions were made using six chambers on a weekly basis from 1 January 2002 to 12 September 2002 following *Sass et al.* [1990]. The straw was distributed in the field in rows approximately 1 m wide, with smaller volumes of straw between the rows. A random placement of chambers would have led to a high amount of measurement variability due to the effect of organic matter on CH₄ emissions. Therefore two chambers were placed on an area with a large amount of straw, two chambers were placed on an area between the rows with little straw, and the final two chambers were placed on an area with an intermediate amount of straw. Emissions from the latter two chambers were considered representative of the field as a whole, while the other chambers provided a bound on the approximate minimum or maximum emissions. F_{CH_4} was determined by placing chambers over the collars and allowing emitted gases to accumulate in the enclosed volume. An initial 50 mL gas sample from the enclosure was taken with a 60 mL syringe immediately after chamber placement. Four subsequent samples were taken at 6- to 7-min intervals. The chambers were surrounded with foam insulation to prevent large (>2°C) temperature increases during enclosure. The chambers were equipped with small battery powered fans that were operated for 1 min prior to syringe sampling to ensure adequate mixing of the internal volume. Temperature was measured inside and outside the chamber throughout sampling. Syringes were shipped to UC-Irvine and analyzed for CH₄ within 24 hours of collection using GC-FID. F_{CH_4} was then calculated from the following equation:

$$F_{CH_4}(\text{g CH}_4\text{-C m}^{-2}\text{d}^{-1}) = [V/A][\Delta s/\Delta t], \quad (1)$$

where V is the above-water volume of the chamber, A is the area sampled, $\Delta s/\Delta t$ is the least squares fit to increase in the density of CH₄ (g CH₄-C m⁻³), s , as a function of time, where s was calculated from the molar mixing ratio and the temperature inside the chamber at the time of sampling using the ideal gas law.

2.6. Meteorological Measurements

[16] Relative humidity and air temperature were measured with a Vasaila HMP45C probe (Vasaila, Woburn, MA). Incoming and reflected photosynthetically active radiation (PAR) were measured with silicon quantum sensors (Licor, Lincoln, NE). Incoming and outgoing solar irradiance were measured with thermopile pyranometers (CM3, Kipp and Zonen, Bohemia, NY). Net radiation at 3 m was measured with a REBS Q * 7 thermopile net radiometer (REBS, Seattle, WA). Soil temperature at 10 cm

depth was measured using a soil thermistor probe (T107, Campbell Scientific, Logan, UT).

2.7. Biomass Measurements

[17] Biomass harvests were used to estimate the production of dry matter by the rice plants during the 2002 growing season. Two representative 0.5 m² sections of rice were removed and shipped to UC Irvine for dry matter analysis at 21-day intervals. Plants were gently pulled from the soil and, although roots appeared intact, a small amount of root material may have remained in the soil. Soil particles were removed by cleansing the roots under running water. A negative exponential function based on the ratio of the root dry matter to the shoot dry matter ($DM_{\text{root}}/DM_{\text{shoot}} = 1.346 * \exp[-0.021 * \text{days after planting}]$, $r^2 = 0.963$) was used to calculate root biomass for the three dates when measurements of DM_{root} were not obtained directly.

3. Data Analysis

3.1. Calculation of Flux Using the “Scalar Ratio” Method

[18] The scalar ratio approach assumes that the eddy diffusivity term that relates a vertical profile of a gas to its rate of exchange with a surface is the same for both CH₄ and CO₂ and eliminates the need for measuring the diffusivity directly. F_{CH_4} can be calculated from measurements of the vertical concentration profile of both CO₂ and CH₄ combined with measurements of F_{CO_2} by eddy covariance using (equation (2)).

$$F_{CH_4} = F_{CO_2} * \frac{\Delta CH_4}{\Delta CO_2}, \quad (2)$$

where the fluxes, F_{CH_4} and F_{CO_2} , are related by the ratio of the vertical gradients of the mixing ratios of the respective gases above the rice canopy. *Miyata et al.* [2000] employed this approach to determine the fluxes of CH₄ and CO₂ in a paddy over an 8-day period.

[19] The diurnal pattern of F_{CO_2} , the vertical concentration profiles of CO₂ and CH₄, and the regression between CO₂ and CH₄ concentration for 14 June 2002 at 1:30 PM and 10:30 PM, illustrate the CH₄ flux calculation (Figure 2). The correlation between CH₄ and CO₂ forms the basis for the flux calculation. The gradients of CO₂ and CH₄ were generally steeper at night than during well-mixed daytime conditions. In these cases the vertical CO₂ gradient exceeded 18 ppmv m⁻¹ at night (Figure 2e), while the CH₄ gradient exceeded 0.2 ppmv m⁻¹. During the times of peak photosynthetic uptake (1 PM, Figure 2b), the CH₄ gradients were about six times smaller and the CO₂ gradient was positive with increasing height. In both cases, the gas concentrations at different heights were tightly correlated with each other (Figures 2d and 2e) ($r^2 > 0.98$). The flux was calculated from the ratio of the individual regressions of the mixing ratio with height such that

$$F_{CH_4} = F_{CO_2} * (dCH_4/dz)/(dCO_2/dz). \quad (3)$$

[20] During some periods, CH₄ and CO₂ were tightly correlated even when the change in concentration with height was not monotonic. In these cases, we multiplied

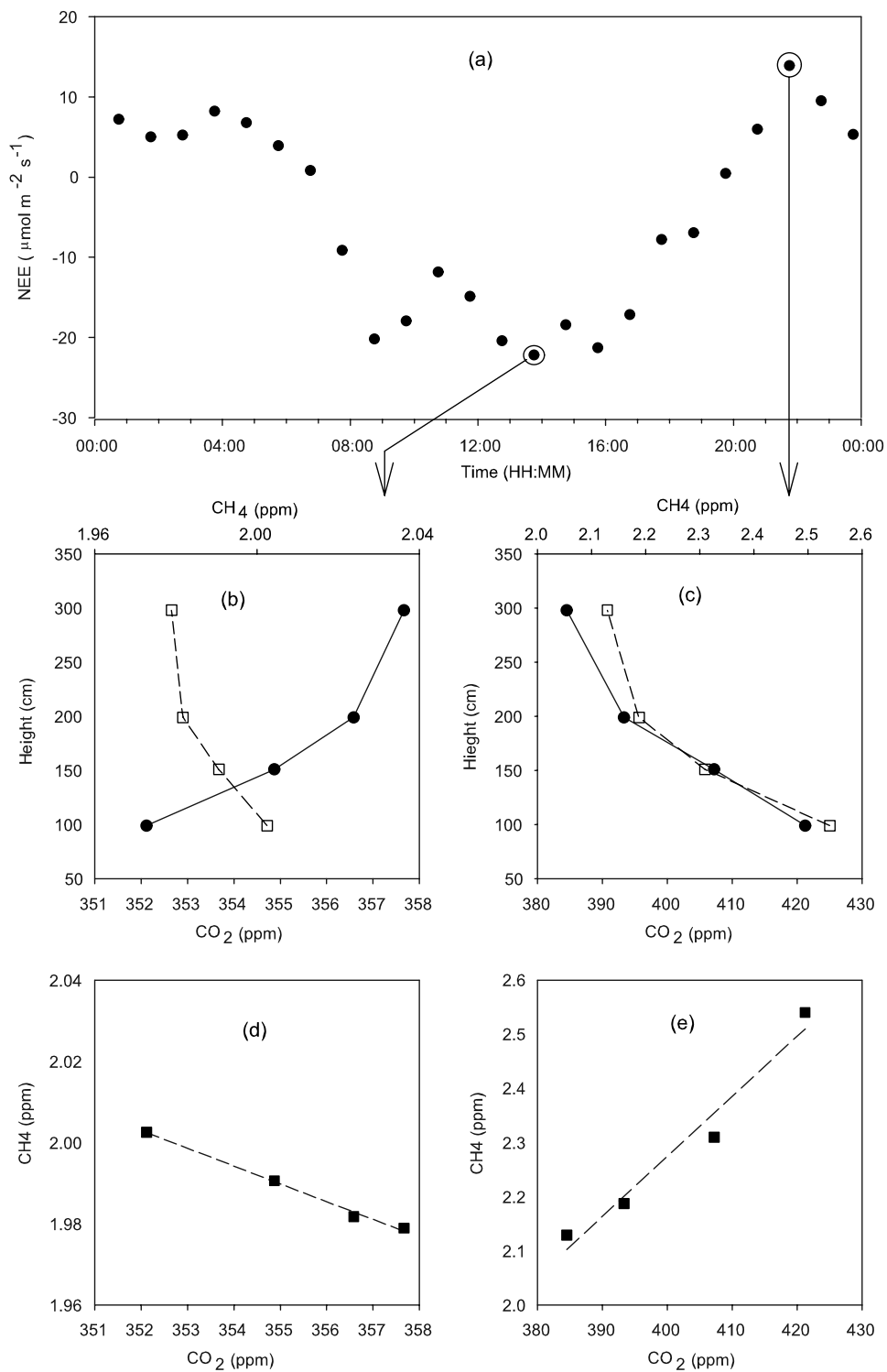


Figure 2. Daytime and nighttime eddy covariance and flux gradient measurements taken on 14 June 2002. (a) Diurnal course of net CO₂ exchange measured by eddy covariance. (b, c) Vertical profile of the mixing ratio of CH₄ and CO₂ at 1:30 PM and 10:30 PM. (d, e) Correlation between CH₄ and CO₂ concentrations across the four heights for these periods.

the slope of best fit line to the CH₄ and CO₂ (irrespective of height) by the NEE for that hour to obtain the CH₄ flux,

$$F_{\text{CH}_4} = F_{\text{CO}_2} * d\text{CH}_4/d\text{CO}_2. \quad (4)$$

3.2. Calculation of CH₄ Flux Using the Aerodynamic Method

[21] The aerodynamic flux gradient method provided a second approach for calculating the diffusivity [Miyata *et al.*, 2000]. From Monin-Obhukov similarity theory, the vertical flux of a gas is related to the mean vertical gradient of the mixing ratio,

$$F = -\bar{\rho}_a K_g(z) \frac{\partial \bar{s}}{\partial z} = -\bar{\rho}_a \frac{ku^*(z-d)}{\phi_g(\zeta)} \frac{\partial \bar{s}}{\partial z}, \quad (5)$$

where $\bar{\rho}$ is the density of dry air (mol m⁻³), K_g is a turbulent exchange coefficient with dimensions of m² s⁻¹, s is the molar mixing ratio of the gas of interest, z is vertical elevation, k is the von Karman constant, d is the zero plane displacement height (the height at which the mean wind is zero, taken here as 0.7 times the mean plant height). The denominator of the right-hand side equation ($\Phi_g(\zeta)$) is the dimensionless Monin-Obhukov stability parameter, which corrects the diffusivity under nonneutral conditions.

[22] The CH₄ flux, F_{CH_4} , was then calculated by

$$F_{\text{CH}_4} (\text{gCH}_4 - \text{Cm}^{-2}\text{d}^{-1}) = \frac{-\bar{\rho}_a ku^* [s_2 - s_1]}{\ln(z_2/z_1) - [\Psi(\zeta_2) - \Psi(\zeta_1)]} \cdot (86400)(1 \times 10^{-6})(12), \quad (6)$$

where s_1 and s_2 are the concentration of CH₄ (in $\mu\text{mol CH}_4/\text{mol dry air}$) at heights z_1 and z_2 respectively and Ψ is the integrated form of Φ , calculated as $\Psi = 2 \ln \left[\frac{1 + [1 - 16(z_2 - d)/L]^2}{1 + [1 - 16(z_1 - d)/L]^2} \right]$ for unstable conditions ($\zeta \leq 0$) [Paulson, 1970; Dyer and Hicks, 1970], and $\Psi = -\frac{5}{4} \zeta (z_2 - z_1)$ for stable conditions ($\zeta \geq 0$) [Panofsky and Dutton, 1984; Dyer and Hicks, 1970].

4. Results

4.1. Net Ecosystem Exchange

[23] Net ecosystem exchange (NEE) was measured from 1 July 2000 to 22 November 2002 (Figure 3). Continuity of measurements was good over most of the study period except for a 21-day period at the beginning of the growing season in 2002, when communication problems between the datalogger and the IRGA occurred. We obtained valid fluxes 61% of time over this entire period and 68% of the time when F_{CH_4} and F_{CO_2} were measured simultaneously (October 2001 to October 2002). Clear seasonal trends associated with the growth of the rice and fallow period management practices were observed over the study. Peak uptake occurred in mid July of each year, when net daytime uptake of CO₂ exceeded 40 $\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$. NEE increased in an approximately linear fashion from the time of germination until the seasonal peak, and then declined until the harvest. Respiratory losses (positive fluxes of CO₂) were highest following the drainage of standing water from the paddy, which occurred prior to seed bed preparation and

also ~ 20 days prior to harvesting. The average nocturnal respiratory F_{CO_2} was $4.8 \pm 3.8 \mu\text{mol m}^{-2} \text{ s}^{-1}$ during the growing season and the average daytime NEE was $-10.2 \pm 7.4 \mu\text{mol m}^{-2} \text{ s}^{-1}$. The cumulative NEE over the 149-day growing season was $-789 \text{ g CO}_2\text{-C m}^{-2}$. The NEE integrated over the period 10 October 2001 to 9 October 2002 was $-549 \text{ g CO}_2\text{-C m}^{-2}$.

4.2. Biomass Measurements

[24] The seasonal biomass increase was fit with a 3 parameter sigmoid function (Figure 4a). The derivative of this function was then compared to the daily uptake of carbon measured by eddy covariance (Figure 4b). The rate of biomass accumulation agreed reasonably well with measurements of net daily F_{CO_2} over the early part of the season whereas the rate of biomass accumulation exceeded the net uptake measured by eddy covariance during the middle and latter parts of the season. The decoupling of F_{CO_2} from biomass accumulation indicated that the heterotrophic component of the respiratory flux increased during the later part of the growing season. As a result, net carbon uptake was smaller relative to biomass accumulation. We suspect that there was a pool of carbon in the soil derived from photosynthates of previous seasons (probably straw) that contributed to respiratory fluxes in the latter part of the growing season.

4.3. Weekly Chamber Measurements of F_{CH₄}

[25] The chamber measurements showed a clear seasonal pattern of F_{CH_4} (Figure 5). The presence of straw in the chamber frames strongly affected flux. The medium straw chambers emitted less CH₄ than the pooled average during periods when overall fluxes were high. The cumulative CH₄ emitted over our study was 19.3 g CH₄-C m⁻² for the medium straw chambers, 40.0 g CH₄-C m⁻² for the high straw chambers and 14.7 g CH₄-C m⁻² for the low straw chambers. The cumulative sum of CH₄ for all chambers was 25.6 g CH₄-C m⁻² over the entire period of measurement and 15.5 over the course of the growing season. 2.6 g of CH₄-C was released during the flooded period at the beginning of measurements (1/9/02). Over the dry period prior to planting 1.0 g CH₄-C was emitted. These rates are comparable to the rates of 17–27 g CH₄-C m⁻² reported by Fitzgerald *et al.* [2000] in a nearby field studied in 1994–1995 that was subject to similar management. These emission rates are slightly above average values found during an intensive sampling campaign conducted in five Asian countries [Wassmann *et al.*, 2000] but typical of fluxes measured from paddies in the southern United States [Sass *et al.*, 1999].

4.4. Comparison of the Flux Gradient and Chamber Approaches

[26] The weekly time series of F_{CH_4} measured with chambers was linearly interpolated and compared to the daily fluxes measured by the flux gradient system (Figure 6). The timing and magnitude of F_{CH_4} measured by the flux gradient method agreed broadly with F_{CH_4} measured by the chambers. The largest discrepancies occurred from mid-April to mid-May when chamber fluxes showed a gradual increase in F_{CH_4} whereas the flux gradient system showed a faster rate of increase. The aerodynamic approach agreed

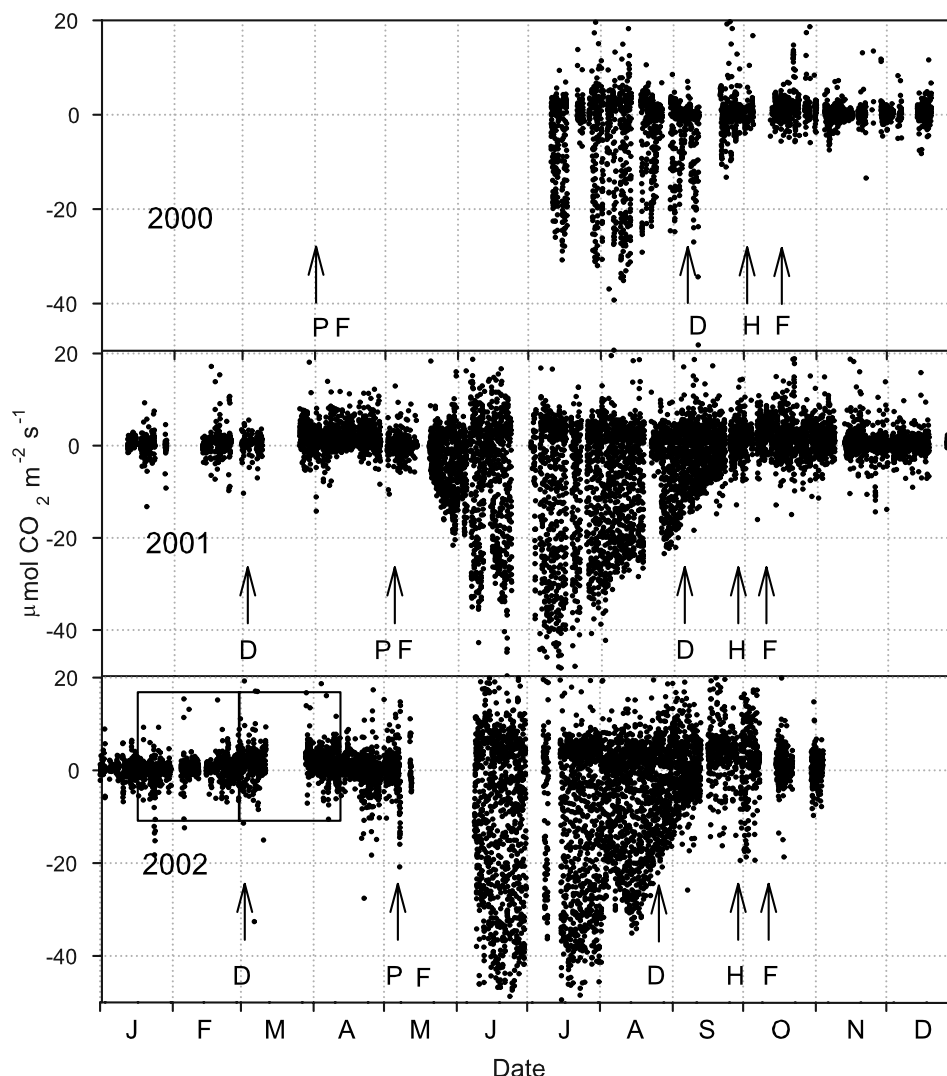


Figure 3. Half-hourly values of F_{CO_2} for 2.8 years. A negative value indicates the loss of CO₂ from the atmosphere to the crop. Arrows indicate timing of planting (P), crop harvest (H), post-harvest flooding (F) and drainage prior to planting or harvest (D). The two boxes in the bottom panel indicate the 45-day period prior to drainage when the daily average of F_{CO_2} was $0.3 \mu\text{mol m}^{-2} \text{s}^{-1}$ (left box) and the 45-day period after drainage when the daily average of F_{CO_2} was $1.7 \mu\text{mol m}^{-2} \text{s}^{-1}$ (right box).

favorably with the chamber method during the time of peak emissions. Unfortunately, we were unable to calculate F_{CH_4} using the scalar ratio method during this period since the closed-path IRGA was malfunctioning.

[27] Past chamber measurements have often reported fluxes that are 60–100% higher than those measured using micrometeorological techniques [Miyata *et al.*, 2000; Werle and Kormann, 2001]. We obtained comparatively good agreement between techniques during this study. The scalar ratio approach gave values on average 30% lower than the chamber method and the aerodynamic approach gave values on average 25% higher than the chamber method. The chamber measurements indicated that $25.6 \text{ g CH}_4\text{-C m}^{-2}$ were emitted from 9 January to 17 October, while the aerodynamic method indicated $31.2 \text{ g CH}_4\text{-C m}^{-2}$ emitted over this period and the scalar ratio method indicated $22.7 \text{ g CH}_4\text{-C m}^{-2}$. Annual sums of F_{CH_4} were $26.1 \text{ g CH}_4\text{-C m}^{-2}$ for the scalar ratio method and $31.0 \text{ g CH}_4\text{-C m}^{-2}$ for the

aerodynamic method (integrating over the period 17 October 2001 to 16 October 2002).

4.5. Exchange of CH₄ and CO₂ Over the Fallow Period and Growing Season

[28] Rates of CO₂ efflux over the flooded fallow period indicated slow but steady rates of organic matter decomposition. When the floodwater was removed in the spring, there was an abundant supply of labile fermentation products that were mineralized rapidly once oxic conditions were established. This, together with the higher soil temperatures, accounted for the large increase in daily F_{CO_2} during the spring drained period (Figure 3).

[29] Miyata *et al.* [2000] suggested that the presence of floodwater acts as an almost complete diffusion barrier to CO₂ efflux based on 9 days of observations. In the present study, the slow yet sustained rate of CO₂ efflux over the flooded period resulted in a significant loss of carbon. As a

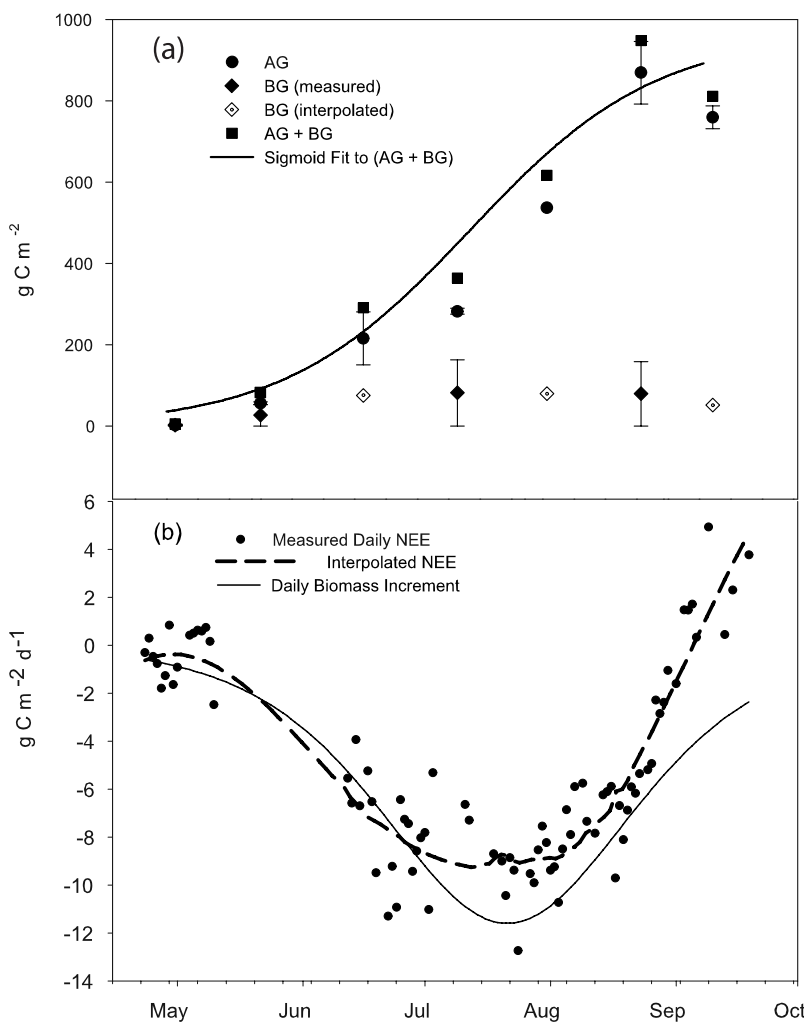


Figure 4. (a) Aboveground (AG) and belowground (BG) biomass measured by destructive sampling during the 2002 growing season. Solid circles are measured biomass from 0.5 m² quadrates (error bars are 1 SD, n = 2). Solid diamonds are measured belowground biomass. Missing values for belowground biomass are estimated using a function fit to the time series of belowground biomass: aboveground biomass (open diamonds). The dashed line is a three-parameter sigmoid curve fit to the sum of the belowground and aboveground biomass (biomass = 2797/[1 + exp{-(DAS - 89.9)/20.8}], $r^2 = 0.96$) where DAS = days after seeding. (b) Daily growth rate (the daily change in biomass) and daily NEE ($\text{g CO}_2\text{-C m}^{-2} \text{ d}^{-1}$) over the same period (solid circles). The dashed line is a negative exponential smoothing function fit to the daily NEE.

result, the ratio of CH₄ efflux to CO₂ uptake for the whole year ($F_{\text{CH}_4} : F_{\text{CO}_2} = 0.048$ to $0.056 \text{ g CH}_4\text{-C} [\text{g CO}_2\text{-C}]^{-1}$) was twice that calculated for the growing season alone ($F_{\text{CH}_4} : F_{\text{CO}_2} = 0.019$ to $0.024 \text{ g CH}_4\text{-C} [\text{g CO}_2\text{-C}]^{-1}$) (Table 1). We believe that the floodwater provided only a temporary restriction to gaseous transport and over time acted as a steady state reservoir so that emissions reflected the belowground rate of production (minus consumption, in the case of CH₄).

[30] F_{CO_2} and F_{CH_4} were tightly correlated during the growing season (Figure 7). The slope of this relationship was $-0.015 \text{ g CH}_4\text{-C} [\text{g CO}_2\text{-C}]^{-1}$ ($r^2 = 0.82$), indicating that about 1.5% of recently fixed carbon was returned to the atmosphere as CH₄. Chanton *et al.* [1997] also measured the relationship between CH₄ emission and net CO₂ exchange over the course of a growing season (using phyto-

chambers) and reported a larger ratio of CH₄ release to net CO₂ uptake ratio of 4.5%.

5. Discussion

5.1. What Is the Stoichiometry of CH₄ and CO₂ Exchange?

[31] From October 2001 to October 2002, the large net flux of CO₂ into the plant-soil system during the growing season ($789 \text{ g CO}_2\text{-C m}^{-2}$) exceeded the combined losses of rice grain harvesting (482 g C m^{-2}) and heterotrophic respiration over the fallow period ($240 \text{ g CO}_2\text{-C m}^{-2}$) leaving 67 g C m^{-2} remaining in the field. Over the same period the paddy released 26.1 to 31.0 g CH₄-C (equivalent to 4.5% to 5.6% of preharvest NEP). During the growing season only, the stoichiometric ratio was 1.9% to 2.4%, and

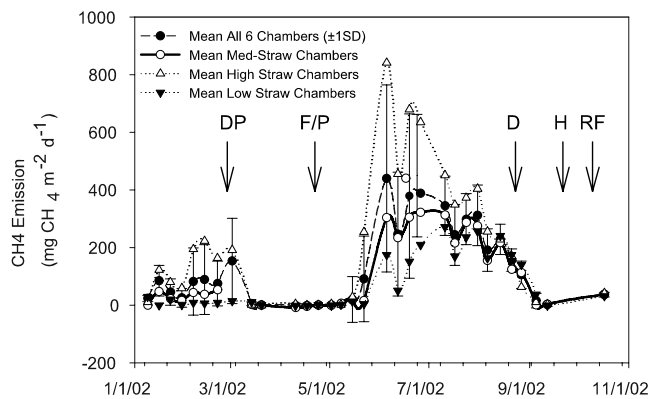


Figure 5. Methane emissions measured with static chambers. Solid circles are the pooled mean of all six chambers. Arrows indicate drainage prior to seed bed preparation (DP), flooding and planting of the rice crop (F/P), drainage prior to harvest (D), harvest (H), and reflooding over the winter (RF).

was relatively constant throughout crop development. When the C removed by harvest is accounted for, F_{CH_4} is equal to 39.0% to 46.3% of C remaining in the field.

[32] Incremental gains in biomass over the course of the growing season were moderately well correlated with daily F_{CO_2} . The residual variation from this relationship was probably due to the production of plant litter which contributed to the substrate source for the heterotrophic community. Biomass did not appear to be the major factor driving F_{CH_4} in this paddy over the entire growing season. Peak F_{CH_4} occurred early in the season and was probably derived from recent photosynthates allocated to the roots and then transferred to the soil as root litter or exudates. Substrate limitation appears to have limited F_{CH_4} in the latter part of the growing season. The assumption that there is a constant $F_{CO_2} : F_{CH_4}$ ratio over the course of the season for rice paddies is not supported here. Differences in cultivation practices will have a large impact on this ratio.

[33] Strong correlations between biomass and daily F_{CH_4} can result from increased substrate availability and/or increased plant transport [Sass *et al.*, 1990, 1991; Chanton *et al.*, 1997; Huang *et al.*, 1997]. A more complex relationship was found in this study: F_{CH_4} was positively correlated

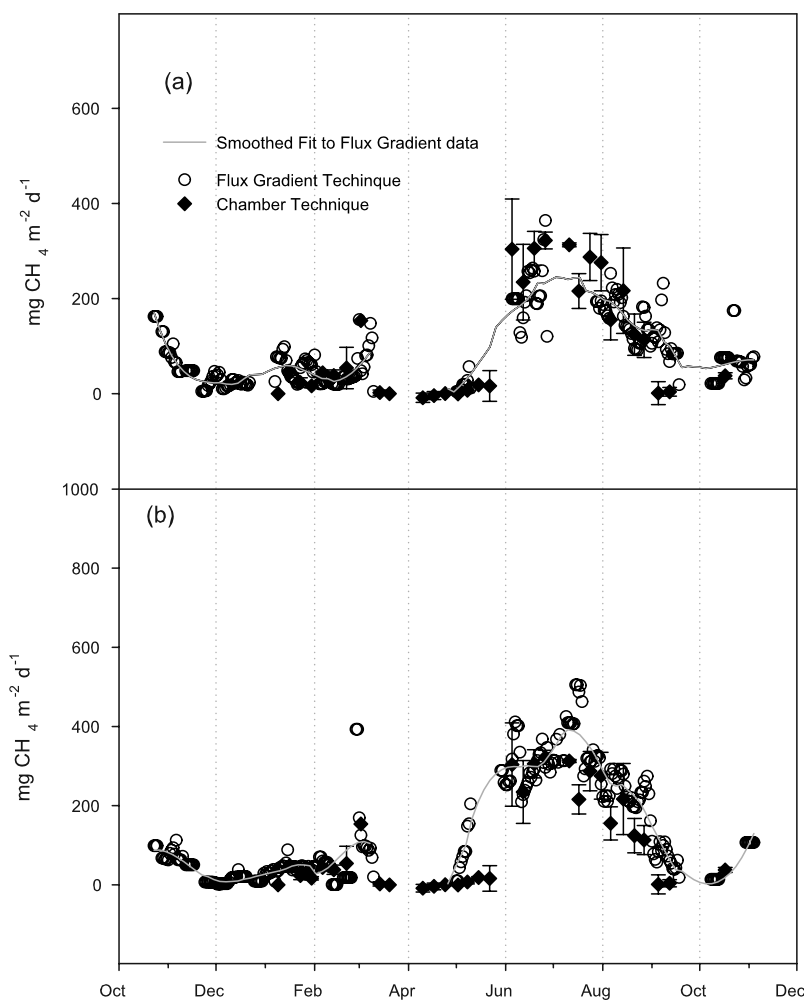


Figure 6. CH₄ emissions from the rice paddy measured by the flux gradient technique using (a) the scalar ratio and (b) the aerodynamic approach. Emissions measured using chamber are shown for comparison.

Table 1. Cumulative F_{CH_4} and F_{CO_2} and Stoichiometry Over the Period 10 October 2001 to 9 October 2002^a

Period ^b	Length, days	State of Paddy	Net Exchange of CO ₂ or CH ₄ (by the Three Methods Described in Text), g C m ⁻²				F_{CH_4} : F_{CO_2} Stoichiometry, g CH ₄ -C/ g CO ₂ -C		
			CO ₂	CH ₄			Chamber	SR	AD
			EC	Chamber	SR	AD			
10/10/01–1/8/02	91	flooded/bare	109.6	n.c.	10.4	8.5	0.0%	9.5%	7.7%
1/9/02–3/1/02	52	flooded/bare	10.8	1.4	2.4	2.4	13.5%	22.4%	22.5%
3/2/02–3/24/02	23	draining/bare	38.5	1.1	0.8	2.1	2.6%	1.7%	4.9%
3/24/02–4/16/02	23	drained/tillage	46.6	0.0	n.c.	n.c.	0.0%	0.0%	0.0%
4/17/02–4/22/02	6	flooded before seeding	4.7	0.0	n.c.	n.c.	0.2%	0.0%	0.0%
4/23/02–5/15/02	23	seedling	-18.4	0.1	n.c.	n.c.	-0.6%	0.0%	0.0%
5/16/02–6/8/02	24	mid-vegetative	-88.6	2.4	n.c.	n.c.	-2.7%	0.0%	0.0%
6/9/02–7/2/02	24	late vegetative	-226.5	4.3	3.6	4.1	-1.9%	-1.6%	-1.8%
7/3/02–7/15/02	13	early reproductive	-133.5	2.8	n.c.	n.c.	-2.1%	0.0%	0.0%
7/16/02–7/27/02	13	late reproductive	-131.7	2.2	n.c.	3.8	-1.5%	0.0%	-2.7%
7/28/02–8/22/02	25	ripening until drain	-195.2	3.6	3.1	3.2	-1.9%	-1.6%	-1.7%
8/23/02–9/14/02	23	ripening after drain	-18.9	1.0	3.0	3.0	-5.6%	-16.1%	-16.3%
9/15/02–9/21/02	7	maturity	23.6	0.1	0.3	0.3	0.3%	0.8%	0.8%
9/22/02–10/9/02	19	post harvest	30.3	0.3	0.4	0.4	1.0%	1.3%	1.2%
4/23/02–9/21/02	152	growing season	-789.3	16.4	15.2	18.6	-2.1%	-1.9%	-2.4%
10/10/01–10/9/02	365	over whole year	-548.9	26.3	26.1	31.0	-4.8%	-4.8%	-5.6%

^aCH₄/CO₂ ratios are only calculated when data exist for that interval. For the stoichiometry of the growing season and the entire year, missing data were filled by interpolation. F_{CO_2} values in the two lowermost rows include the assumption that the harvested rice grains are remineralized within 1 year. All other rows consider rice grains as biomass that remains in the field. When chamber measurements were zero or missing, flux gradient measurements were also assigned to zero. SR refers to the scalar ratio method and AD refers to the aerodynamic method.

^bDates are given as mm/dd/yy.

during the vegetative period, but negatively correlated after panicle initiation ($r^2 = 0.72$) (Figure 8). Primary production controlled CH₄ production in the early part of the growing season, but substrate depletion and CH₄ oxidation are likely causes for the limited emissions in later growth stages. CH₄ oxidation increased throughout the growing season because larger plants transport more oxygen to the rhizosphere. *Lu et al.* [2002] showed that the greatest deposition of photosynthates occurs during early plant growth suggesting that substrate availability should be greater in the vegetative stage than at later stages.

5.2. Are Paddies an Important Global Carbon Sink?

[34] The strength of a carbon sink is often measured using net ecosystem production (NEP): the difference between net primary production (NPP) and heterotrophic respiration [Woodwell and Whittaker, 1968]. In an agricultural field, the loss of biomass C via harvesting must also be included if it is envisaged that the remineralization of the removed C will be rapid. *Stallard* [1998] used a range of fixed stoichiometries between F_{CH_4} and F_{CO_2} to conclude that rice paddies were capable of sequestering 0.4 to 1.0×10^{15} g of carbon globally. The global area of rice cultivation is 147.5×10^{10} m² [Aselmann and Crutzen, 1989] and *Stallard's* estimate would therefore suggest a NEP of 271–678 g C m⁻² yr⁻¹. In this study, we measured an NEP of 549 g C m⁻² yr⁻¹ but our value does not include the C loss via harvest. The NEP measured here falls in the upper part of the range that *Stallard* reported but, when the C loss via harvest is included, the paddy sequesters a much smaller value of 67 g C m⁻² yr⁻¹.

[35] *Aselmann and Crutzen* [1989] estimated that the global NPP of rice was 0.56×10^{15} g C yr⁻¹ (1.4×10^{15} g dry matter yr⁻¹ assuming an average C content of 40%) or 380 g C m⁻² yr⁻¹. Similarly, *Bachelet et al.* [1995] estimated the NPP of China's rice paddies to be 135–222 $\times 10^{12}$ g C yr⁻¹ or 419–689 g C m⁻² yr⁻¹ (where the area of

rice cultivation in China is 3.22×10^{11} m²). NEP cannot exceed NPP, by definition [Woodwell and Whittaker, 1968], implying that the estimate by *Stallard* [1998] of 10^{15} g NEP is unfeasible with respect to the estimate by *Aselmann and Crutzen* [1989] and only marginally possible with the upper limit of the estimate by *Bachelet et al.* [1995].

[36] Our results imply a F_{CH_4} : F_{CO_2} ratio of 0.048 to 0.056 if we do not account for C removed via harvest and a higher ratio of 0.390 to 0.463 if we assume that harvested C is remineralized to CO₂ within 1 year (Table 1). *Stallard* [1998] assumed a ratio of 0.071 in the calculation where

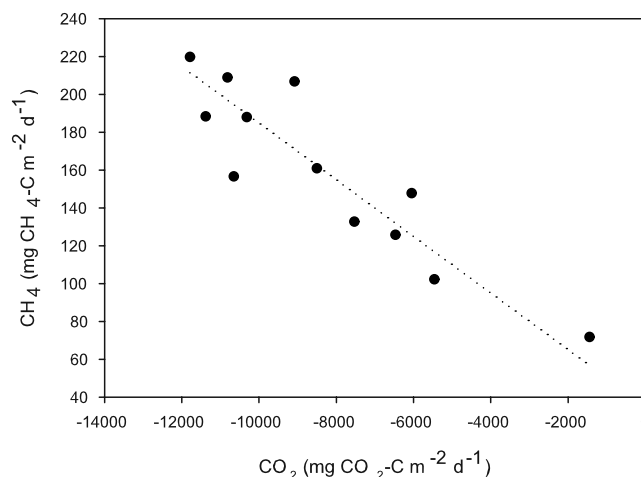


Figure 7. Relationship between CO₂ exchange (eddy covariance) and CH₄ flux (static chambers). The values for CO₂ exchange are the mean daily exchange for the 7-day period surrounding the time at which the chamber measurement of CH₄ was taken. Calculated using a Model II regression, the slope of the line is -0.015 (mg CH₄-C: mg CO₂-C) and $r^2 = 0.82$.

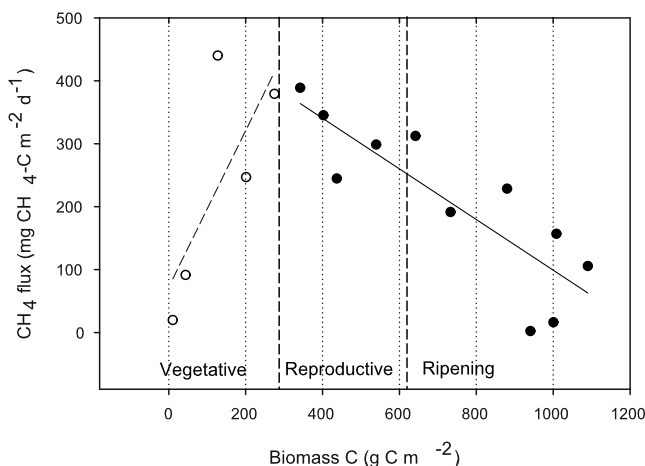


Figure 8. Relationship between CH₄ flux and biomass during the growth phases of the rice. One data point taken at the beginning of the growing season was excluded from the regression (open circle). The solid line is a least squares fit to the data such that: CH₄ Emission = $-0.301 \times \text{biomass} + 392.5$, $r^2 = 0.83$.

rice paddies bury 1×10^{15} g C. However, *Stallard* [1998] used close to the upper limit (148 Tg CH₄) of the range of global CH₄ emission rates estimated by *Aselmann and Crutzen* [1989] (60–160 Tg C). More importantly, by not including the effect of harvesting the rice on the net C balance, *Stallard* [1998] overestimated the sequestration potential to an extent determined by the ratio of the C content of rice grains to annual NEP. More recent estimates of global CH₄ flux from rice paddies are considerably smaller, for example, 25–54 Tg CH₄ yr⁻¹ [*Sass et al.*, 1999]. Using the midpoint of this range (39.5 Tg CH₄) and a stoichiometry of 0.071 (g CH₄-C/g CO₂-C) would lead to an estimate of global carbon storage for rice paddies of 0.41 Pg C (or 266 g C m⁻²). Using the stoichiometry found here and assuming all rice grain carbon is remineralized within 1 year leads to a much lower storage term of 0.10 Pg C (or 64 g C m⁻²).

[37] The annual stoichiometry found in the current study was largely controlled by the ratio of the length of the growing season to the length of the fallow period. To extrapolate the results of this study globally, one must account for agricultural practices in other regions. In particular, the length of the growing season, number of rice crops (or other crops) per year, the use of organic amendments, and the seasonal pattern of flooding must all be taken into account. For instance, NEP increased by 25–56% by growing a ratoon (secondary) crop of rice [*Campbell et al.*, 2001].

[38] The stoichiometry reported here was in a single year of measurement (2002). In 2001, the carbon sequestered by the rice over the same period was 70 g C m⁻² (assuming the 492 g of harvested C was mineralized within 1 year) which is within 5% of the 2002 carbon gain. The year to year variability in carbon accumulation was small for the two years of F_{CO_2} measurement reported here, and we would expect that the organic matter content of the soil would increase with sustained addition of this magnitude. The soil

organic C content (loss on combustion) was 9% (g C/g dry soil) between 0 and 1 cm depth and was 1.6–1.9% between 1 and 28 cm depth. These measurements indicated an inventory exceeding 6 kg C m⁻². The annual addition of 60 to 70 g C m⁻² was therefore a modest addition (1% to 2% per year) relative to the existing soil C pool.

5.3. Do Rice Paddies Have a Net Positive or Negative Radiative Balance?

[39] The annual stoichiometry is an estimate of the balance of radiatively important gases that are exchanged with the atmosphere. Long-lived greenhouse gases (CO₂, CH₄, N₂O and CFCs) have contributed 2.6 W m⁻² to the global radiative budget over the past 150 years with CO₂ accounting for 1.6 W m⁻² and CH₄ accounting for 0.57 W m⁻² [*Lelieveld et al.*, 1998]. To derive the radiative forcing of rice would require knowledge of changes in the source sink balance of radiatively active gases over the last ~150 years in addition to historical land-use changes. Calculating radiative forcing of rice agriculture is beyond the scope of this paper. Here we compare F_{CO_2} and F_{CH_4} on a CO₂-equivalent basis to estimate their current radiative impact. Rice agriculture contributes 6 to 17% of the total global CH₄ source [*Khalil and Shearer*, 2000]. The global warming potential of CH₄ on a mole for mole basis is 22.5 for a 20 year time period, 8.36 for a 100 year time period and 2.55 for a 500 year time period [*Intergovernmental Panel on Climate Change*, 2001]. The annual stoichiometry for the rice paddy was 0.390–0.463 assuming the C removed as rice grain was mineralized after a year. This stoichiometry suggests that rice paddies are a net source of CO₂ equivalents on 20 year and 100 year horizons. Only by using a 500 year horizon can the sequestration of atmospheric CO₂ come close to fully negating the radiative impact of the emitted CH₄.

[40] The seasonal pattern of CO₂ exchange, CH₄ and CH₄ expressed as CO₂ equivalents is shown in Figure 9. The release of CO₂ equivalents in the form of CH₄ was offset and exceeded by the strong net downward flux of CO₂ during the growing season. The paddy was drained during parts of March, April and October, soil temperatures were high, and rapid mineralization of carbon led to elevated CO₂ fluxes. It was during these periods that the paddy was the strongest source of CO₂ equivalents. Because CO₂ is chemically inert in the troposphere, its radiative impact is unimportant on subannual timescales. However, owing to the seasonal nature of the chemical sink processes for CH₄, the seasonal pattern of CH₄ emissions has relevance on shorter timescales. During the growing season, plant physiological processes involved in the allocation of carbon between aboveground and belowground tissue early in the season appeared to control the seasonal pattern of CH₄ release. Over the entire year, the net amount of carbon sequestered by the paddy, the sum of the net carbon uptake over the growing season (549 g C m⁻²) minus the carbon in the harvested rice grains which was assumed to be remineralized after 1 year (482 g C m⁻²), was 67 g C m⁻². The emitted CH₄ (26.1–31.0 g C m⁻²) was multiplied by 8.36 to transform its radiative effect to 219–259 g CO₂-C equivalents m⁻² (on a 100 year time basis). This indicates that 26% to 31% of the radiative impact of the emitted CH₄ was offset by the sequestration of atmospheric CO₂ in the rice paddy.

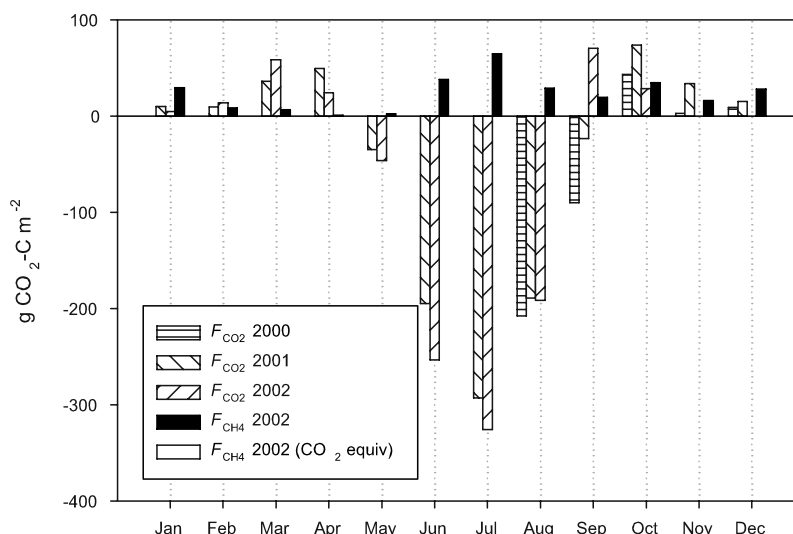


Figure 9. Monthly sums of net ecosystem exchange (September 2000 to October 2002) and CH₄ flux (October 2001 to October 2002). The white bars are the same data as the black bars multiplied by the global warming potential for CH₄ on a 100-year time horizon (8.36 mol/mol), and plotted as “CO₂ equivalents.”

[41] A more comprehensive treatment of the exchange balance of radiatively active gases should also include measurements of N₂O emissions. Rice paddies may be a globally important N₂O source [Bronson *et al.*, 1997a, 1997b; Zou *et al.*, 2005] but N₂O emissions are less intimately linked with photosynthesis than CH₄ emissions and more associated with episodic events such as nitrogen fertilizer application and field drainage. We would therefore not expect N₂O flux to exhibit similar dependence on CO₂ uptake as that which exists for CH₄ flux. Bronson *et al.* [1997a] showed that strategies to mitigate CH₄ production, such as using ammonium sulfate as a source of N (instead of urea) or midseason drainage, may increase N₂O emissions. Under certain treatments, stimulation of N₂O emission negated the savings achieved in reduced CH₄ flux. Typically 0.5% to 1.5% of applied N is emitted as N₂O and emission rates range from 2 to 290 g CO₂ equivalent m⁻² yr⁻¹ [Bronson *et al.*, 1997a; Zou *et al.*, 2005]. Using the mineral N application rates for this paddy, we can calculate that 0.17 g N₂O-N m⁻² yr⁻¹ was emitted (using a 1% conversion of applied N to emitted N₂O-N), equivalent to 0.26 g N₂O m⁻² yr⁻¹. Multiplying this by the GWP of N₂O (296, 100 year time horizon) [Intergovernmental Panel on Climate Change, 2001] gives an emission rate of 77 g CO₂-equivalents m⁻² yr⁻¹, roughly a third of that of CH₄. Clearly, continuous, year-round measurements of N₂O emissions would be valuable in constructing the complete greenhouse gas budget of rice agriculture.

6. Conclusions and Implications

[42] Continuous measurements of F_{CH_4} and F_{CO_2} in a California rice paddy were made using micrometeorological and chamber techniques in 2002. F_{CH_4} was 26.1–31.0 g CH₄-C m⁻² yr⁻¹ and was positively correlated to biomass accumulation during early growth but was negatively correlated during later growth. Over the growing season, the amount of carbon released as CH₄ was 4.8% to 5.6% of the

net CO₂ assimilated by the paddy. Over the entire year, the F_{CO_2} measurements indicated that the paddy was a carbon sink even when the carbon removed by harvest was accounted for. We provide an upper constraint for the quantity of C that paddies are likely to sequester globally. The CO₂ sequestration offset the CH₄ emission by 26% to 31% in terms of CO₂ equivalents.

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