Contribution of Ebullition to Methane and Carbon Dioxide Emission from Water between Plant Rows in a Tropical Rice Paddy Field

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1. Introduction

Although bubble ebullition through water in rice paddy fields dominates direct methane (CH\textsubscript{4}) emissions from paddy soil to the atmosphere in tropical regions, the temporal changes and regulating factors of this ebullition are poorly understood. Bubbles in a submerged paddy soil also contain high concentrations of carbon dioxide (CO\textsubscript{2}), implying that CO\textsubscript{2} ebullition may occur in addition to CH\textsubscript{4} ebullition. We investigated the dynamics of CH\textsubscript{4} and CO\textsubscript{2} ebullition in tropical rice paddy fields using an automated closed chamber installed between rice plants. Abrupt increases in CH\textsubscript{4} concentrations occurred by bubble ebullition. The CO\textsubscript{2} concentration in the chamber air suddenly increased at the same time, which indicated that CO\textsubscript{2} ebullition was also occurring. The CH\textsubscript{4} and CO\textsubscript{2} emissions by bubble ebullition were correlated with falling atmospheric pressure and increasing soil surface temperature. The relative contribution of CH\textsubscript{4} and CO\textsubscript{2} ebullitions to the daily total emissions was 95–97% and 13–35%, respectively.
Emission by bubble ebullition is considered to be greater than that by diffusion from paddy water [6]. The bubbles usually contain a high concentration of CH$_4$ ranging between 1 and 82% (v/v) [10, 11] and comprise most of the total CH$_4$ pool in flooded paddy soil [12]. Bubble production and ebullition are enhanced by applied organic materials during the initial plant growth period [6, 13, 14] and by organic substances originating from rice roots during later growth stages [6, 12, 14]. 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 [15].

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 [16–19]. Falling atmospheric pressure has been shown to be the most important contributor to CH$_4$ bubbling in peatlands [18, 19]. 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 [20].

In contrast, CO$_2$ exchange through paddy water is the result of photosynthesis of aquatic plants and respiration of both the plants and the soil microorganisms [21]. Emission due to soil respiration is suppressed by paddy water during flood irrigation [21, 22], but the CO$_2$ concentration in soil bubbles is between 2.2 and 13.0% (v/v) [11, 23], 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.

2. 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 18 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 18 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.

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 (Figure 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 (Figures 2(a), 2(c), and 2(e)) or a slow-constant increase (Figures 2(c) and 2(e)). Emission by bubble ebullition events was defined as a sudden increase in concentration ($\Delta$C/Δt) of ≥0.29 ppm min$^{-1}$, whereas emission by diffusion was defined as a slow-constant increase ($\Delta$C/Δt) 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 (Figures 2(b) and 2(f)), a steady increase (Figure 2(d)), or a decrease by plant uptake (Figure 2(f)). 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 (Figure 2(f)) 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 (Figures 2(a), 2(b), 2(c), 2(e), and 2(f)), 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 (Figure 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 (Figure 2). The gas flux
$F$ (mg m$^{-2}$ h$^{-1}$) was calculated using temporal changes in gas concentration as [24]

$$F = \frac{V}{A} \left[ \frac{dC(t)}{dt} \right]_{t=0},$$  \hspace{1cm} (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

$$C(t) = C_{\text{max}} - (C_{\text{max}} - C_0) \exp(-kt),$$  \hspace{1cm} (2)

where $C_{\text{max}}$ 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 $C_{\text{max}}$, $C_0$, and $k$ were iteratively obtained using the data of observed gas concentration versus time. Substituting (2) at $t = 0$ into (1) means that the gas flux $F$ (mg m$^{-2}$ h$^{-1}$) can be calculated as [24]

$$F = \frac{V}{A} k (C_{\text{max}} - C_0).$$  \hspace{1cm} (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 (eTape Vaisala Inc., Helsinki, Finland), respectively. Water depth in the rice field was measured with a water level sensor (eTape Vaisala Inc., Helsinki, Finland). 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.

3. Results and Discussion

3.1. CH$_4$ Emission. Episodic and rapid increases in CH$_4$ concentration were identified in 21 out of the 46 measurements (Figures 2(a), 2(c), and 2(e)). 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$^{-1}$ [25].

The large CH$_4$ emissions via bubble ebullition mainly occurred between 10:00 a.m. and 5:00 p.m. local time (Figure 3(a)). During this period, atmospheric pressure markedly decreased and reached a minimum value (Figure 3(b)). A night-time CH$_4$ ebullition event also occurred at 2:50 a.m. local time on September 21 (Figures 2(c), 3(a), and 3(b)), 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 (Figure 4; $r = -0.77, p < 0.001$). 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 Tokida et al. [18, 19] 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 [16]. Reduced air pressure also increases the CH$_4$ concentration of gas bubbles by degassing dissolved CH$_4$ in soil solution [16, 26, 27]. 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, are 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 [17, 27]. In the current study, soil surface temperature increased from around 6:30 a.m. and reached
Figure 2: Examples of the changes in CH\textsubscript{4}, CO\textsubscript{2} concentrations (7-point running average) in the closed chamber measured at 2:50 p.m. on September 20 ((a), (b)), at 2:50 a.m. on September 21 ((c), (d)), and at 4:50 p.m. 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\textsubscript{4}, CO\textsubscript{2} emission/uptake rates, before respective increase or decrease events.
a maximum value at 3:00–3:30 p.m. on each day (Figure 3(b)). This period approximately corresponded to that when \( \text{CH}_4 \) ebullition events frequently occurred. The positive and significant correlation between soil surface temperature and \( \log_{10} \) \( \text{CH}_4 \) emission via bubble ebullition \( (r = 0.66; p < 0.005; \text{Figure } 4(b)) \) indicates that the increase in soil surface temperature contributed to \( \text{CH}_4 \) ebullitions in the daytime. Ebullition events occurred at 8:50 a.m. on both days and at 9:50 a.m. on September 21, even though atmospheric pressure did not fall between 6:30 a.m. and 10:00 a.m. 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 \( \text{CH}_4 \) production in soil [28]. Therefore such increased biological activities might have also increased the \( \text{CH}_4 \) concentration in the bubbles.

\( \text{CH}_4 \) emission via bubble ebullition (546–617 mg m\(^{-2}\) d\(^{-1}\)) contributed 95–96% of total daily \( \text{CH}_4 \) emission (567–647 mg m\(^{-2}\) d\(^{-1}\)) through flooded water (Table 1). These \( \text{CH}_4 \) ebullitions mainly occurred in the daytime and were associated with falling atmospheric pressure and increasing soil temperature, as discussed above (Figures 3(a) and 3(b)). In contrast, \( \text{CH}_4 \) emission by diffusion (21–30 mg m\(^{-2}\) d\(^{-1}\)) accounted for only 3.7–4.7% of total daily \( \text{CH}_4 \) emission from flooded water (Table 1). The \( \text{CH}_4 \) emissions by diffusion were mostly observed at nighttime when soil temperature decreased (Figures 3(a) and 3(b)). Therefore, these results clearly show that \( \text{CH}_4 \) emission in rice paddy fields is predominant by daytime ebullition from flooded water with much lower \( \text{CH}_4 \) emissions at nighttime by diffusion.

### Table 1: Cumulative \( \text{CH}_4 \) emissions and relative contribution of bubble ebullition and diffusion processes to total emissions.

| Date  | \( \text{CH}_4 \) ebullition (mg m\(^{-2}\) d\(^{-1}\)) | Via \( \text{CH}_4 \) ebullition (%) | \( \text{CH}_4 \) diffusion (mg m\(^{-2}\) d\(^{-1}\)) | Via \( \text{CH}_4 \) diffusion (%) | Total \( \text{CH}_4 \) emission (mg m\(^{-2}\) d\(^{-1}\)) |
|-------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|----------------------------------|
| Sep. 20 | 617.4 | 95.3 | 30.3 | 4.7 | 647.7 |
| Sep. 21 | 546.2 | 96.3 | 20.9 | 3.7 | 567.1 |

3.2 \( \text{CO}_2 \) Emission. Episodic increases in \( \text{CO}_2 \) concentration were found in 14 of the 21 measurements when \( \text{CH}_4 \) ebullition events occurred. During these 14 chamber closure periods, the \( \text{CO}_2 \) concentration in the chamber air increased abruptly (Figures 2(b) and 2(f)) at about the same time as \( \text{CH}_4 \) concentration increased (Figures 2(a) and 2(e)). These similar patterns indicate that \( \text{CO}_2 \) was released to the atmosphere in the bubbles along with the \( \text{CH}_4 \). In the other 7 measurements, there was a steady increase in \( \text{CO}_2 \) concentration but no episodic increase, as shown in Figure 2(d), while \( \text{CH}_4 \) concentration abruptly increased (Figure 2(c)). This suggests these bubbles did not contain much \( \text{CO}_2 \).

\( \text{CO}_2 \) 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 \( \text{CO}_2 \) from flooded water to the atmosphere by diffusion, likely due to the gradient in \( \text{CO}_2 \) concentration at the interface between the flooded water and the atmosphere and also due to respiration of the aquatic plants [21]. The values of \( \text{CO}_2 \) 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\(^{-1}\) [29].

On September 20, most of the \( \text{CO}_2 \) fluxes were outgoing emissions due to bubble ebullitions. The highest \( \text{CO}_2 \) emission (196.2 mg m\(^{-2}\) h\(^{-1}\)) occurred at 2:50 p.m. (Figures 2(d) and 3(a)), coinciding with a high \( \text{CO}_2 \) concentration in the bubbles of up to 11.74% (v/v). However, at 1:50 p.m., there was a negative (incoming) \( \text{CO}_2 \) flux, even though there was a \( \text{CH}_4 \) ebullition event. This overall negative flux must have been due to the fact that \( \text{CO}_2 \) uptake by photosynthesis of the aquatic plants exceeded emissions by bubble ebullition, as shown in Figure 2(f) for \( \text{CO}_2 \) transfer.
Figure 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.

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 ($r = -0.72; p < 0.05$; Figure 4(c)) and soil surface temperature ($r = 0.72; p < 0.05$; Figure 4(d)). 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 [16, 17]. In addition, the soil surface temperature was between 27 and 40°C during the measuring period which was optimal for respiratory soil microbes in the submerged paddy soil [28]. 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 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 CO₂ uptake by aquatic plants would have exceeded CO₂ emission by bubble ebullition. Moreover, the very low concentration of CO₂ in the bubbles also contributed to lower CO₂ emission by bubble ebullition. The CO₂ emissions by diffusion mostly occurred at nighttime just like for CH₄. The nighttime CO₂ emissions by diffusion were mostly attributed to the gradient in CO₂ concentrations between the atmosphere and the flooded water and also to CO₂ respiration by small aquatic plants [21].

4. Conclusions

Our study found that daytime CH₄ 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 CH₄ ebullition because soil temperature was low compared with that in the daytime. The fact that CH₄ and CO₂ concentrations in the chamber air increased abruptly when bubbles were released suggests that bubble ebullition events caused not only CH₄ emission but also CO₂ emission. The CO₂ 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 CH₄ and CO₂ ebullitions in tropical rice paddy fields.

We also found that CH₄ emission was predominant due to daytime ebullition, whereas only a small proportion of CO₂ emissions was due to daytime ebullition. The low CO₂ ebullition throughout the day was due to CO₂ photosynthesis and respiration by aquatic plants, meaning that CO₂ emission was mainly by diffusion between flooded water and the atmosphere.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Table 2: Cumulative CO₂ emissions and relative contributions of bubble ebullition and diffusion processes to total emissions.

| Date   | CO₂ ebullition (mg m⁻² d⁻¹) | Via CO₂ ebullition (%) | CO₂ diffusion (mg m⁻² d⁻¹) | Via CO₂ diffusion (%) | Total CO₂ emission (mg m⁻² d⁻¹) |
|--------|-----------------------------|------------------------|----------------------------|-----------------------|---------------------------------|
| Sep. 20| 648.2                       | 35.0                   | 1203.8                     | 65.0                  | 1852.0                          |
| Sep. 21| 159.7                       | 13.3                   | 1040.4                     | 86.7                  | 1200.1                          |
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