

Redox Range with Minimum Nitrous Oxide and Methane Production in a Rice Soil under Different pH

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ABSTRACT

A Louisiana rice soil was incubated from the most oxidizing to the most reducing conditions that could be maintained. Four different pH levels were used. Nitrous oxide production initiated shortly after the incubation started under oxidized conditions. As the soil suspension became more reducing, a large amount of CH₄ was produced at a critical reducing point and increased exponentially with a further decrease of redox potential (E_H). The results indicated that there was no statistically significant difference between the theoretically predicted decrease of E_H with increase of pH and the observed change of E_H with pH for N₂O production (60 mV, $P = 0.932$), and for significant CH₄ production (93 mV, $P = 0.204$), respectively. Consequently, the E_H range with minimum N₂O and CH₄ production shifted to lower values of the E_H scale when pH increased. Global warming potential (GWP) contribution from the studied soil mainly comes from N₂O production at moderately reducing conditions, and from CH₄ production under very reducing conditions. There was a slight production of CH₄ at high E_Hs soon after incubation started, but this CH₄ production was not a significant source of GWP from soils because of its small quantity and transient occurrence. If pH is neutral, the calculated E_H range with minimum GWP is generally in the range of -150 to +180 mV. This redox window accounts for >40% of the entire E_H range in this study, which makes appropriate management of irrigated rice fields possible that will minimize both N₂O and CH₄ production.

NITROUS OXIDE (N₂O) and methane (CH₄) are two important greenhouse gases only secondary to carbon dioxide (CO₂) in their contribution to radiative forcing of the Earth's atmosphere [Intergovernmental Panel on Climate Change (IPCC), 2001]. Tropical and subtropical irrigated rice fields are considered a major anthropogenic source of atmospheric CH₄ during the flooded period of the fields, and an important source of N₂O during the remaining unflooded season. Fluctuation of soil water content determines soil aerobic and anaerobic conditions, which can be characterized by E_H. In flooded rice soil, there are two aerobic/anaerobic interfaces—flooded soil surface layer maintained by O₂ dissolved in the standing water, and plant rhizosphere maintained by O₂ diffusing through the rice plant. These aerobic/anaerobic interfaces control many redox reactions including nitrification, denitrification, cycling of iron and manganese compounds, sulfate reduction and sulfide oxidation, and CH₄ formation and oxidation (Patrick and DeLaune, 1972; Ponnampereuma, 1972; Smith and DeLaune, 1984; Reddy et al., 1989; Patrick and Jugsujinda, 1992). Nitrous oxide is mainly produced

from denitrification under moderately reducing conditions where the reduction intensity is not great enough to completely reduce nitrate to nitrogen gas (N₂). Significant CH₄ formation in soils generally occurs when E_H declines below -150 mV (Wang et al., 1993) or even below -300 mV (Cicerone and Oremland, 1988). Soils in irrigated rice fields will undergo a significant fluctuation of pH because of organic matter (OM) addition and fertilization, flooding and drainage cycle, plant development and metabolism, and soil microbial activities (Granli and Bøckman, 1994). The inverse relationship of E_H and pH is described by the Nernst equation. Redox potential change per pH unit may vary from 59 to 177 mV, depending on redox couples and kinetic of the reaction (Bohn, 1971). Since E_H values represent mixed potentials, a simple correction of 59 mV per pH unit may be adequate.

The concentration of greenhouse gases in the atmosphere is increasing in an unprecedented rate since industrialization (IPCC, 2001). Agriculture plays an important role in the global fluxes of these greenhouse gases and has been suggested as a potential effective approach for slowing further increases in radiative forcing (Duxbury et al., 1993). The trade-off relationship of N₂O and CH₄ production in rice soils, as observed by Chen et al. (1997), makes it a real challenge to reduce the production of one gas but not to increase the production of the other. Our recent study indicates that both N₂O and CH₄ productions can be low in a specific soil redox potential range of +120 to -170 mV (pH varies between 6.5 and 7.2 among four different soils) where the soil is reducing enough to favor complete denitrification to N₂, but is still oxidizing enough to inhibit methanogenesis (Yu et al., 2001). However, the effect of pH on E_H was not well considered, thus the conclusion may be more case specific. A small amount of CH₄ production was recently observed during the initial phase of reduction in rice soils despite a high E_H and presence of soil oxidants (Roy et al., 1997; Yao and Conrad, 1999). Rapid release of H₂ from OM decomposition makes it thermodynamically possible to produce CH₄ by H₂/CO₂ utilizing methanogens at beginning of soil submergence. The implication of this initial CH₄ production to greenhouse gas production in rice soils was not assessed in our previous study as well as elsewhere. More comprehensive analysis in technique and statistics was conducted in this study with the following expectations: (i) to verify the existence of an optimum E_H range where both N₂O and CH₄ productions are not significant, (ii) to study the effect of pH on such a E_H range,

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Abbreviations: E_H, soil redox potential; IPCC, Intergovernmental Panel on Climate Change; FID, flame ionization detector; GC, gas chromatography; GWP, global warming potential; OM, organic matter.

(iii) to evaluate the relative contribution of the early CH_4 production in overall greenhouse gas production in rice soils, and (iv) to draw a more general conclusion on the E_H range with minimum greenhouse gas productions in soils when pH is in neutral.

MATERIALS AND METHODS

Sample Soil and Incubation Procedure

A Crowley silt loam soil (fine, smectitic, hyperthermic Typic Albaqualfs) was taken from the field surface layer (0–20 cm) at the Rice Experiment Station, Crowley, LA. The soil was air-dried, sieved (1 mm), thoroughly mixed, and stored at room temperature (20°C) before the experiment. Basic soil characteristics were analyzed and provided in Table 1.

The microcosm technique of Patrick et al. (1973) was used in this study with some modification. Four hundred grams of the air-dried Crowley rice soil was weighted into a 2300-mL Erlenmeyer flask, to which 1600 mL of deionized water was added to make a soil suspension. Then four grams of ground rice straw was added to the soil suspension as an energy source for the microorganisms, and KNO_3 was added to provide 50 mg N kg^{-1} soil. Each flask was capped with a rubber stopper, in which a septum was installed for gas sampling. A gas inlet and outlet was installed so that the accumulated gases in the headspace could be purged if needed. The soil suspension was maintained homogenous by continuous stirring with a magnetic stirrer, and kept anaerobic by maintaining a slow flow ($\approx 20 \text{ mL m}^{-1}$) of pure N_2 during the incubation.

Treatment and Measurement

Four treatments with different pH values were established: (A) control without pH adjustment, (B) pH 5.5, (C) pH 7.0, and (D) pH 8.5. Normally, pH was measured and then adjusted to each target pH value with 1.0 N HCl or 1.0 N NaOH where appropriate after gas sampling, but sometimes it was adjusted according to the deviation of pH reading without gas sampling. Since it is not practical to maintain two soil suspensions to be at the same pH and redox condition because of variations of the soil and incubation environment, a single microcosm system was used for each of the above four treatments. Instead of using treatment replication to ensure the duplicability and accuracy of the experiment, an approach of frequent sampling and measurement was used in this study.

It is critical to ensure the accuracy of the E_H and the pH measurements in such a frequent sampling approach. The E_H of each soil suspension was measured by two Pt electrodes and a calomel reference electrode that were connected to a millivolt meter (Cole-Parmer, Chicago, IL). All Pt electrodes were prechecked (deviation < 10 mV) with standard pH 4.0 and pH 7.0 buffer solutions saturated with quinhydrone before installation to the microcosms (Bohn, 1971). A Handheld pH meter with a combination pH electrode (Accumet AP62, Fisher Scientific, Pittsburgh, PA) was used for pH measurement of the soil suspensions, and the electrode was calibrated with standard pH 4.0 and pH 7.0 buffer solutions before each measurement.

Gas Sampling and Analysis

Gas samples were taken whenever E_H in the microcosm systems changed by >10 mV. It was necessary for such frequent samplings, especially for N_2O measurement, because it is unknown when N_2O production would occur at each pH and redox condition, and N_2O production can only be moni-

Table 1. Selected physical and chemical characteristics of the sample soil.

Texture	pH	Organic matter	Total N	Total Fe	Total Mn	Total S
		g kg^{-1}			mg	
Silt loam	7.3	16.7	0.7	68.2	19.5	10.7

tored for a short period of time if no additional nitrate supply is available. The microcosms were purged with pure N_2 at a higher flow rate (at least double than normal) for two hours before each gas sampling. Then, a gas sample in the headspace of each microcosm was withdrawn with a syringe with an airtight valve three times after purging, 0 (immediately after closing the purging gas), 0.5, and 1 h, respectively. The gas samples were stored in the syringes for no more than 48 h before analysis. Nitrous oxide and CH_4 were analyzed with a Tremetrics 9001 gas chromatograph (GC) with dual channel system with an electron capture detector for N_2O and a flame ionization detector (FID) for CH_4 and CO_2 . A methanizer catalyst column was installed after the sample separation column of the GC, which reduced CO_2 to CH_4 for FID detection. The sensitivity of the detectors was ensured to detect the atmospheric level of N_2O (0.3 $\mu\text{L L}^{-1}$), CH_4 (1.7 $\mu\text{L L}^{-1}$), and CO_2 (370 $\mu\text{L L}^{-1}$). Each gas analysis was calibrated by its corresponding certified standard.

Calculation and Statistical Analysis

Gas production rate was calculated by linear regression of the three analyses in 1 h, and expressed as μg gas per kg soil (air dried) per hour. Such linear regression approach is the best to ensure the accuracy of gas production rate measurement, because gas production rate is calculated exactly as the amount of gas flux within the sampling time, no matter if any interested gas remains in the system at the zero-time gas sampling. The amount of gas dissolved in the liquid phase was calculated by taking mole fraction solubility of 7.07×10^{-4} for CO_2 , 5.07×10^{-4} for N_2O , and 2.81×10^{-5} for CH_4 (Handbook of Chemistry and Physics, 1991), but the effect of pH on the gas solubility was not considered. Significant effect of pH on CO_2 solubility in the water phase was expected, but it is difficult to precisely calculate total CO_2 production because of likely imbalance of CO_2 –carbonate system during the 1-h measurement (note: the system was flushed with N_2 before the measurement). Redox potential was standardized to the standard H_2 electrode by adding 247 mV (the correction factor for calomel reference electrode at 20°C) to the observed instrument reading.

Data were processed with Excel (Microsoft 2000), and statistical analysis was conducted with SAS (SAS Institute, Inc., Cary, NC). Analysis of variance with PROC GLM was conducted to determine the difference of means between different treatments. Simple linear regression with PROC REG was conducted to test if the slope of a regression was significantly different from that of a theoretical model. The significant level was chosen at $\alpha = 0.05$ for all statistical analysis.

RESULTS AND DISCUSSION

pH Treatment

Soils undergo pH change in reaching anaerobic conditions because of a series of oxidation-reduction reactions. The increase in pH of flooded soils is largely because of reduction of iron and manganese in form of oxides or hydroxides. Carbon dioxide production in the various reactions was probably responsible for the de-

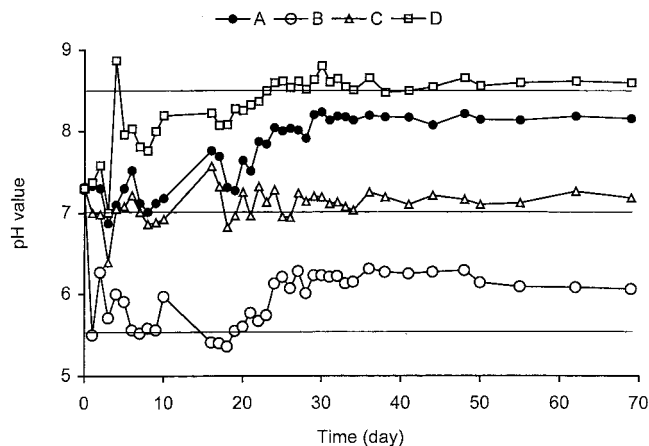


Fig. 1. Variation of pH during the incubation. (A) control without pH adjustment, (B) pH 5.5, (C) pH 7.0, and (D) pH 8.5.

crease of soil pH. In a prolonged flooding situation, soils tend to be near neutral in pH for both originally acidic and alkaline soils (Ponnamperuma, 1972). During the first 3 wk of the incubation, pH in the soil suspensions varied significantly regardless of the pH adjustment, which reflected dramatic degradation of the OM and the initiations of reduction processes of various soil oxidants in the anaerobic condition (Fig. 1). Without adjustment (Treatment A), pH in the soil suspension tended to increase by about one unit (from 7.3 to 8.2) by the end of the experiment. Continuous flushing of the microcosm with N_2 might substantially diminish the CO_2 level in the system, which would consequently increase the soil pH to some extent. Because of such tendency of the soil pH change, pH in the other three pH-adjusted soil suspensions stabilized at higher levels than that expected: 6.2 for Treatment B, 7.2 for Treatment C, and 8.6 for Treatment D, respectively. It seems that the pH buffering capacity of the sample soil is high because pH was adjusted even more frequently than gas samples were taken. However, we only needed to ensure that the soils were incubated at different pH conditions in this experiment so that we could study the effect of pH on N_2O and CH_4 production. It did not matter that the incubated soils did not reach their target pH levels in this study. Redox potentials are interpreted with their corresponding pH in the following discussion.

Redox Potential Measurement

The soils were incubated across a E_H range where both N_2O and CH_4 productions could be observed in

Table 2. Redox potential (E_H) measurement.

Treatment	Measurement	Mean [†]	Range	Regression		
				Equation	r^2	P value [‡] (n)
A	E_{H-1}	129.4	-335 to 495	$E_{H-1} = 0.912 \times E_{H-2}$	0.992	0.012 (77)
	E_{H-2}	136.4	-335 to 525			
B	E_{H-1}	147.3	-160 to 520	$E_{H-1} = 1.109 \times E_{H-2}$	0.960	<0.001 (58)
	E_{H-2}	126.8	-180 to 545			
C	E_{H-1}	113.5	-285 to 395	$E_{H-1} = 1.020 \times E_{H-2}$	0.975	0.230 (98)
	E_{H-2}	116.4	-285 to 445			
D	E_{H-1}	90.4	-305 to 425	$E_{H-1} = 1.041 \times E_{H-2}$	0.938	0.167 (85)
	E_{H-2}	90.3	-335 to 385			

[†] There was no significant difference in mean value of each treatment (ANOVA, $P > 0.05$).

[‡] P value was the statistic of the slope test (simple linear regression) against the theoretical model $E_{H-1} = E_{H-2}$.

all four treatments. The E_H range differed between different treatments depending on the pH levels reached, but was generally as wide as 700 to 800 mV. Two replicate electrodes in the four treatments showed no statistically significant difference ($P = 0.775$, $n = 318$) when they were plotted and analyzed together. However, individual analysis of the four treatments indicated that the two replicate electrodes for Treatments A and B were, respectively, significantly different in E_H reading, but no significant differences were found for Treatments C and D, respectively (Table 2). Variations of E_H readings are expected because of the mixed potential measurement and the reaction kinetics. Larger deviations between the two replicate electrodes were found at the beginning of the incubation when E_H was high. The largest SDs between the two replicate measurements observed were up to 67.2 for Treatment A, 91.9 for Treatment B, 56.6 for Treatment C, and 70.7 mV for Treatment D, respectively. However, most of the SDs of the two replicate measurements were <20 mV when E_H s were below -100 mV, giving more reliable results under reducing conditions. All E_H values are presented by means of the two replicate E_H measurements, which probably represented the best estimates.

CO_2 Production

Redox potential of a soil after flooding represents the progressive development of reducing intensity. Soil respiration can yield energy for soil microorganisms by oxidizing OM with production of CO_2 . In anaerobic conditions, the availability of major soil electron acceptors (nitrate, manganic, and ferric oxides or hydroxides, and sulfate) is limited, compared with unlimited O_2 supply in aerobic conditions. A quantitative relationship between CO_2 production and E_H was attempted in this study. The results indicated a statistically significant decrease of CO_2 production in logarithmic scale with the decrease of E_H in all four different treatments (Fig. 2, Table 3). The exponential relation obtained cannot be fully interpreted by the decrease of soil OM content (not determined) during the incubation. Least amount of CO_2 production was found in Treatment D that had the highest pH adjustment mainly because of higher solubility of CO_2 under higher pH. One of the striking characteristics of wetland soil is the smaller production of CO_2 and the accumulation of organic C in the sediment (Smith et al., 1983). It is expected that soil respira-

Table 3. CO₂ production and its relation to soil redox potential (E_H, mV).

Treatment	CO ₂ production		Regression		
	Mean	Range	Equation	r ²	P value† (n)
	mg kg ⁻¹ h ⁻¹				
A	11.2a‡	0.0 to 61.6	Log CO ₂ = 0.0020 × E _H + 0.534	0.777	<0.001 (46)
B	7.5a,b	0.0 to 37.1	Log CO ₂ = 0.0022 × E _H + 0.215	0.711	
C	10.9a	0.2 to 61.3	Log CO ₂ = 0.0034 × E _H + 0.042	0.638	
D	4.1b	0.0 to 17.5	Log CO ₂ = 0.0011 × E _H + 0.410	0.311	

† P value was the statistic of the slope test (simple linear regression) against zero (no relationship).

‡ Data labeled with the same letter were not significantly different (ANOVA, *P* > 0.05).

tion will be weakened with less CO₂ production if soils are maintained flooded, and consequently there will be a substantial decrease of energy yield in such an anaerobic condition.

N₂O and CH₄ Production

Nitrous oxide and CH₄ production in the four treatments showed a similar pattern, as found in our previous study (Yu et al., 2001). Nitrous oxide production occurred shortly after the incubation started, while most of the CH₄ production occurred one or two months later, depending on different pH treatments (Fig. 3). Denitrification is believed to be the major source of N₂O production. Nitrous oxide production formed a bell-shape pattern, featuring an accelerating phase followed by a declining phase as the E_H decreased. The N₂O production generally tended to increase exponentially with the decrease of E_H in the accelerating phase. With no additional supply of nitrate, N₂O production would go to the declining phase after reaching a maximum at a particular redox level. The dynamics of N₂O production will also be affected by the development of denitrifying enzymes during the incubation, especially N₂O reduction enzyme that controls the N₂O/N₂ ratio of denitrification (Rudaz et al. 1991; Dendooven and Anderson 1995). Small amounts of CH₄ production was found at an early phase of the incubation in all treatments when E_H was still high (Fig. 3). This initial CH₄ production has been studied and reported by other researchers (Fetzer and Conrad, 1993; Roy et al., 1997). Yao and

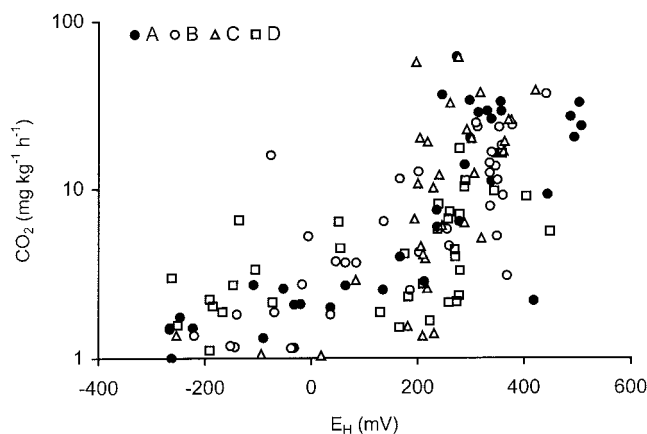


Fig. 2. CO₂ production under different soil redox conditions. (A) control without pH adjustment, (B) pH 5.5, (C) pH 7.0, and (D) pH 8.5. The figure was plotted in logarithmic scale. CO₂ production below 1.0 mg kg⁻¹ h⁻¹ was considered insignificant and not illustrated in the figure for clarity.

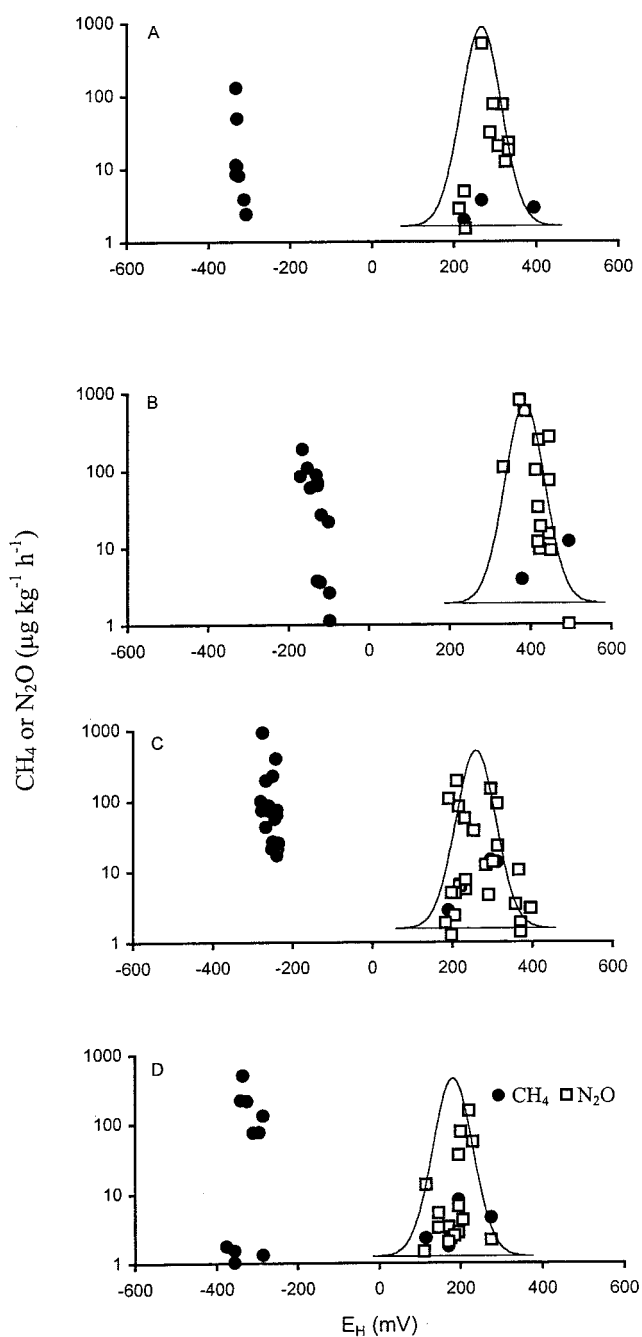


Fig. 3. N₂O and CH₄ production under different soil redox conditions. (A) control without pH adjustment, (B) pH 5.5, (C) pH 7.0, and (D) pH 8.5. The figure was plotted in logarithmic scale. N₂O and CH₄ production below 1.0 µg kg⁻¹ h⁻¹ was considered insignificant and not illustrated in the figure for clarity.

Table 4. N₂O and CH₄ production and their relation to soil redox potential (E_H).†

Treatment	N ₂ O production		Initial CH ₄ production		Significant CH ₄ production observation
	Observation	E _H range	Observation	E _H range	
	μg kg ⁻¹ h ⁻¹	mV	μg kg ⁻¹ h ⁻¹	mV	μg kg ⁻¹ h ⁻¹
A	1.5 to 520.0	213 to 333	2.0 to 3.7	225 to 395	2.4 to 130.0
B	1.0 to 804.8	333 to 495	3.9 to 12.1	380 to 495	1.1 to 190.0
C	1.2 to 190.5	183 to 395	2.9 to 14.6	190 to 295	17.1 to 929.5
D	1.5 to 152.8	110 to 275	1.7 to 8.2	170 to 275	1.0 to 503.4

† N₂O and CH₄ production below 1.0 μg kg⁻¹ h⁻¹ was considered insignificant and not included in the table.

Conrad (1999) identified three sequential phases in soil reduction dynamics: (i) H₂-dependent methanogenesis at positive E_H (360–510 mV), then (ii) sulfate or Fe (III) reductions when the first phase methanogenesis is becoming thermodynamically unfavorable, and (iii) vigorous acetate-dependent methanogenesis with a constant rate. The early initiation of methanogenesis has been overlooked because of its small quantity, as it becomes evident only when CH₄ is detected around the atmospheric level (1.75 μL L⁻¹), and is plotted on a logarithmic scale. Large quantities of CH₄ was produced after a critical point of the E_H in each treatment. The later significant CH₄ production was not limited by the soil OM, and the production rate increased exponentially with the decrease of E_H, as shown by the linear relation in a logarithmically scaled figure.

Detailed analyses of the results in Fig. 3 are summarized in Table 4. The E_H range where N₂O was produced varied in each treatment, but was uniformly as wide as 100 to 150 mV. In each soil, the E_H range for N₂O production generally overlapped with that for the initial CH₄ production. Highest N₂O production was observed in Treatment B, probably because of the inhibition of N₂O reduction activity by the lower pH (Burford and Bremner, 1975). The amount of amended nitrate provides substrate for denitrification only enough for 2 or 3 d at the highest observed production rate (804.8 μg kg⁻¹ h⁻¹); thus, frequent sampling at the beginning of the incubation is very important to avoid missing N₂O and CH₄ production signatures and to obtain enough data for statistical analysis. In most case studies, CH₄ production from soils refers to the significant CH₄ production under anaerobic conditions. Both initial and later significant CH₄ productions were observed in this study. The results showed that the significant CH₄ production rate was ≈15 to 60 times higher than that of the initial CH₄ production. The source of CH₄ from soils is dominantly contributed by the significant CH₄ production under anaerobic conditions. The critical E_H for such significant CH₄ production was obtained by linear regression of the CH₄ production in logarithmic scale with E_Hs. The intercept of the linear equation at the E_H axis where the CH₄ production rate equals 1 μg kg⁻¹ h⁻¹ is defined as the critical value of E_H, after which CH₄ is produced in a significant amount [the results are presented in Fig. 4 (iii)]. Previously, CH₄ production in a normal scale was used for such estimation (Yu et al., 2001). The approach was modified in this study to make better estimation because of the actual logarithmic relationship. The critical E_H value for significant CH₄ production should be higher if the criteria for significant

CH₄ production were chosen at a lower rate (<1 μg kg⁻¹ h⁻¹), as in our previous estimation (the criterion was chosen at theoretical zero CH₄ production). The current criterion fits the objective of this study because the maximum observed CH₄ production is up to two or even three orders of magnitude higher than the chosen criteria.

Soil redox chemistry is largely affected by soil pH. The effects of pH on the critical E_Hs for the N₂O production, the initial CH₄ production, and the significant CH₄ production were examined, respectively (Fig. 4). The results showed a significant inverse relationship between each of the above three critical E_Hs and soil pH ($P < 0.001$). Further statistical analysis indicated that there was no significant difference between the theoretical E_H change per pH unit (59mV) and the observed change of critical E_H with pH for N₂O production (60 mV, $P = 0.932$) for initial CH₄ production (83 mV, $P = 0.733$) and for significant CH₄ production (93 mV, $P = 0.204$), respectively. In an acidic condition, significant CH₄ production can take place at a remarkably high redox condition, as seen in Treatment B, with critical E_H up to -69 mV. It emphasizes the importance to understand the close linkage between pH and E_H. Despite the difficulties of E_H application and its interpretation of soil redox reactions, it seems that the theoretical relation of E_H and pH applies to N₂O and CH₄ production under different redox and pH conditions very well. We predict that it might be also applicable to different soils with originally different pH. We are planning to conduct a further experiment to verify such a hypothesis.

Redox Potential Range with Minimum N₂O and CH₄ Production

The results verified our previous finding of the existence of a favorable E_H range, where both N₂O and CH₄ production were low (<1 μg kg⁻¹ h⁻¹): +200 to -300 mV for A, +310 to -100 mV for B, +180 to -220 mV for C, and +110 to -280 mV for D, respectively (Fig. 3). The E_H range spans ≈400 to 500 mV, and there is no indication of what governs the width of such E_H range, which depends on further investigation with more different soils. There was an expected shift of such a E_H range to the reducing end of the E_H scale when pH increased. Linear regression of the midpoint of the E_H range with minimum N₂O and CH₄ production and the corresponding pH of the four treatments indicated that the E_H range shifted by 94 mV to the lower end of the redox scale when pH increased by 1 unit. Such an inverse relationship ($r^2 = 0.957$) was also not significantly differ-

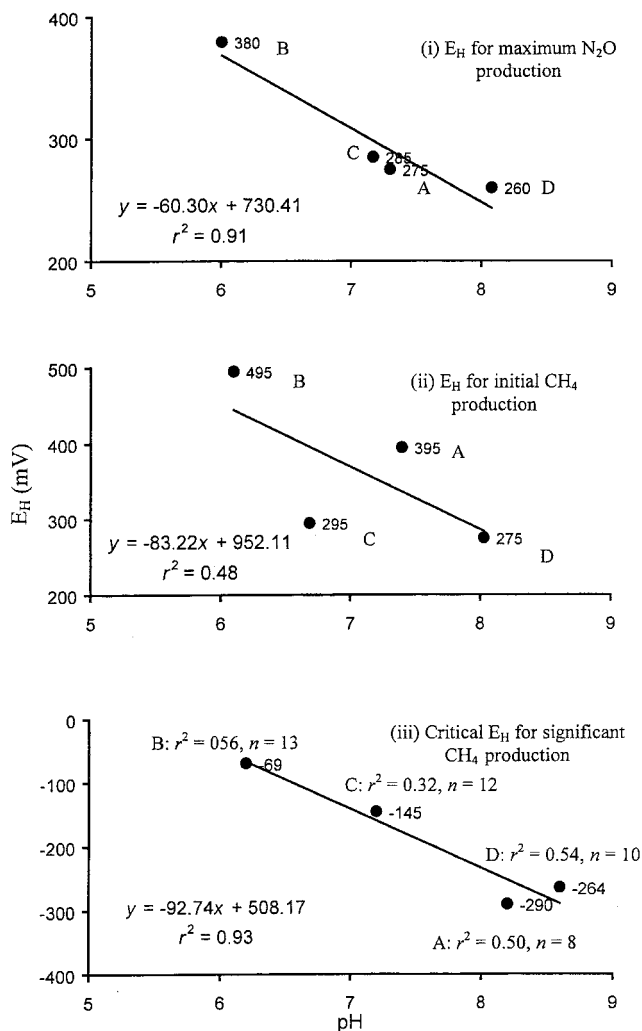


Fig. 4. Effect of pH on the critical redox potential (E_H) for N_2O production, initial CH_4 production, and significant CH_4 production. (A) control without pH adjustment, (B) pH 5.5, (C) pH 7.0, and (D) pH 8.5. (i) Redox potential for maximum N_2O production was estimated from vertex of the bell-shape pattern of the N_2O production. (ii) Highest E_H for initial CH_4 production was obtained directly from the original observations. (iii) Critical E_H for significant CH_4 production was labeled with regression coefficient (r^2) and sample size (n).

ent from the theoretical change of 59 mV per pH unit ($P = 0.130$).

According to the IPCC, GWP provides a measure of the cumulative radiative forcing of various greenhouse gases relative to some reference gas, usually CO_2 , across a specific time horizon. To draw a more general conclusion on the results of this study, GWP of N_2O and CH_4 , expressed as CO_2 equivalent, were calculated by mass factors of 275 for N_2O and 62 for CH_4 in a 20-yr time horizon (IPCC, 2001). In addition, converting E_H s at different pH to the values at pH 7.0 will provide more representative information, as wetland soil is characterized by the neutral pH under prolonged flooding situation (Ponnamperuma, 1972). Theoretical value of 59 mV per pH unit was used for such conversion regardless of the difference found in the regressions (Fig. 4). The results indicated that at the beginning of the submer-

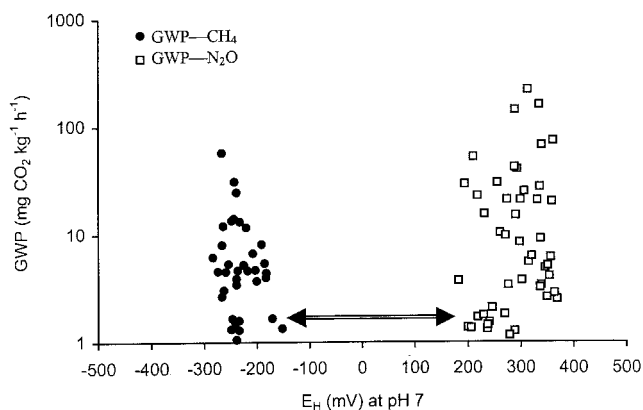


Fig. 5. Soil redox potential range at pH 7 with minimum global warming potential (GWP) contributions. The figure was plotted in logarithmic scale. N_2O and CH_4 contributions to the GWP below $1.0\ mg\ CO_2$ equivalent $kg^{-1}\ h^{-1}$ were considered insignificant and not illustrated in the figure for clarity.

gence, GWP in the soils mainly came from the contribution of N_2O production (1.2 to $225.4\ mg\ CO_2\ kg^{-1}\ h^{-1}$), and later from CH_4 production (1.2 to $52.1\ mg\ CO_2\ kg^{-1}\ h^{-1}$) when strictly reducing conditions prevailed. The early initiation of CH_4 production in the four treatments did not contribute to the GWP by more than $1.0\ mg\ CO_2\ kg^{-1}\ h^{-1}$. This confirms the early conclusion that the initial CH_4 production at a high redox condition is not a significant source of greenhouse gas from soils because of its temporal occurrence and smaller quantity. The relative portion of N_2O production in the overall greenhouse gas production of the soils largely depends on the amount of available nitrate, while the portion of CH_4 production probably depends more on the intensity of reduction. Figure 5 showed a more general case that the E_H range with minimum contribution of GWP was between -150 to $+180$ mV at a neutral pH condition. The E_H range was narrowed down to 330 mV compared with the individual analysis of the four treatments (400 – 500 mV) because of two reasons: (i) The criterion was chosen at a higher level; both N_2O and CH_4 productions at a rate of $1\ \mu g\ kg^{-1}\ h^{-1}$ are $<1\ mg\ kg^{-1}\ h^{-1}$ of CO_2 equivalent. (ii) The E_H range with minimum N_2O and CH_4 production of different pH treatments might slightly overlap each other after converting to pH 7.0.

It is a great challenge to abate greenhouse gas production in rice fields while maintaining grain yields. Carbon dioxide is the leading greenhouse gas, but controlling this gas is extremely difficult because of the global energy requirement and economic development. In addition to the enormous effort to increase soil C storage to reduce the atmospheric CO_2 level, mitigation of N_2O and CH_4 deserves attention because of their greater greenhouse effect and their longer residence time (for N_2O) in the atmosphere (IPCC, 2001). Proper agricultural management practice could be a valuable option to sustain the intensive irrigated rice agroecosystem without producing more greenhouse gases. The favorable E_H range with minimum GWP contribution accounts for $>40\%$ of the entire range covered from the most oxidized to the most reducing conditions in this study. It suggests a possibility for controlling E_H in such

a range to lessen GWP in rice paddy fields, possibly by proper management of irrigation, OM incorporation, and fertilizer applications. The best scenario will be that OM addition will favor N_2O reduction, but will not create reducing conditions strong enough to stimulate CH_4 production. Additionally, OM addition may increase the anaerobic zones in the soil, which may stabilize fertilizer N in the form of ammonium instead of nitrate (Patrick and Mahapatra, 1968). If an exponential relationship between CO_2 production and E_H also exists in the field as found in this laboratory study, there will be a substantial CO_2 contribution to GWP in a higher redox range. In this study, average CO_2 production of the four treatments under specific redox range was 14.2 ($E_H > +180$ mV), 2.7 ($+180 > E_H > -150$ mV), and 0.8 ($E_H < -150$ mV) $mg\ kg^{-1}\ h^{-1}$ of CO_2 , respectively (Fig. 2). Seasonal rice plant development and root exudates will affect soil redox status and greenhouse gas production and transportation to the atmosphere, which deserves careful evaluation especially in the field application. Field study should also integrate the short-term and the long-term effect of such management practice on rice plant metabolism and on rice yield.

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