Redox Window with Minimum Global Warming Potential Contribution from Rice Soils

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ABSTRACT

Eight different rice (Oryza sativa L.) soils were incubated using a microcosm technique to study CO₂, CH₄, and N₂O contribution to global warming potential (GWP) at different redox potential (E_H) conditions. Cumulative GWP from these three greenhouse gases reached a minimum at a redox "window" of +180 to -150 mV. Within the redox window, CO₂ production accounted for 86% of the cumulative GWP, because both N₂O and CH₄ production were low. When E_H was higher than +180 mV, both CO₂ and N₂O production made a significant contribution to the cumulative GWP, whereas CH₄ production was a dominant contributor when E_H was lower than -150 mV. During the incubation, each soil exhibited a unique signature of developing such an optimum redox window with a minimum GWP. Multiple regressions showed that initial soil organic matter (OM) and S content might have a significant control (P = 0.02) on the time required for the soils to reach the redox window when the incubation started from aerobic conditions. The results of this integrated study on productions of the three greenhouse gases provide a theoretical base for abating soil GWP loading into the atmosphere by regulating soil E_H conditions.

ETHANE AND N_2O are the most important atmo- \mathbf{I} spheric trace gases, next to CO₂, contributing to global greenhouse effect. Agriculture accounts for about 20% of the projected anthropogenic greenhouse effect, producing about 50 and 70%, of overall anthropogenic CH₄ and N₂O emissions, respectively. Agricultural activities (not including forest conversion) also account for approximately 5% of anthropogenic emissions of CO₂ (Intergovernmental Panel on Climate Change [IPCC], 2001). To meet the demand of increasing world population, agriculture is expected to intensify in the next several decades, probably with more greenhouse gas loading into the atmosphere. However, agriculture is probably one of the few ecosystems that human beings can directly manage for mitigation of greenhouse gas production and emission.

Biological N₂O can be produced from nitrification under aerobic conditions, and denitrification under moderately reducing conditions where the reduction intensity is not strong enough to completely reduce nitrate to N₂ gas. Denitrification is the final step of the N cycle by which fixed N in the biosphere returns to the atmospheric N₂ pool, and is the major source of N₂O. Significant CH₄ formation (methanogenesis) in soils generally occurs under strictly reducing conditions when soil reduction intensity decreases below a critical point. Soil reduction intensity can be characterized by soil E_H. Soils tend to undergo a series of sequential biogeochemical reactions in a homogenous environment when soil redox

Published in Soil Sci. Soc. Am. J. 68:2086–2091 (2004). © Soil Science Society of America 677 S. Segoe Rd., Madison, WI 53711 USA status changes from aerobic (high E_H) to anaerobic (low E_H) conditions. Major reactions include, in order of E_H from high to low, nitrification, denitrification, Mn (IV) reduction, Fe (III) reduction, SO²⁻₄ reduction, and methanogenesis (Patrick and DeLaune, 1972; Ponnamperuma, 1972; Reddy et al., 1989). The relative order of reactions when E_H decreases can be theoretically predicted by soil redox chemistry, but overlapping between different reactions and simultaneous occurrence of reactions exist at a particular E_H , especially under field conditions.

Rice fields provide a unique aerobic and anaerobic environment because of irrigation and drainage practices, making it a major source of CH₄ during the flooded season, and an important source of N₂O during the drained season as reported in numerous field studies (Abao et al., 2000; Cai et al., 1997; Chen et al., 1997; Tsuruta et al., 1997). To mitigate CH₄ emission from submerged rice fields, drainage and aeration during the rice growing season may effectively reduce CH₄ emission, but with the potentially adverse effect of stimulating higher N2O emission (Bronson et al., 1997; Wassmann et al., 2000). The different E_H conditions required for N_2O and CH_4 formations and the trade-off pattern of their emissions as found in rice fields makes it a challenge to abate the production of one gas without enhancing the production of the other. Our previous studies indicate that both N₂O and CH₄ productions can be minimized in a specific soil E_H range where the soil is reducing enough to favor complete denitrification to N2, but not so reduced as to initiate significant methanogenesis. The optimum E_H range with minimum N₂O and CH₄ production, using a U.S. rice soil (pH 5.7), a Chinese rice soil (pH 6.7), and two Belgian upland soils (pH 6.0 and 7.0), was found to be between +120 to -170 mV (Yu et al., 2001). Using the same U.S. rice soil incubated at four different pH levels (between 5.5 and 8.5), Yu and Patrick (2003) concluded that the E_{H} range with minimum GWP from N_2O and CH_4 production was between +180 to -150 mV (pH 7.0). The objectives of this study, using eight different rice soils, are to (i) validate the existence of such an optimum soil E_H range with minimum N_2O and CH₄ production in a broader range of rice soils under laboratory conditions, (ii) evaluate the contribution of CO_2 production in cumulative soil GWP within and beyond this $E_{\rm H}$ range, and (iii) explore what redox related soil characteristic(s) (OM, pH, Mn, Fe, and S) govern the dynamics of this $E_{\rm H}$ range.

MATERIALS AND METHODS

Sample Soils

Eight rice soils (surface 20 cm) from different rice cultivating regions of the world were collected for this study, including

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Abbreviations: E_H , redox potential; GWP, global warming potential; IPCC, Intergovernmental Panel on Climate Change; OM, organic matter.

from five major rice-cultivating states in the USA (Arkansas, California, Louisiana, Mississippi, and Texas), and from three international regions (Hangzhou/China, West Java/Indonesia, and Pathumthani/Thailand). The soils were air-dried, sieved (1 mm), thoroughly mixed and stored at room temperature (20°C) before the experiment. Soil characteristics of interest were analyzed and showed large variation among regions (Table 1).

Soil Incubation and Measurement

Soils were incubated using a microcosm system where soil E_H and pH could be monitored, and gas samples could be taken as needed (for detailed description, see Yu and Patrick, 2003). For each of the eight rice soils, a soil suspension was made by adding 400 g soil to a 2300-mL Erlenmeyer flask containing 1600 mL of deionized water. To each soil suspension, 4 g ground rice straw was amended as additional source of OM, and potassium nitrate (KNO₃) was amended to provide an additional source of nitrate at rate of 50 mg N kg⁻¹ soil. An independent set of microcosm systems was used for each of the eight soils, and all the eight microcosms were incubated for about 4 mo under the same condition (i.e., temperature 20°C). Soil incubation was started at oxidized conditions with no further O₂ supply thereafter. To monitor detail dynamics of gas production under different E_H conditions, gas samples were frequently taken whenever E_H in the microcosm system changed by more than 10 mV. The E_H level of each soil suspension was measured by two replicate Pt working electrodes with a calomel reference electrode. Water-soluble Mn, Fe, and sulfate concentrations in the soil suspensions were monitored during the incubation by withdrawing soil solution at different E_{H} conditions. Soil solution (10 mL each time) was taken using a syringe without contact to the ambient air, and filtered immediately through a GF/F filter paper (Whatman Inc., Clifton, NJ) into a 10-mL test tube with three drops of 2 M nitric acid to preserve the sample for later analysis. The same volume of deionized water was replenished to maintain the initial volume of liquid phase and headspace in the microcosms.

Sample Analysis

Nitrous oxide, CH₄, and CO₂ concentrations were analyzed with a Tremetrics 9001 gas chromatograph (GC) with dual channel system using an electron capture detector (ECD) for N₂O, and a flame ionization detector (FID) for CH₄ and CO₂. A methanizer catalyst column was installed after the sample separation column of the GC, which reduced CO₂ to CH₄ for FID detection. Each gas analysis was calibrated using certified gas standards (Scott Specialty Gases, Inc. Plumsteadville, PA). Initial soil pH was measured in soil/water (1:1) slurry. Initial soil total OM was measured colorimetrically after oxidizing with K₂Cr₂O₇ and concentrated sulfuric acid. Soil total N was analyzed in dry combustion by a Leco N analyzer (Leco Corp., St. Joseph, MI). Soil extractable Mn and Fe were analyzed by inductively coupled plasma (ICP) after extracting with diethylene triamine pentaacetic acid (DTPA) solution to remove soluble and labile solid phases. Soils also were extracted with ammonium acetate and acetic acid solution to remove S that was presumed to be mostly sulfate. Water-soluble Mn, Fe, and S concentrations in the soil solutions were analyzed directly using ICP after filtration.

Calculations and Statistical Analysis

Gas production rate was determined by linear regression of the three gas concentration measurements in 1 h after closure of the microcosm. The amount of gas dissolved in the

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

| Soil | pН | Total OM [†] | Total N | Fe | Mn | S |
|-------------|-----|-----------------------|---------|---------------------|-----|-----|
| | | % | | mg kg ⁻¹ | | |
| Arkansas | 6.0 | 1.46 | 0.07 | 134 | 105 | 13 |
| California | 6.7 | 4.08 | 0.16 | 224 | 107 | 45 |
| Louisiana | 7.3 | 1.67 | 0.07 | 68 | 19 | 11 |
| Mississippi | 7.7 | 2.53 | 0.10 | 71 | 9 | 12 |
| Texas | 5.1 | 2.54 | 0.11 | 115 | 35 | 38 |
| China | 5.6 | 4.64 | 0.27 | 190 | 102 | 66 |
| Indonesia | 5.3 | 2.37 | 0.10 | 211 | 280 | 65 |
| Thailand | 4.7 | 2.58 | 0.12 | 173 | 40 | 190 |

† Organic matter.

liquid phase was calculated by taking mole fraction solubility of 5.07×10^{-4} for N₂O, 2.81×10^{-5} for CH₄, and 7.07×10^{-4} for CO₂ (Lide, 1991). Redox potential (E_H) was standardized to the standard H₂ electrode by adding 247 mV (the correction factor for calomel reference electrode at 20°C) to the observed instrument reading. All E_H data were reported as their corresponding values at pH 7.0 that were calculated according to the inverse relationship of E_H and pH as described by Nernst equation (59 mV per pH unit, Bohn, 1971). Global warming potentials in a 100-yr time horizon were calculated by taking conversion factors that 1 mg CH₄ and N₂O are equivalent to 23 and 296 mg CO₂, respectively (IPCC, 2001). All GWP results were expressed as mg CO₂ equivalent per kg soil (air dry) per hour.

Statistical analysis was conducted using SAS software (version 8.02, 1999-2001, SAS Institute, Cary, NC). Simple linear regression using PROC REG was conducted to test if the slope of a regression was significantly different from zero (no relationship). Multiple regression was conducted when more than one variables were considered in the model with stepwise analysis to identify the most significant factor(s). Regression analysis was applied including the eight soil measurements together, due to limitation of statistical analysis for the single measurement of each soil. The significance level was chosen at α equals 0.05 for all statistical analysis.

RESULTS AND DISCUSSION Change of Soil pH and Redox Potential During the Incubation

Flooded soils tend to approach near neutral pH for both originally acidic and alkaline soils (Ponnamperuma, 1972). At the beginning of the study, pH of the eight soils varied by three pH units (pH = 4.7 to 7.7). After the 4-mo incubation period, the difference in pH among the eight soils was only 1.1 pH units [Fig. 1 (i)]. Fluctuations of pH were generally minor for the four soils with initial pH near neutral (Arkansas, California, Louisiana, and Mississippi). However, a dramatic pH increase for the four acidic soils (Texas, China, Indonesia, and Thailand) was observed during the incubation. After the incubation was started, the most significant pH increase occurred in the first 10 d for the China soil (from 5.4 to 7.0), between Day 10 to 40 for the Texas soil (5.8 to 7.0), between Day 20 to 50 for the Indonesia soil (5.6 to 7.2), and between Day 50 to 70 for the Thailand soil (5.6 to 7.3), respectively. In general, the period when significant soil pH increase was observed was also the time when soil $E_{\rm H}$ decreased rapidly (Fig. 1).

The soil samples were air-dried before the experi-



Fig. 1. Changes in pH and E_H during the incubation. Soil pH was based on a single measurement each time. Soil E_H was based on duplicate measurements, but standard deviations were not included in the figure for clarity.

ment, which eventually transformed all the soil redox active components into their oxidized form. The incubation was initiated in aerobic conditions with no further O_2 supply. Thus, our incubations are analogous to flooding a thoroughly drained soil. The soil E_H conditions during the incubation spanned more than 800 mV (+530 to -310 mV), which represented a normal E_H range that wetland soils generally experience under natural conditions. The most rapid decrease in E_H was observed in the China soil where the E_H declined to 0 mV by the end of the third week during the incubation. In contrast, the Thailand soil required 9 wk to reach an E_H of 0 mV [Fig. 1 (ii)]. Dynamics of soil E_H decrease during the incubation was discussed in more detail later.

Redox Window with Minimum Global Warming Potential Contribution

Each of the eight rice soils exhibited a unique pH and E_H pattern during the incubation from aerobic to anaerobic conditions (Fig. 1). However, production of N₂O, CH₄, and CO₂ showed a similar pattern when all soils were plotted against soil E_H (Fig. 2), even though their production rates varied significantly under the similar incubation conditions (Table 2). Nitrous oxide production, probably from both nitrification and denitrification, began immediately after the incubation started, but most significantly between +400 to +200 mV [Fig. 2





(i)]. Only small amount of N₂O was generated when the soil E_H was below +180 mV, due to stronger reduction of N_2O to N_2 at lower E_H (Masscheleyn et al., 1993). The critical E_{H} value for the initiation of significant CH_{4} production was about -150 mV at neutral pH (Masscheleyn et al., 1993; Wang et al., 1993; Yu et al., 2001). Although significant CH₄ production occurred at different time of the incubation for each soil, for all soils it happened only when soil E_H decreased below -150 mV[Fig. 2 (ii)]. Thus, major CH₄ production occurred in a narrow $E_{\rm H}$ range of -150 to about -300 mV, and the production rate increased greatly as soil $E_{\rm H}$ decreased within this range [Fig. 2 (ii)]. In addition to low E_{H} , the near neutral pH conditions that developed at the later phase of the incubation probably enhanced methanogenesis in our soils (Wang et al., 1993). Soil microbial respiration activities generated CO_2 in the entire E_H range studied [Fig. 2 (iii) and Table 2]. Carbon dioxide production rates decreased exponentially when the soil $E_{\rm H}$ shifted from high to low ($r^2 = 0.25, P < 0.01, n = 261$).

| N2O, CH4, and CO2 at unrefent Eff lange. | | | | | | | | |
|---|----------------------|---------------------|---------------------|-------|--|--|--|--|
| Soil | GWP-N ₂ O | GWP-CH ₄ | GWP-CO ₂ | Total | | | | |
| mg CO ₂ equivalent kg ⁻¹ soil h ⁻¹ | | | | | | | | |
| $\mathbf{E}_{\mathrm{H}} > +180 \mathrm{mV}$ | | | | | | | | |
| Arkansas | $8.2 \pm 10.1^{+}$ | 0.1 ± 0.1 | 17.2 ± 20.6 | 25.4 | | | | |
| California | 14.6 ± 19.2 | 0.0 ± 0.0 | 25.3 ± 20.2 | 39.9 | | | | |
| Louisiana | 8.6 ± 6.6 | 0.1 ± 0.1 | 13.8 ± 18.6 | 22.5 | | | | |
| Mississippi | 2.0 ± 1.9 | 0.7 ± 0.0 | 17.5 ± 14.3 | 19.3 | | | | |
| Гехаз | 32.5 ± 49.1 | 0.0 ± 0.0 | 12.9 ± 11.3 | 45.4 | | | | |
| China | 250.6 ± 130.5 | 0.0 ± 0.0 | 31.8 ± 36.7 | 282.3 | | | | |
| Indonesia | 7.0 ± 3.3 | 0.0 ± 0.0 | 8.3 ± 11.2 | 15.3 | | | | |
| Fhailand | 3.6 ± 2.4 | 0.0 ± 0.0 | 5.6 ± 7.6 | 9.3 | | | | |
| Subtotal | 326.0 | 1.0 | 132.3 | 459.3 | | | | |
| $+180 \ mV > E_{H} > -150 \ mV$ | | | | | | | | |
| Arkansas | 0.0 ± 0.0 | 0.2 ± 0.2 | 0.9 ± 0.5 | 1.1 | | | | |
| California | 0.3 ± 0.1 | 0.1 ± 0.0 | 6.0 ± 14.7 | 6.4 | | | | |
| Louisiana | 0.9 ± 0.4 | 0.0 ± 0.0 | 1.9 ± 2.2 | 2.9 | | | | |
| Mississippi | 0.2 ± 0.0 | 0.1 ± 0.1 | 1.3 ± 0.9 | 1.6 | | | | |
| Гехаз | 0.4 ± 0.2 | 0.1 ± 0.0 | 0.8 ± 0.8 | 1.3 | | | | |
| China | 2.5 ± 0.7 | 0.1 ± 0.1 | 34.2 ± 54.3 | 36.8 | | | | |
| Indonesia | 1.5 ± 0.7 | 0.1 ± 0.1 | 2.8 ± 2.5 | 4.3 | | | | |
| Fhailand | 1.8 ± 0.7 | 0.1 ± 0.0 | 1.6 ± 1.7 | 3.4 | | | | |
| Subtotal | 7.6 | 0.6 | 49.6 | 57.8 | | | | |
| $E_{\rm H} < -150~{ m mV}$ | | | | | | | | |
| Arkansas | 0.0 ± 0.0 | 2.3 ± 1.2 | 1.3 ± 1.4 | 3.62 | | | | |
| California | 0.0 ± 0.0 | 2.1 ± 2.0 | 0.5 ± 0.4 | 2.52 | | | | |
| Louisiana | 0.0 ± 0.0 | 12.0 ± 15.0 | 0.9 ± 0.7 | 12.90 | | | | |
| Mississippi | 0.0 ± 0.0 | 9.6 ± 11.1 | 0.0 ± 0.2 | 9.54 | | | | |
| Гехаз | 0.0 ± 0.0 | 9.8 ± 10.0 | 1.9 ± 2.3 | 11.68 | | | | |
| China | 0.8 ± 0.3 | 14.5 ± 6.0 | 2.2 ± 2.0 | 17.51 | | | | |
| Indonesia | 2.6 ± 0.6 | 16.2 ± 15.6 | 1.4 ± 1.0 | 20.18 | | | | |
| Fhailand | 0.0 ± 0.0 | 2.8 ± 2.0 | 0.0 ± 0.1 | 2.76 | | | | |
| Subtotal | 3.4 | 69.1 | 8.2 | 80.7 | | | | |
| Fotal | 337.0 | 70.7 | 190.1 | 597.8 | | | | |
| | | | | | | | | |

Table 2. Global warming potential (GWP) contributions from N_2O , CH_4 , and CO_2 at different E_H range.

 \dagger Values represent mean \pm standard deviation.

Our results validated the existence of an E_H range where the cumulative GWP from these three greenhouse gases reached a minimum (Fig. 2). In this E_H range, the reducing conditions in the soils were favorable for complete denitrification with N₂ as the end product, but were still not intense enough to initiate significant CH₄ production. In addition, CO₂ production was substantially decreased in such anaerobic conditions compared with aerobic conditions. The E_H "window" with minimum GWP contribution from the soils slightly varied for each soil, but generally located between +180 and -150 mV at pH 7 as was found in our previous investigation (Yu and Patrick, 2003).

Total GWP from the eight soils at different E_{H} ranges and relative contributions of each individual gas (N_2O_1 , CH_4 , and CO_2) to the cumulative GWP are summarized in Table 2. The results showed that 77% of the total GWP from the eight rice soils during the 4-mo incubation was produced when the E_{H} was higher than +180 mV, and 13% when the $E_{\rm H}$ lower than -150 mV. The remaining 10% of the total GWP was produced in the $E_{\rm H}$ range of +180 to -150 mV that accounted for about 40% of the entire $E_{\rm H}$ range studied. When the $E_{\rm H}$ was higher than the optimum range ($E_{\rm H} > +180 \text{ mV}$), about 2/3 of the GWP came from soil CO₂ production, except in the China and Texas soils where higher N2O production was measured. In the optimum $E_{\rm H}$ range (+180 > $E_{\rm H} > -150$ mV) where the cumulative GWP reached a minimum, about 86% the GWP came from soil CO₂ production because both soil N₂O and CH₄ production were low. Significant CH_4 production from the eight different soils was consistently observed only when E_H was below -150 mV, making CH_4 a dominant contributor in the GWP in this lower E_H range.

Our results showed that contribution of N₂O, CH₄, and CO_2 to the cumulative GWP at each E_H range were highly variable among the eight soils. Nitrous oxide production mainly depends on denitrification intensity and N_2O/N_2 ratio in denitrification products. Inhibition of N_2O reduction activity by low pH, resulting in higher $N_2O/$ N₂ ratio of acidic soils, has been well studied (Firestone et al., 1980). Extremely high N₂O production found in the China soil was likely due to its high soil OM and N contents, as well as low pH (Table 1 and 2). Organic matter decomposition and evolution of CO_2 generally decrease when soil $E_{\rm H}$ changes from high to low. However, the cumulative GWP from C gas (CO_2 and CH_4) production may actually increase if significant CH₄ production is initiated after soil E_H decreased below the critical point (-150 mV). In this study, C gas (sum of CO₂ and CH₄) productions from the eight soils were 36.1 ($E_H > +180$ mV), 13.6 (+180 > $E_H > -150$ mV), and 4.5 mg C kg⁻¹ h⁻¹ ($E_H < -150$ mV), respectively (calculation based on 1 mg CH_4 is equivalent to 23 mg CO_2). The results have a significant implication in evaluating the overall benefit of soil C sequestration effort in terms of CO2 equivalent, because part of the C captured in soils may be substantially offset by enhanced CH₄ production under reducing conditions. In addition, increasing soil C content, as the result of soil C sequestration, may stimulate higher N₂O production in moderately reducing conditions if soil denitrification activity is limited by soil OM as an electron donor. The amount of easily degradable OM in soils plays a critical role in developing reducing conditions in soils, as well as in CH₄ production. Increased CH₄ emissions corresponded to the development of soil reducing condition and release of degradable OM from rice plant roots during the growing season (Inubushi et al., 2003). If additional OM were provided in the later phase of the incubation, higher production of CH_4 (possibly CO_2 as well) would be expected, which would increase the relative contribution of each gas to total GWP.

Initiation and Duration of the Optimum Redox Window

The results of this study also indicated that there existed a large variation among the eight different rice soils in the time needed for the soil $E_{\rm H}$ to decrease below +180 mV, and further below -150 mV. Each soil exhibited a unique dynamic signature of developing such an $E_{\rm H}$ window with minimum GWP during the incubation. For example, it took 19 d of incubation for the China soil to reach the optimum $E_{\rm H}$ range (+180 > $E_{\rm H} > -150$ mV), and the soil remained in this $E_{\rm H}$ range for only 5 d. In contrast, it took 47 d for the Thailand soil to enter such an $E_{\rm H}$ range, and the soil remained in this $E_{\rm H}$ range for an average of 61 d (Fig. 3). Highest initial OM content was found in the China soil (Table 1), which might partially explain the shortest time needed



Fig. 3. Duration of soil in the $E_{\rm H}$ range (+180 > $E_{\rm H}$ > -150 mV) during the incubation. Values in each bar represent the time (in days) that each soil remained in the above $E_{\rm H}$ range. Lower end of the bar represented the time when an individual soil $E_{\rm H}$ decreased below +180 mV, and upper end of the bar represented the time when the soil $E_{\rm H}$ decreased below -150 mV.

for the China soil $E_{\rm H}$ to decrease below +180 mV. However, regression (n = 8) between the durations for the soil remaining in the above $E_{\rm H}$ range and the initial soil OM contents ($r^2 = 0.06$, P = 0.58) was weak.

Multiple regression analysis (n = 8) indicated that initial soil OM and S was significantly related to the time required for the soils to reach the redox window from the initial aerobic conditions (Time [day] = $-0.63 \times \text{OM} + 0.13 \times \text{S} + 39.8, r^2 = 0.78, P = 0.02$). The Thailand soil required the longest time to span the entire E_H range during the incubation, possibly mainly due to its high S content (Table 1). Sulfate, which is highly soluble and redox active, plays a multiple roles in soil redox biogeochemistry and CH₄ production. Inhibition effect of sulfate on CH₄ production is well known (Kumaraswamy et al., 2001; Scholten et al., 2002) and significant CH₄ production can start only when sulfate is nearly depleted in the media. Inherent differences in microbial community composition might also play a significant role in soil redox dynamics, but it was not explored at this stage. To decrease cumulative GWP in rice fields by controlling irrigation and drainage, it is essential to understand the general redox buffer capacity (such as OM, Fe, Mn, and S content) of the soils, so that such the management can be adjusted accordingly to make the soil remain in this favorable E_{H} range as much as possible.

There was a linear relationship between the soluble Fe content in the soil suspensions and soil $E_{\rm H}$ ($r^2 = 0.11$, P = 0.08, n = 60), indicating a significant role of Fe in buffering the soil redox conditions. It appears that Fe was more geochemically active than Mn, since Fe in the soil solution was four to five fold higher than that of Mn (Fig. 4), despite soil Fe and Mn levels that were the same order of magnitude at the beginning of the incubation (Table 1). It is difficult to interpret the results for S (mostly in form of sulfate), because the microcosm system used in this study was an open system for gas produced in the soils by continuous flushing the system with N₂ (Yu and Patrick, 2003). Also, H₂S produced during reduction of sulfate might react with ferrous Fe



Fig. 4. Dynamics of soluble Mn, Fe, and sulfate during progressive reduction.

 (Fe^{2+}) to produce Fe mono- and disulfides. This could explain why soluble Fe and sulfate concentrations declined at the end of the incubation when the reducing conditions were fully developed (Fig. 4). In contrast to soluble Fe, Mn generally showed a continuous increase when soil E_H decreased because there are no major processes to remove the soluble Mn, as is the case with Fe. Longest time required for initiation of significant CH₄ production was found in the Thailand soil where highest sulfate concentration in the soil solution (Fig. 4), and highest initial S content in the soil (Table 1) was observed.

Implications

Our results clearly delineated a wide redox window with minimum soil N_2O and CH_4 production, as well as lower CO_2 production between +180 to -150 mV, which have implications for mitigating GWP in soils. Appropriate management of irrigation, OM, and fertilization is likely a feasible approach, at least for conventionally submerged rice soils, to minimize both N_2O and CH_4 productions. The implication of abating N_2O and CH_4 production may be more important than sequestering C in these soils, because (i) recent evidence suggests that the capacity of soils, as a C sink, is limited or unlikely on a long-term basis (IPCC, 2001; Gill et al., 2002; Schlesinger and Lichter, 2001), and (ii) higher C stocks through conservation and sequestration can lead to higher future C emissions under either natural or human-induced disturbance (IPCC, 2001). Furthermore, N₂O and CH₄ production should also be taken into account in evaluation of soil C sequestration, because part of the stored C may be offset by higher N₂O and CH₄ production (Roulet, 2000; Smith, 1999).

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