# **Redox Potential Control on Cumulative Global** Warming Potentials from Irrigated Rice Fields

Kewei Yu\*

Department of Biological and Environmental Sciences, Troy University, Troy, AL 36082 \*E-mail: kyu@troy.edu

Rice cultivation shifts between aerobic and anaerobic environment, making it a potential CH<sub>4</sub> source during flooding and a N2O source during drainage. A favorable redox "window" of +180 to -150 mV was found where both N<sub>2</sub>O and CH<sub>4</sub> productions were low. The trade-off emissions of CH<sub>4</sub> and N<sub>2</sub>O found in rice field can be minimized by manipulating the soil profile through proper irrigation and drainage to maintain a favorable redox distribution. Various soil redox active components can effectively buffer the soil Eh change, in which Iron (Fe) probably plays a critical role. Development of best management practice in irrigated rice fields to mitigate greenhouse gas (GHG) emissions should consider reaching an overall minimum cumulative global warming potential (GWP) from CH<sub>4</sub> and N<sub>2</sub>O emissions but not decreasing rice yield.

### Introduction

Rice (Oryza sativa) is the most important food for more than half of the world's population. Rice cultivation area is about 155 million ha, making flooded rice (paddy) fields the largest man-made wetlands on earth. World rice production in 2008 was approximately 661 million tons. More than 90% rice production is taking place in Asia, with China accounting for 30% of total world production, followed by India (22%), Indonesia (9%), and Bangladesh (7%) (1).

Next to carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) are the most important atmospheric greenhouse gases (GHGs) contributing to the enhanced global greenhouse effect. In 2005, the CH<sub>4</sub> concentration in

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the atmosphere reached 1774 ppb, more than double its pre-industrial level. Meanwhile the N<sub>2</sub>O concentration reached 319 ppb, about 18% higher than its pre-industrial level (2). To compare the potential climate impact of the emissions of different greenhouse gases with CO<sub>2</sub>, Intergovernmental Panel on Climate Change (IPCC) introduced a metric of Global Warming Potential (GWP). Using CO<sub>2</sub> as a reference gas, GWP compares the integrated radiative forcing of different greenhouse gases over a specified period (e.g., 100 years), and the results can be expressed as CO<sub>2</sub> equivalent. In a 100-year time horizon, 1 kg of CH<sub>4</sub> and N<sub>2</sub>O have been determined to be equivalent to 25 and 298 kg of CO<sub>2</sub>, respectively, in radiative forcing of the global greenhouse effect (2).

Overall, wetland rice fields contribute more than 1/4 to global anthropogenic CH<sub>4</sub> emission (2). Nitrogen fertilization and drainage practice in rice fields also provide opportunities for N<sub>2</sub>O emission. Rice fields, as well as other agriculture fields, can play an important role in mitigation of production and emission of CH<sub>4</sub> and N<sub>2</sub>O to reach a sustainable food production because of the accessibility of direct management of this ecosystem. This chapter discusses critical soil factors that control CH<sub>4</sub> and N<sub>2</sub>O emissions from rice ecosystems and summarizes several studies that attempted to identify the optimum rice growth conditions that minimize GHG emissions and the overall global warming potential from rice cultivation.

#### **Redox Window with Minimum GWP from Soils**

Nitrous oxide can be produced from nitrification under aerobic conditions, and denitrification under moderately reducing conditions. Significant CH<sub>4</sub> production generally needs strictly reducing conditions. The intensity of soil reducing condition can be instrumentally measured as soil oxidation-reduction (redox, Eh) potential (3). In natural environments, redox potential (Eh) can vary from well oxidizing conditions (Eh up to +700 mV) to strictly reducing conditions (Eh down to -300 mV).

Most of the soil redox reactions occur in an Eh range where water (H<sub>2</sub>O) is stable, and the reactions are sequentially initiated as predicted in theory of redox chemistry (Table I). After flooding, microbial reduction processes sequentially use  $O_2$ ,  $NO_3^-$ , Mn(IV), Fe(III),  $SO_4^{2-}$  and  $CO_2$  as electron acceptors as Eh decreases, accompanied by the emission of various trace gases.

Aerobic (high Eh) and anaerobic (low Eh) conditions may be dominant for a certain period in rice soils depending on irrigation and drainage practice, making rice fields a major source of CH<sub>4</sub> during the flooded season, and an important source of N<sub>2</sub>O during the non-flooded season (5–7). Such a trade-off relationship between CH<sub>4</sub> and N<sub>2</sub>O emission makes mitigation of cumulative GWP from rice fields a great challenge. To explore the optimum redox conditions where the cumulative GWP from soils reaches the minimum, Yu and Patrick (3) conducted a soil incubation study with eight paddy soils (Table II) using a homogenous soil microcosm equipped with automatic monitoring of soil Eh and pH (Figure 1) (8). The Eh and pH conditions of the soil microcosm were closely monitored and controlled. Gas samples of GHGs (CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O) were frequently taken,

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whenever Eh in the microcosm system changed by more than 10 mV, to monitor the dynamics of gas production under different Eh conditions.

The studied rice soils showed a large variation in pH and Eh change during the incubation from aerobic to anaerobic conditions. However, productions of N<sub>2</sub>O and CH<sub>4</sub> in the soils showed a quite similar pattern when they were plotted against Eh, even though their production rates varied significantly under the similar incubation conditions due to large variations in soil characteristics (Table II). Nitrous oxide production, probably from both nitrification and denitrification, began immediately after the incubation started, but was mostly produced in an Eh range of +400 to +200 mV. Only a small amount of N<sub>2</sub>O was present when the Eh was below +180 mV, due to stronger reduction of  $N_2O$  to  $N_2$  at lower Eh (10). The critical Eh value to initiate a significant  $CH_4$  production was about -150 mVat neutral pH (10, 11). Although significant CH<sub>4</sub> production occurred at different time of the incubation for each soil, for all soils it happened only when the soil Eh decreased below -150 mV. Thus, major CH<sub>4</sub> production occurred in a narrow Eh range of -150 to about -300 mV, and the production rate increased greatly with Eh decrease within this Eh range. The results delineated a wide Eh range where the cumulative GWP from N<sub>2</sub>O and CH<sub>4</sub> emissions reached a minimum (Figure 2). In this Eh range, soils were reducing enough to favor complete denitrification with  $N_2$  as end product, but were still oxidizing enough to inhibit significant methanogenesis. The Eh "window" with minimum GWP contribution slightly varied for each soil, but generally located between +180 and -150 mV at pH 7. Carbon dioxide production showed an exponential decrease with decrease of soil Eh during the incubation. This favorable "redox window" remains valid even when  $CO_2$  emissions were considered for total cumulative GWP (8).



Figure 1. Soil microcosm system with redox and pH control ((9) with modification).

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Typical Reaction	Standard Eh (mV)
$O_2 + 4H^+ + 4e^- = 2H_2O$	1229
$2NO_{3} + 12H^{+} + 10e^{-} = N_2 + 6H_2O$	1240
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1230
$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	1060
$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O$	300
$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O$	170
$2H^+ + 2e^- = H_2$	0

Table I. Redox potential of important reactions in soils (4)



Figure 2. Soil Eh range with minimum GWP contribution ((8) with modification).

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Soil	рН	ОМ	Total N	Fe	Mn	S	
			mg kg-1				
Arkansas	6.0	14.6	0.7	134	105	13	
California	6.7	40.8	1.6	224	107	45	
Louisiana	7.3	16.7	0.7	68	19	11	
Mississippi	7.7	25.3	1.0	71	9	12	
Texas	5.1	25.4	1.1	115	35	38	
China	5.6	46.4	2.7	190	102	66	
Indonesia	5.3	23.7	1.0	211	280	65	
Thailand	4.7	25.8	1.2	173	40	190	

Table II. Selected characteristics of the sample soils

Relative contributions of N<sub>2</sub>O and CH<sub>4</sub> in the cumulative GWP at different Eh range were highly variable for each soil. On average of the eight soils, 57% of the total GWP was produced when Eh was higher than +180 mV, and 38% when Eh lower than -150 mV. Only 5% of the total GWP was produced in the Eh range of +180 to -150 mV that accounted for about 40% of the entire Eh range studied (8).

In a separate experiment using the same system, the Louisiana rice soil was incubated at different pH conditions (pH = 5.5, 7.0 and 8.5). The favorable Eh range with minimum N<sub>2</sub>O and CH<sub>4</sub> production shifted to lower values of the Eh scale when pH increased as predicted by the Nernst equation (*12*). All above experiments were conducted from oxidizing to reducing conditions (an analog of flooding in rice fields). An incubation from reducing to oxidizing conditions (an analog of drainage in rice fields) was conducted using six of the above eight soils, resulting in the same conclusion on the favorable redox window with minimum N<sub>2</sub>O and CH<sub>4</sub> emissions (*13*).

## Drainage and Role of Iron (Fe) on CH<sub>4</sub> and N<sub>2</sub>O Emissions

Early field-scale studies have observed the trade-off relationship between CH<sub>4</sub> and N<sub>2</sub>O emissions during flooding periods and drainage periods (5, 6, 14). Redox potential oscillations due to rice field management control microbial community structure and function for various biogeochemical processes. The laboratory microcosm studies provide some guidelines for an optimistic perspective in mitigating GWP in rice soils if the soils could be maintained in this favorable redox range.

Mid-season drainage has been shown the most effective approach to reduce CH<sub>4</sub> emission from flooded rice fields, but with a potentially adverse effect of stimulating higher N<sub>2</sub>O emission (14, 15). Following the guidance of an optimum redox range with minimum CH<sub>4</sub> and N<sub>2</sub>O productions, Johnson-Beebout and Olivyn (16) conducted a soil pot study was conducted to explore the possibility

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of maintaining a "healthy redox" to reach simultaneous reduction of GWP from CH<sub>4</sub> and N<sub>2</sub>O emissions in soil by irrigation/drainage control. The experimental pots contained soil without rice plant, and the Eh measurements were used to determine various irrigation schedules for different treatments. Surprisingly, the results found that more CH<sub>4</sub> emissions were found in two treatments with drainage/flooding cycle than in corresponding continuous flooding treatment. Unlike in rice fields where most of  $CH_4$  emission is through rice plant (17, 18), in soil pots the only pathway for CH<sub>4</sub> emissions is through soil/water surface. Consequently, less CH<sub>4</sub> surface emission from the continuous flooding treatment resulted in higher CH<sub>4</sub> concentration in the soil solution. On the other hand, drainage/flooding cycle facilitated CH<sub>4</sub> surface emission with less CH<sub>4</sub> dissolved in the soil solution (16). Due to heterogeneity of soil pots/fields conditions, interpretation of Eh measurements and gas emissions deserves careful attention. In soil microcosm studies, soils are in homogeneous slurry conditions where Eh measurements reflect the actual redox status of the system and all gases of interest are in equilibrium between headspace and soil slurry. Large Eh gradients exist in soil aggregates under natural conditions with aerobic (high Eh) outer layers and anaerobic (low Eh) inner layers (19). Frequent drainage/flooding cycle in soil pots/fields can significantly alter soil hydrological conditions that ultimately enhance gas release to the atmosphere by physical disturbance.

At a drainage event, atmospheric  $O_2$  will enter soil pore space resulting in re-oxidation of various reduced redox active compounds in soils (20, 21). Next to  $O_2$  in soil pore space, Iron (Fe) could be the most important oxidant (electron acceptors) in rice fields. As seen in Table II, most of the soils have higher Fe content than that of Mn or S. The redox couple of Fe(III)/Fe(II) plays an important role in buffering redox status of rice fields (22). Methanogenesis can be controlled by inhibition due to the presence of  $O_2$ , and by competition for substrates (electron donors) due to the presence of alternative electron acceptors (23).

It has been observed that higher total Fe contents were found in paddy soils compared to in non-paddy soils (24, 25). Thompson et al. (26) observed an increasing crystallinity of iron oxides during soil redox alternation (200–700 mV) in short-term batch experiments, which could be one of the reasons for the paddy soils to retain Fe. The critical Eh value for Fe(III)/Fe(II) conversion is about 100 mV at pH 7 (27). When Eh falls below 100 mV, Fe reduction and consequent dissolution occurs. Iron oxidation and immobilization occurs when Eh reaches higher than 100 mV.

Reducible Fe plays an important role to regulate soil redox status, and thus production and emission of both CH<sub>4</sub> and N<sub>2</sub>O. Huang and Yu (*28*) studied the role of amendment of reducible Fe in soil on efficacy of drainage-based management to mitigate CH<sub>4</sub> emissions in a soil plot experiment. The results show that drainage, single or double, could greatly reduce CH<sub>4</sub> emissions, especially in Fe-amended treatments (Figure ()). In this study, Fe amendment showed no significant effect on rice yield (p > 0.05). Similar results were found in a study without continuous flooding (*29*). In a clay loam soil with original Fe content 3.9 g kg<sup>-1</sup>, Fe(OH)<sub>3</sub> amendment by 3.3 g kg<sup>-1</sup> reduced the cumulative CH<sub>4</sub> emission by 52%. Similar study conducted by Jäckel et al. (*30*) showed that ferrihydrite amendment 1046 g

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 $m^{-2}$  reduced CH<sub>4</sub> emission by 50% in a sandy loam soil with original Fe content 2.5 g kg<sup>-1</sup>.

The presence of Fe(III) can significantly delay the initiation of methanogenesis. The threshold concentration for H<sub>2</sub> and acetate utilization (two major CH<sub>4</sub> production pathways) by Fe(III) reducing bacteria is lower than that for methanogens (*31*). Exposure of soils to O<sub>2</sub> by temporal drainage allows regeneration of Fe(III) from its reduced form Fe(II). Therefore, the above inhibition of Fe(III) reduction on methanogenesis resumes. Aeration could result in higher CO<sub>2</sub> and N<sub>2</sub>O production in general. However, proper management of drainage can minimize such increase. A case study by Ratering and Conrad (*32*) showed that the increase of CO<sub>2</sub> and N<sub>2</sub>O production were <10% of the decreased production of CH<sub>4</sub>, and did not represent a trade-off in terms of CO<sub>2</sub> equivalent.

### Integration of Rice Yield and Reducing GWP from Rice Fields

Flooding a field for rice cultivation greatly limits the  $O_2$  supply from the atmosphere, the microbial activities switch from aerobic (i.e. oxic condition) to facultative (i.e. hypoxic condition) and to anaerobic (i.e. anoxic condition) fermentation of organic matter, where alternative electron acceptors, such as Mn(IV) and Fe(III), are used. In such submerged soils, rice plants form aerenchyma that can enable the transport of atmospheric  $O_2$  to the roots (21). Thus there exist two aerobic/anaerobic interfaces with large Eh gradients in rice ecosystem, water/soil interface and plant rhizosphere/bulk soil interface (20).



Figure 3. Methane emission (mean  $\pm$  SD, n = 3) from cultivated rice. The arrows indicate the 2-day drainage ((28) with modification).

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The different Eh conditions required for N<sub>2</sub>O and CH<sub>4</sub> formation and the trade-off pattern of their emissions as found in above laboratory and pot experiments make it a great challenge to abate the production of one gas but not enhance the production of the other. Irrigation and drainage management can induce temporal and spatial variations in soil redox conditions that affect not only trace gas emissions but also rice yield. Thus, to propose feasible mitigation approaches, both cumulative GWP from N<sub>2</sub>O and CH<sub>4</sub> emissions and rice yield need to be considered simultaneously.

In a field study conducted at Shenyang, China (41°32' N, 122°23' E) by Yu and Chen (33), effects of soil management on soil redox potential, GHG emissions, as well as rice yield were investigated. The soil had an OM content of 2.12% and 1.51%, respectively, for the field with and without annual application of organic manure ( $\delta$ ). A major regional cultivar of rice was used for the study with a single growing season of about 120 days, during which three ammonium based nitrogen fertilizer applications were made, with a total N application rate of 170 kg N ha-1. The fields were kept under flooded and non-flooded conditions. The four treatments were: (A) No OM addition, flooded, (B) No OM addition, non-flooded, (C) OM addition, flooded, and (D) OM addition, non-flooded. The flooded fields kept 5 to 10 cm standing water, while the soil surface in the non-flooded fields was wet with water table fluctuating between the soil surface to approximately 5 cm below ground. The non-flooded treatments prevent great fluctuations of soil redox conditions as in conventional flooding/drainage cycle. Soil Eh was measured at depths of 1, 2, 4, 8, 14, and 22 cm below the soil surface. CH<sub>4</sub> and N<sub>2</sub>O emissions in the rice field were measured at least once a week using a static chamber technique. Detailed experimental methodology is provided by Yu and Chen (33).

#### Effect of Field Management on Soil Redox Status

The variation of soil Eh in the rice fields is shown in Figure 4. Values of the measured Eh generally spanned a range of +700 to -300 mV. Unlike homogeneous soil suspensions used in a previous study by Yu and Patrick (8), both oxidizing and reducing conditions existed simultaneously in the rice fields, due to the heterogeneous nature of the field. Soil redox status under the different treatments showed a similar seasonal pattern (Figure 4). Flooding the field (A and C) and adding OM (C and D) facilitated the development of reducing conditions in the soils. After drainage, soil Eh in the upper layers of the field increased up to +450 mV in just a few days. Strictly reducing conditions (Eh < -150 mV) that were favorable for methanogenesis generally developed at 3 periods after rice transplanting: day 50 to 60 (early), day 67 to 77 (middle), and day 95 to 105 (late). Non-flooding conditions (B and D) provided more aeration to the top layers of the fields than the flooded fields (A and C), and consequently resulted in the strictly reducing zones (Eh < -150 mV) being developed 4 or 5 cm deeper than in the flooded fields.

Irrigation and OM management practice showed a significant impact on the soil redox status. Under the flooding conditions, the bulk soil with Eh < 0 mV accounted for 63 and 50% of the soil (top 22 cm) with (treatment C) and without (treatment A) OM addition, respectively. The non-flooding management enlarged

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the volume of bulk soil with higher Eh, and in compensation reduced the portion of soil with lower Eh (Figure 4 and Figure 5). The lower water table in the treatment B and D aerated the soil surface layers, thus strictly reducing conditions developed at deeper layers of the soil profile where reducing intensity was strong enough to initiate a significant  $CH_4$  production.



Figure 4. Soil Eh profile under different treatments ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.



Figure 5. Relative portion of the soil volume at each Eh range ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.

Methane production mostly occurs in soil microenvironments where the Eh values are lower than what is normally measured (34). However, soil Eh measurement can qualitatively indicate the redox status in the soil microenvironment, especially in flooded soils where soil aggregates tend to break When measured soil Eh is lower, the soil microenvironment is more down. reducing, and vice versa (19). Soil OM is the major electron donor in various soil redox reactions, and is the driving force of developing soil-reducing conditions. Release of new OM from the rice root and degradation of the dead rice roots significantly contributed to developing the middle and late strictly reducing zones, respectively (35). In the fields without receiving OM where the rice was in poor growth (with less rice yield, see Table III), less reducing zones developed in the middle season, probably due to less root exudates or dead root tissues from the rice plants. Oxygen diffusion through the rice plant might play a significant role in elevating the soil Eh level between the three strictly reducing periods of the soils.

#### Effects of Field Management on CH<sub>4</sub> and N<sub>2</sub>O Emission, and on Rice Yield

Major periods with higher CH<sub>4</sub> and N<sub>2</sub>O emission generally remained the same among the different treatments (Figure 6), which also agreed quite well with the previous measurements in the same rice field where more complete seasonal variations of CH<sub>4</sub> and N<sub>2</sub>O emission were recorded ( $\delta$ ). The three periods with major CH<sub>4</sub> emission in the rice fields corresponded to the seasonal development of the strictly reducing conditions in the soils (Figure 6), indicating a close relationship between soil Eh and methanogenesis activity. The highest CH<sub>4</sub>

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emission was found in the treatment C (OM addition, flooded), and the lowest in the treatment B (No OM addition, non-flooded). Flooded fields showed low N<sub>2</sub>O emission, and occasional consumption of ambient N<sub>2</sub>O. Nitrogen fertilization during the rice-growing season stimulated higher N<sub>2</sub>O emission, especially in the non-flooded fields (Figure 6). Drainage at the end of the season also resulted in higher N<sub>2</sub>O emission, but meanwhile terminated CH<sub>4</sub> emission in the fields.

Table III summarizes major results of this field study. When the rice fields were flooded, no addition of OM reduced the CH<sub>4</sub> emission by 57% with no difference in average N<sub>2</sub>O emission. Without OM addition, non-flooding management reduced the cumulative GWP from both CH<sub>4</sub> and N<sub>2</sub>O by 46%, but about one third of the CH<sub>4</sub> emission reduction (176.6 CO<sub>2</sub> equivalent m<sup>-2</sup> d<sup>-1</sup>) was offset by the increase of N<sub>2</sub>O emission (56.2 CO<sub>2</sub> equivalent m<sup>-2</sup> d<sup>-1</sup>). In the OM added fields, non-flooding management reduced the cumulative GWP by 72% as a result of the CH<sub>4</sub> emission reduction by 458.2 CO<sub>2</sub> equivalents m<sup>-2</sup> d<sup>-1</sup>, and the N<sub>2</sub>O emission increase by 29.6 CO<sub>2</sub> equivalents m<sup>-2</sup> d<sup>-1</sup>. Although the local traditional management (treatment C) showed the highest GWP, appropriate irrigation (e.g., treatment D) could effectively reduce the cumulative GWP by a significant reduction of CH<sub>4</sub> emission with little enhancing N<sub>2</sub>O emission from the rice field. More O<sub>2</sub> was available for the soils under the non-flooding conditions, thus a larger portion of the soil OM converted to CO<sub>2</sub>, instead of converting to CH<sub>4</sub> by methanogenesis under the strictly anaerobic conditions.



Figure 6. Seasonal CH<sub>4</sub> and N<sub>2</sub>O emissions in the rice fields ((33) with modification). Treatment: (A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded.

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Maggungen aut	Treatment					
Measurement	A	В	С	D		
CH <sub>4</sub> (mg m <sup>-2</sup> d <sup>-1</sup> )	10.80 (95)	3.12 (51)	25.20 (98)	5.28(75)		
N <sub>2</sub> O (mg m <sup>-2</sup> d <sup>-1</sup> )	0.04 (5)	0.23 (49)	0.04 (2)	0.14(25)		
GWP (mg m <sup>-2</sup> d <sup>-1</sup> )	260	140	591	163		
Yield (ton ha-1)	9.7	8.8	11.5	10.9		

 Table III. Summary of the rice field study results ((33) with modification)

(A) No OM addition, flooded; (B) No OM addition, non-flooded; (C) OM addition, flooded; (D) OM addition, non-flooded. Data in parenthesis denotes the relative contribution (%) of  $CH_4$  or  $N_2O$  in the cumulative GWP.

Soil OM played an important role in rice yield (Table III). When additional OM was provided, rice plants showed a more healthy growth as observed in the field and higher yield at harvest regardless of irrigation conditions. This was probably due to the additional nutrients (e.g., phosphorus) in the organic manure and a generally beneficial effect of OM on soil fertility. Compared with the local traditional management (treatment C), the rice yield was significantly decreased (P < 0.05) by 16% if no additional OM was applied (treatment A), and by another 9% if the field was non-flooded (treatment B). Therefore, addition of OM should be included in the field management practice, at least for this region, because of the top priority for higher rice yield. Non-flooded management didn't show any water stress to the rice plant growth, and the rice yield was not decreased in this field trial. With OM addition, non-flooding treatment (D) showed no significant (P > 0.05) reduction in rice yield (5%).

The wide Eh range (+180 to -150 mV) with minimum N<sub>2</sub>O and CH<sub>4</sub> production found in the laboratory studies can be used to guide field management to achieve a maximum reduction of cumulative GWP from CH<sub>4</sub> and N<sub>2</sub>O in rice fields. Although soil Eh in entire soil profile of the rice fields cannot be regulated within such an Eh range, proper irrigation management can make the soil Eh distribute in a desirable way to largely reduce CH<sub>4</sub> emission with little enhancing N<sub>2</sub>O emission.

Irrigation and drainage showed a critical impact on controlling the soil redox status, and on CH<sub>4</sub> and N<sub>2</sub>O production and emission. The best management practice proposed in this field study, in order to reduce the cumulative GWP from the rice field without decreasing the rice yield, is to keep the field non-flooded with OM addition (treatment D). This is a minor modification of the current local management practice (treatment C), which would make it more feasible in application. Less water used for the non-flooded fields may provide some additional benefits to the farmers with less labor, water, and electricity expenses. This management approach may also be feasible for the rice fields with no information available on seasonal variation of CH<sub>4</sub> and N<sub>2</sub>O emission, because irrigation control is adjusted according to the wetness of the soil surface, instead of any instrumental measurement.

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Increasing N<sub>2</sub>O production and emission can significantly offset CH<sub>4</sub> reduction during the drainage or non-flooded practice in mitigating CH<sub>4</sub> emission, resulting in low efficacy in overall GWP reduction. However, higher N<sub>2</sub>O production and emission is always associated with N-fertilization during the rice-growing season. The results also suggest a possible modification to the currently proposed management practice (treatment D) to reduce the short-term higher N<sub>2</sub>O emission by temporarily flooding the fields upon fertilization (only applied to ammonium-based fertilizers). Such temporary flooding condition may prevent the undesirable nitrification activity that makes the fertilizer N unstable, and limits N<sub>2</sub>O production and emission as found under the flooding conditions (Figure 6, and Table III). This modification will not affect the feasibility of the proposed field management, but how long the field should be flooded after fertilization, without introducing significant CH<sub>4</sub> emission, deserves further investigation.

#### Conclusion

Mitigating GHG emission from agricultural ecosystem is a promising approach to abate the current global climate change, because this ecosystem is under direct human management. The theoretical redox window with minimum cumulative GWP emission from soils provides an important guidance in irrigation and fertilization management of rice field. Due to the heterogeneous nature of rice field, Eh measurement and critical Eh condition for CH<sub>4</sub> and N<sub>2</sub>O emission should be carefully interpreted. Irrigation control should minimize significant methanogenesis and nitrification, while favoring complete denitrification with N<sub>2</sub> as the end product. Timing and duration of drainage should be field specific, depending on the soil Eh buffering capacity. All management practice should consider rice yield as a high priority. Significant reduction of GWP by proper management will greatly compensate the projected higher GHG emissions from rice fields due to demand increase by growing population, which will make the rice ecosystem environmentally sustainable.

#### References

- 1. Internal Rice Research Institute (IRRI), **2010**, URL http://beta.irri.org/ statistics.
- Intergovernmental Panel on Climate Change (IPCC), Technical Summary. In Climate Change 2007; Cambridge University Press: New York, 2007
- 3. Bohn, H. L. Soil Sci. 1971, 112, 39-45.
- Lide D. R. In *Handbook of Chemistry and Physics*, 72nd ed.; CRC Press: Boca Raton, FL, 1991.
- 5. Cai, Z. C.; Xing, G. X. Plant Soil 1997, 196, 7-14.
- 6. Chen, G. X.; Huang, G. H. Nutr. Cycling Agroecosyst. 1997, 49, 41–45.
- 7. Tsuruta, H.; Kanda, K. Nutr. Cycling Agroecosyst. 1997, 49, 51-58.
- 8. Yu, K. W.; Patrick, W. H. Soil Sci. Soc. Am. J. 2004, 68, 2086–2091.
- 9. Patrick, W. H.; Williams, B. G. Soil Sci. Soc. Am. Proc. 1973, 37, 331–332.

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In Understanding Greenhouse Gas Emissions from Agricultural Management; Guo, L., et al.; ACS Symposium Series; American Chemical Society: Washington, DC, 2011.

- 10. Masscheleyn, P. H.; DeLaune, R. D. Chemosphere 1993, 26, 251-260.
- 11. Wang, Z. P.; Delaune, R. D. Soil Sci. Soc. Am. J. 1993, 57, 382-385.
- 12. Yu, K. W.; Patrick, W. H. Soil Sci. Soc. Am. J. 2003, 67, 1952-1958.
- 13. Yu, K. W.; Böhme, F. Soil Sci. Soc. Am. J. 2007, 71, 1406–1417.
- 14. Bronson, K. F.; Neue, H. U. Soil Sci. Soc. Am. J. 1997, 61, 981-987.
- 15. Wassmann, R.; Lantin, R. S. Nutr. Cycling Agroecosyst. 2000, 58, 23–36.
- 16. Johnson-Beebout, S. E.; Olivyn, R. A. Geoderma 2009, 149, 45–53.
- 17. Yu, K. W.; Wang, Z. P. Biol. Fert. Soils 1997, 24, 341-343.
- 18. Sass, R. L.; Fisher, F. M. Global Biogeochem. Cycles 1990, 4, 47-68.
- 19. Tiedje, J. M.; Sexstone, A. J. Plant Soil 1984, 76, 197-212.
- 20. Reddy, K. R.; Patrick, W. H. Limnol. Oceanogr. 1989, 34, 1004-1013.
- 21. Begg, M. B.; Kirk, G. D. New Phytol. 1994, 128, 469-477.
- 22. Yao, H.; Conrad, R. Biogeochemistry 1999, 47, 269-295.
- 23. Kimura, M.; Murakami, H. Soil Sci. Plant Nutr. 1991, 37, 55-60.
- 24. Zhang, G. L.; Gong, Z. T. Geoderma 2003, 115, 15–29.
- 25. Cheng, Y. Q.; Yang, L. Z. Geoderma 2009, 151, 31-41.
- 26. Thompson, A.; Chadwick, O. A. Geochim. Cosmochim. Acta 2006, 70, 1710–1727.
- 27. Patrick, W. H.; Jugsujinda, A. Soil Sci. Soc. Am. J. 1992, 56, 1071-1073.
- 28. Huang, B.; Yu, K. W. Chemosphere 2009, 74, 481-486.
- 29. Watanabe, A.; Kimura, M. Commun. Soil Sci. Plant Anal. 1999, 30, 2449–2463.
- 30. Jäckel, U.; Russo, S. Soil Biol. Biochem. 2005, 37, 2150-2154.
- 31. Lovley, D. R.; Phillips, E. J. Appl. Environ. Microbiol. 1989, 55, 700-706.
- 32. Ratering, S.; Conrad, R. Global Change Biol. 1998, 4, 397-407.
- 33. Yu, K. W.; Chen, G. X. *Global Biogeochem. Cycles*, 2004, *18*, GB3018, doi:10.1029/2004GB002251.
- 34. Neue, H. U. Soil Use Manage. 1997, 13, 258-267.
- 35. Schutz, H.; Seiler, W. Biogeochemistry 1989, 7, 33-53.

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