Chemosphere 74 (2009) 481–486

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effects of ferric iron reduction and regeneration on nitrous oxide and methane emissions in a rice soil

Bin Huang *, Kewei Yu, Robert P. Gambrell

Department of Oceanography and Coastal Sciences, Louisiana State University, Baton Rouge, LA 70803, USA

ARTICLE INFO

Article history:
Received 19 May 2008
Received in revised form 8 October 2008
Accepted 9 October 2008
Available online 22 November 2008

Keywords:
Drainage
Ferric iron
Methane
Mitigation
Flooded rice field
Nitrous oxide

ABSTRACT

A laboratory soil slurry experiment and an outdoor pot experiment were conducted to study effects of ferric iron (Fe(III)) reduction and regeneration on nitrous oxide (N_2O) and methane (CH_4) emissions in a rice (*Oryza sativa* L.) soil. The anoxic slurry experiment showed that enhancing microbial Fe(III) reduction by ferrihydrite amendment (40 mol Fe g^{-1}) transitionally stimulated N_2O production and lowered CH_4 production by 16% during an initial 33-day incubation. Increased regeneration of Fe(III) through a 4-day aeration period in the Fe-amended slurry compared to the control slurry reduced CH_4 emission by 30% in the subsequent 15-day anaerobic incubation. The pot experiment showed that ferrihydrite amendment (63 μmol Fe g^{-1}) stimulated N_2O fluxes in the days following flooding. The Fe amendment suppression on CH_4 emission was obscured in the early season but became significant upon reflooding in the mid- and late-seasons. As a result, seasonal CH_4 emission in Fe-amended pots was 26% lower than the control with a single 2-day drainage and 69% lower with a double 2-day drainage. The reduction in CH_4 emission upon reflooding from the Fe-amended pots was mainly attributed to the increased Fe(III) regeneration during drainage showing a mechanism of Fe(III) regeneration in mitigating CH_4 emission by short-term drainage in flooded soils.

Published by Elsevier Ltd.

1. Introduction

Flooded rice (*Oryza sativa* L.) fields are a major biogenic source of methane (CH_4), a potent greenhouse gas second only to carbon dioxide (CO_2) contributing to the current enhanced global warming (Intergovernmental Panel on Climate Change, 2001). Methane emission from flooded rice fields, as the net result of production and oxidation, is regulated by various factors including soil properties, fertilization, water management, and rice cultivars (Wang et al., 1993; Sigren et al., 1997; Yagi et al., 1997; Watanabe and Kimura, 1999; Huang et al., 2002).

The level of microbially reducible ferric iron (Fe(III)) was found to be a major soil characteristic regulating CH_4 emission from rice soils (Watanabe and Kimura, 1999; Cheng et al., 2007). The pool of reducible Fe(III) in soil is comprised of various Fe compounds with various reducibilites (Van Bodegom et al., 2003). Water soluble Fe(III) and exchangeable Fe(III) are reducible but generally low in concentration. Amorphous Fe(III) oxides like ferrihydrite are partly reducible and presumably the dominant component of reducible Fe(III) (Lovley, 1991). Crystalline Fe(III) oxides like magnetite and goethite have much less reducibilites (Lovley and Phillips, 1988). Nevertheless, due to a high abundance of iron, microbial reducible Fe(III) is normally the dominant alternative electron acceptor (AEA) in rice soil (Yao et al., 1999). More importantly, it is capable of regeneration by chemical and microbial oxidation at the soil–water interface and rice plant rhizosphere (Frenzel et al., 1999; Neubauer et al., 2007, 2008), and during soil drainage (Ratering and Conrad, 1998). Microbial Fe(III) reduction competitively suppresses CH_4 production to regulate CH_4 emission from flooded rice fields (Wang et al., 1993; Frenzel et al., 1999).

Increasing the microbially reducible Fe level by amending with Fe materials has been used to assess the effect of Fe(III) reduction on reducing CH_4 emission in flooded rice fields (Furukawa and Inubushi, 2002). A few pot studies and one field study have shown that the influence of Fe amendment on lowering CH_4 emission in rice soils, mostly investigated under continuously flooded conditions, varied from being effective in Fe-low rice soils to being negligible in Fe-rich soils (Furukawa and Inubushi, 2002, 2004; Jäckel et al., 2005).

Ferric iron regeneration during drainage has been suggested to be important in reducing CH_4 emission upon reflooding (Ratering and Conrad, 1998), but not substantially effective in some treatments in two Fe amendment experiments (Furukawa and Inubushi, 2002, 2004). More studies are needed for evaluating the role of Fe(III) regeneration during drainage in reducing CH_4 emission and in determination of suitable drainage durations to reduce CH_4 emission without increasing N_2O emission and reducing rice

* Corresponding author. Tel.: +1 225 578 6427; fax: +1 225 578 6423.
E-mail address: bhuang3@lsu.edu (B. Huang).

0045-6535/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2008.10.015

yield (Yagi et al., 1997; Cai et al., 1999). In this study, we focused on the effect of Fe(III) reduction and regeneration on CH_4 emission from both soil slurries and rice pots. The effect of Fe(III) reduction and regeneration on N_2O flux in the soil was also investigated.

2. Materials and methods

2.1. Soil

A silt loam soil (fine, smectitic, hyperthermic Typic Albaqualfs) was used in this study. The soil was taken from the field top layer (0–15 cm) at the Rice Experiment Station, Crowley, Louisiana, United States (30°14.4′ N, 92°20.4′ W). The soil was air-dried, and stored at room temperature (20 °C). The soil sample was passed through a 1-mm mesh sieve for the slurry experiment and through a 4-mm mesh sieve for the pot experiment. The soil pH was 7.3 (soil: water = 1:1), organic matter 1.67%, total nitrogen 0.07%, extractable Mn (with diethylene triamine pentaacetic acid) 19.5 mg kg^{-1}, extractable Fe (with diethylene triamine pentaacetic acid) 68.2 mg kg^{-1}, and extractable *S* (with ammonium acetate and acetic acid) 10.7 mg kg^{-1}.

2.2. Slurry experiment

The microcosm technique of Patrick et al. (1973) was used in the slurry experiment with modification (Yu and Patrick, 2003). A homogenized soil slurry was formed with 1600 mL deionized water and 400 g air-dried soil in a 2300 mL Erlenmeyer flask under constant stirring. The slurry was amended with ferrihydrite at 0 or 40 μmol Fe g^{-1} of soil ($n = 2$). The preparation of ferrihydrite was according to the procedure described by Schwertmann and Cornell (1991). After a 4-day aerobic pre-incubation at 25 °C, the slurry soil was amended with 4 g ground rice straw and KNO_3 at 8 μmol N g^{-1}, and then anaerobically incubated by bubbling the slurry with pure N_2 at a rate of ~10 mL min^{-1}.

Nitrate contents and N_2O production in the slurries were measured at 6, 24, 48 and 72 h after initiation of the anaerobic incubation. Measurements of redox potential (Eh), pH and CH_4 flux in the slurries were conducted on days one, two, four, six and once every three days afterwards until day 52, except when the slurry was aerated from day 33 to 37. On each gas sampling date, the microcosm ($n = 2$) was purged with N_2 at rate of ~30 mL min^{-1} for 2 h and gas samples were taken from the headspace at 0, 20 and 40 min after stopping purging.

2.3. Pot experiment

The outdoor pot experiment was carried out between 3 June and 8 October, 2003. Three kilograms of soil (dry weight) per pot (diameter 15 cm; height 20 cm) were flooded by mixing with 1000 mL fertilizer solution containing 0.98 g KH_2PO_4, 0.48 g urea and 0 or 10.50 g ferrihydrite-Fe. The fertilizer solution was prepared by mixing the fertilizers with ferrihydrite suspension and mixed well with the soil. The pot was planted with three 21-day-old rice seedlings 2 days after flooding (5 June), maintaining a 2–4 cm layer of overlying water in the first month and a 5–7 cm flooding depth afterwards. Weeds in the pots were manually removed weekly. Urea (0.32 g) was applied twice as top dressing on 10 July and 9 August. The pots ($n = 3$) were drained for 2 days either once (on 28 July) or twice (on 28 July and 27 August). The selection of drainage dates was based on CH_4 emissions from the pots and rice growth stage. All pots were drained on 24 September and harvested on 8 October.

Nitrous oxide and CH_4 fluxes in the pots were measured by a closed chamber method. An equilateral triangle-shape frame made of plastic rods was permanently positioned at the soil surface as the base for holding a transparent chamber (height 100 cm; inner diameter 12.5 cm) during gas sampling. The chamber was fitted with a small battery-operated fan for gas mixing and a rubber septum for gas sampling. Gas samples were taken from the chamber by a 10 mL air-tight syringe at 0, 10, 20 and 30 min after closing the chamber. Gas samples were taken between 9:30 and 11:00 AM on days four, six and ten after flooding, and weekly or biweekly afterwards until 23 September.

2.4. Measurements

The redox potential in the slurries was measured with a pH/ISE meter (Orion, Model 290A) using a platinum electrode and a saturated calomel reference electrode. The readings were corrected against the standard hydrogen electrode by adding 242 mV. The soil slurry samples (10 mL) taken at 12, 24 and 48 h during the anaerobic incubation were centrifuged at 2000 *g* for 5 min, the supernatant filtered (<0.45 m) and stabilized for NO_3^- determination with a pH/ISE meter (Orion, Model 290A) using a combination NO_3^- selective electrode (Orion, 9707BN) (American Public Health Association, 1995). Accumulated microbially reduced Fe during the anaerobic soil slurry incubation was measured on day 33 before the starting of aeration. A soil slurry sample (0.5 mL) was anaerobically taken, extracted with 0.5 N HCl (12 mL) for 2 h at room temperature (Lovley and Phillips, 1986) and centrifuged at 2000 *g* for 5 min. The supernatant (0.1 mL) was added to 1 g L^{-1} Ferrozin solution (0.9 mL) in 50 mM *N*-2-hydroxyl-ethylpiperazin-*N*′-2-ethane sulfate buffer at pH 4.0 for measurement of Fe(II) with a spectrometer at 562 nm. Gas samples from the slurry and pot experiments were analyzed within 2 days after sampling, using a Tremetrics 9001 GC with an electron capture detector (ECD) for determining N_2O concentrations and a flame ionization detector (FID) for determining CH_4 concentrations. Gas samples from the pot experiment were analyzed for N_2O during the first 22 days and one day after reflooding of the drained pots, and for CH_4 throughout the study.

2.5. Calculation and statistical analysis

Gas flux was calculated by linear regression of gas concentrations at sampling intervals (Yu and Patrick, 2003). The cumulative gas emission from the soil slurry or rice pot was computed as the sum of the flux on each sampling date multiplied by the interval from the midpoints of two neighboring sampling dates.

Statistical analysis was conducted using SAS (SAS Institute Inc., 1999–2001). Methane and N_2O emissions at sampling dates from the control and ferrihydrite amendment treatments were compared using the Student *t*-test for both slurry and pot experiments. The Student *t*-test was also used for comparison of rice yields in the control and ferrihydrite amendment pots. Temporal variations of CH_4 emission in the control and ferrihydrite amendment treatments were evaluated with one-way repeated measures ANOVA for both slurry and pot experiments. A simple linear regression was conducted between potential of drainage-induced Fe(III) regeneration and cumulative CH_4 emission in the rice pots. The statistical level of significance was chosen at $\alpha = 0.05$ for all statistical analysis.

3. Results

3.1. Redox potential and pH change in soil slurries

When the anaerobic incubation started, the control slurry remained weakly reducing (above 200 mV) for 2 days. Highly reducing conditions (<−290 mV) developed by day nine through 33 (Fig. 1). The slurry Eh increased to >500 mV when the slurry was aerated for 4 days starting on day 33 and decreased to <−280 mV in six days after restarting the anaerobic incubation. The ferrihydrite amendment slightly delayed the redox potential change from being aerobic to being highly reducing (and vice versa) and slightly lowered the Eh under highly reducing conditions. The pH in the control and Fe-amended slurries varied between 7.2 and 7.7 during the study. The pH was more variable under conditions of rapid Eh change than under highly reducing conditions. Ferrihydrite amendment increased pH about 0.1 unit under highly reducing conditions.

3.2. Denitrification, Fe(III) reduction and CH_4 production in soil slurries

The amount of microbially reducible Fe(III) in the soil slurry increased by 53% with Fe amendment, changing from 63.3 ± 1.8 to 97.0 ± 0.42 μmol g^{-1} (mean ± SD, $n = 2$). In the control soil slurry, nitrate declined linearly with time and was depleted 48 h after anaerobic incubation was initiated (Fig. 2). Ferrihydrite amendment significantly increased N_2O fluxes before nitrate depletion (Fig. 2). The N_2O fluxes in the control and Fe-amended treatments were below detection after day two. Significant CH_4 production (>10 nmol $g^{-1}d^{-1}$) in the two treatments was observed on day six and declined after peaking on day 24 through day 33. After a 4-day aeration treatment from day 33 to day 37, significant CH_4 production in the two treatments occurred again on day 43 and peaked on day 49 (Fig. 3). Iron amendment significantly changed the temporal variation of CH_4 flux in the slurry ($p < 0.05$). Methane fluxes in the Fe-amended slurry were significantly lower than in the control slurry on days 15, 18, 24, 47 and 50 ($p < 0.05$), with a cumulative reduction of 15% in the initial 33 days, 30% in the subsequent 15 days after aeration, and 21% in the whole 52 day incubation.

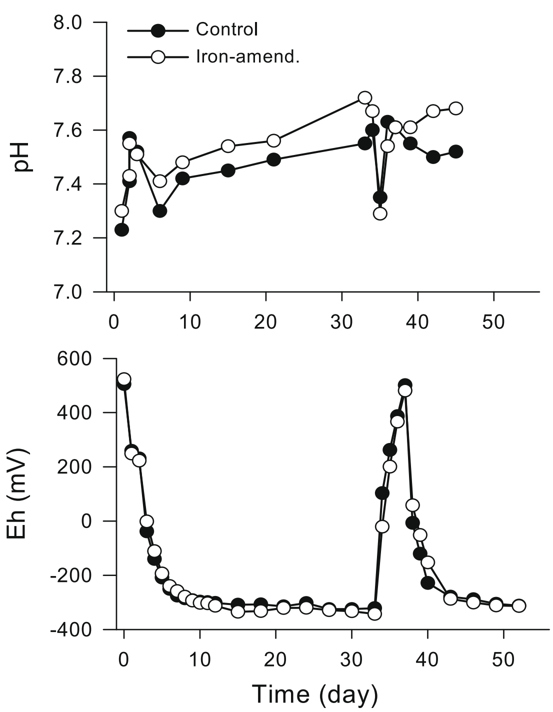

Fig. 1. Eh and pH changes in control and Fe-amended soil slurries. Aeration of the slurries was conducted between days 33 and 37. Data are the means of duplicate measurements.

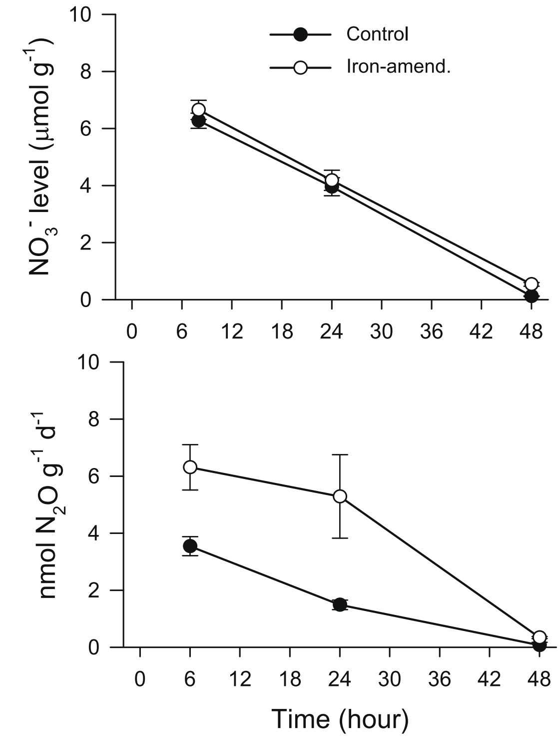

Fig. 2. Nitrate reduction and N_2O production (mean ± SD, $n = 2$) in control and Fe-amended soil slurries.

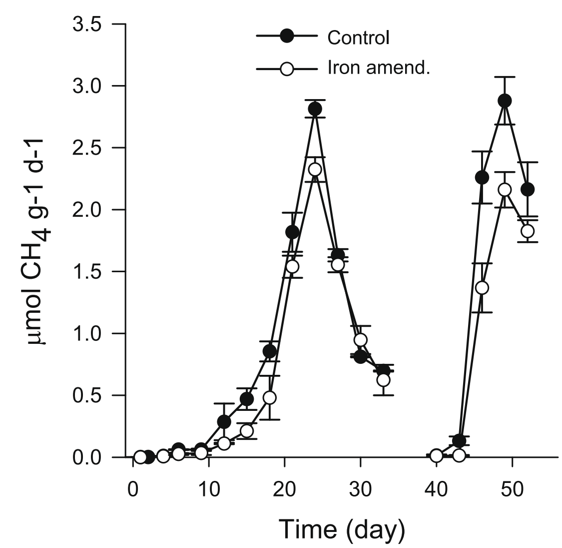

Fig. 3. Methane production (mean ± SD, $n = 2$) in control and Fe-amended soil slurries. Aeration was conducted between days 33 and 37.

3.3. N_2O and CH_4 emissions from pots

Ferrihydrite amendment stimulated N_2O emissions in the early days upon flooding (Fig. 4). Nitrous oxide fluxes became small in all pots after flooding for eight days. No significant N_2O fluxes were observed in the first day after reflooding of the drained pots in the mid- and late-seasons (data not shown).

The initiation of CH_4 emissions from the pots was slow. Methane was emitted at <1.5 mmol CH_4 $m^{-2}d^{-1}$ in all pots until day 40 after flooding (Fig. 5). Iron amendment had little effect on CH_4 emission before the midseason drainage on day 55. Compared to

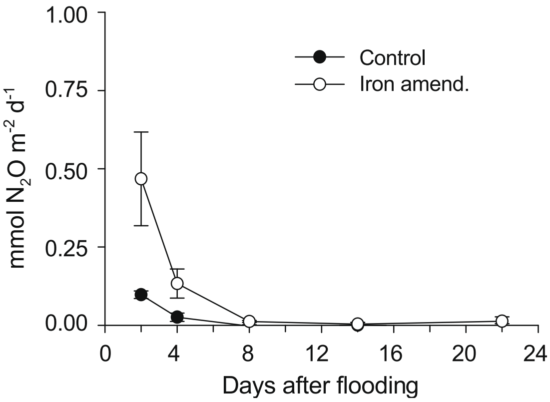

Fig. 4. Nitrous oxide emissions (mean ± SD, $n = 3$) from control and Fe-amended rice pots.

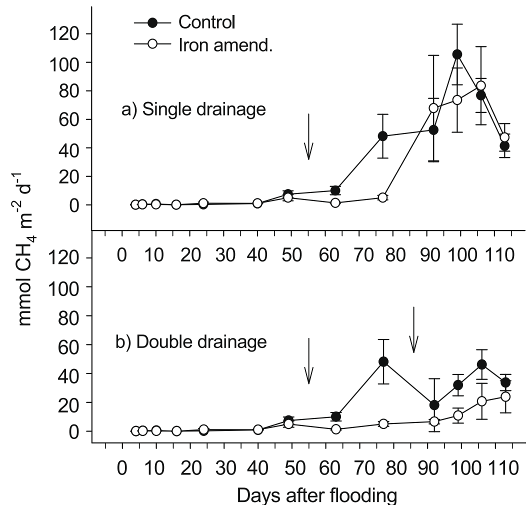

Fig. 5. Methane emission (mean ± SD, $n = 3$) from control and Fe-amended rice pots. The arrows show the dates when 2-day drainage was conducted.

the control pots, CH_4 emissions upon reflooding in the Fe-amended pots were significantly lower on days 63 and 77 ($p < 0.05$) after the pots were drained once on day 55; after day 77 there was no significant difference. When the pots were drained once more on day 85, CH_4 emission upon reflooding was significantly lower on two of four sampling dates (days 99 and 106, $p < 0.05$). As a result, the seasonal CH_4 emission from the rice pots (113 days of measurement) was significantly lowered by Fe amendment when the rice pots were drained once or twice (Table 1) ($p < 0.05$). Regression analysis showed that the cumulative CH_4 emission across the rice pot in the whole measurement period was significantly related to

Table 1
A summary of studies on CH_4 emissions in soil–rice systems as affected by amendment of Fe materials.

Cumulative CH_4 emission relative to control (%)	Drainage	Soil texture	Soil Fe content (g kg^{-1})	Amended Fe material	Fe amendment rate (g kg^{-1})	Source
52	No	Sandy clay loam	3.9[a]	$Fe(OH)_3$	6.4	Watanabe and Kimura (1999)
50	No	Clay loam	3.8[a]	$Fe(OH)_3$	3.3	Same as above
90	No	Coarse medium gley	18.5[b]	Furnace slag	1.5 (490 g m^{-2})[d]	Furukawa and Inubushi (2002)
90	No	Same as above	18.5[b]	Furnace slag	4.2 (980 g m^{-2})	Same as above
89	No	Same as above	18.5[b]	Furnace slag	6.3 (1960 g m^{-2})	Same as above
86	No	Same as above	18.5[b]	Furnace slag	14 (4900 g m^{-2})	Same as above
93	No	Same as above	18.5[b]	Body warmer	4.6 (550 g m^{-2})	Same as above
94	4-day once	Same as above	18.5[b]	Furnace slag	1.5 (490 g m^{-2})	Same as above
66	4-day once	Same as above	18.5[b]	Furnace slag	4.2 (980 g m^{-2})	Same as above
76	4-day once	Same as above	18.5[b]	Furnace slag	6.3 (1960 g m^{-2})	Same as above
81	4-day once	Same as above	18.5[b]	Furnace slag	14 (4900 g m^{-2})	Same as above
93	4-day once	Same as above	18.5[b]	Body warmer	4.6 (550 g m^{-2})	Same as above
77	2-day once	Same as above	18.5[b]	Furnace slag	2.3 (490 g m^{-2})	Furukawa and Inubushi (2004)
75	2-day once	Same as above	18.5[b]	Furnace slag	7.3 (490 g m^{-2})	Same as above
92	2-day once	Same as above	28.5[b]	Furnace slag	490 g m^{-2}	Same as above
99	2-day once	Same as above	28.5[b]	Body warmer	550 g m^{-2}	Same as above
50	No	Same as above	18.5[b]	Furnace slag	2.3 (490 g m^{-2})	Same as above
45	No	Same as above	18.5[b]	Furnace slag	7.3 (980 g m^{-2})	Same as above
111	No	Same as above	28.5[b]	Furnace slag	490 g m^{-2}	Same as above
115	No	Same as above	28.5[b]	Body warmer	550 g m^{-2}	Same as above
50	No	Sandy loam	2.51[c]	Ferrihydrite	1046 g m^{-2}	Jäckel et al. (2005)
74	2-day once	Silt loam	3.5[c]	Ferrihydrite	3.5	This study
31	2-day twice	Silt loam	3.5[c]	Ferrihydrite	3.5	This study

[a] Amorphous Fe.
[b] Total Fe.
[c] Reducible Fe.
[d] Measured increases on soil weight basis in subsequent years after initial Fe amendments on area basis (values in parenthesis.)

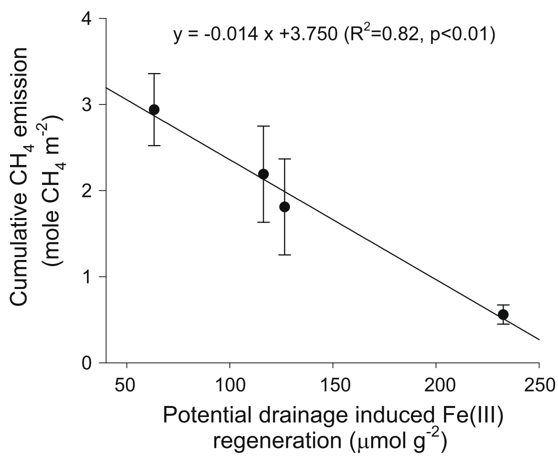

Fig. 6. Relationship between potential of drainage-induced Fe(III) regeneration and cumulative CH_4 emission (mean ± SD, $n = 3$) in 113-days in the rice pots. The potential Fe(III) regeneration during drainage was calculated as the amount of microbial reducible Fe multiplied by its regeneration efficiency during drainage. The amount of the reducible Fe was determined according to the reducibilites of indigenous soil Fe and ferrihydrite from the slurry experiment. The regeneration efficiency of microbial reducible Fe was assumed to be same in the control and Fe-amended pots, and here for simplicity, 100% was adopted.

the potential of Fe(III) regeneration during drainage (Fig. 6) ($p < 0.01$).

3.4. Rice growth

Iron amendment delayed the growth of rice seedlings after transplanting in the first four weeks. No observable differences were found in rice growth between the control and Fe-amended pots in the remaining periods. Rice yields from the control and Fe-amended pots were 11.6 ± 1.4 (mean ± SD, $n = 3$) and 9.9 ± 0.7 with single drainage, and 9.6 ± 1.9 and 9.4 ± 0.7 g per pot with double drainage, respectively. Iron amendment showed no significant effect on rice yield ($p > 0.05$) in either single or double drainage treatments.

4. Discussion

In the soil slurry experiment, nitrate measurement showed a rapid depletion of nitrate in 2 days. Ferric iron amendment showed a small effect on nitrate reduction but transitionally promoted N_2O formation in the slurry, possibly through a toxic effect on enzymatic activity in N_2O reduction (Brons et al., 1991). In the pot experiment, with NO_3^- accumulated under dry conditions being available for denitrification, Fe amendment stimulated N_2O emission in the early days upon flooding. Nitrate generated during the short-term drainage was subject to rapid denitrification or immobilization upon reflooding, but did not lead to significant N_2O emissions one day after reflooding. Overall, N_2O emission in the rice pots throughout the whole rice growing season might be significantly increased by Fe amendment. However, the increase of radiative forcing from N_2O emission was expected to be small compared to the reduction of radiative forcing from CH_4 emission (Furukawa and Inubushi, 2004).

Microbial Fe(III) reduction is an energetically more competitive electron accepting process than methanogenesis (Wang et al., 1993; Frenzel et al., 1999; Yao et al., 1999). Increasing the reducible Fe(III) level by 53% with Fe amendment showed a slight delay in Eh change and a slight increase in pH, but an effective reduction in CH_4 emission in the soil slurry (Fig. 3). Also importantly, this suppressing effect on CH_4 emission remained in the subsequent anaerobic incubation after Fe(III) was regenerated from oxidation of ferrous Fe (Fe(II)) through aeration (Fig. 3).

Our study suggests that the effects of Fe amendment on CH_4 emissions are more complex in soil–rice systems than simple inhibition. Methane emission from the soil–rice system is the net result of production and oxidation and greatly mediated by the rice plant and soil water conditions. (Neue, 1993; Yagi et al., 1997; Aulakh et al., 2000; McLain and Ahmann, 2008). Much of CH_4 produced in the soil-rice system would be microbially oxidized at the oxygenated soil–water interface and rice plant rhizosphere before being emitted to the atmosphere (Neue, 1993). Although Fe amendment could lower the level of acetate to subsequently affect CH_4 oxidation (van Bodegom et al., 2001), its suppression on CH_4 production, as found in the slurry experiment, was expected to be dominant to affect CH_4 emission in the rice–soil system.

In the early rice growing season, the suppression of Fe amendment on CH_4 emission was observed in the study by Furukawa and Inubushi (2002) but obscured in our pot experiment due to low CH_4 emissions in both treatments. With no organic amendment and a relatively small effect of early season rice on CH_4 emission (Aulakh et al., 2000, 2001), the soil from our pot study appeared not to provide sufficient energy source to support strong methanogenic activity, while CH_4 oxidation was expected to be active in the early season (Krüger et al., 2002). Further, the extent of increase of the soil reducible Fe through Fe amendment has been found to be important in reducing CH_4 emissions in soil–rice systems. Studies summarized in Table 1 suggest that the reduction of CH_4 emission by Fe amendment may be significant in low-Fe soils but not in Fe-rich soils. Soil texture could also influence the effect of Fe amendment on reducing CH_4 emission through affecting Fe(II) oxidation, especially during drainage (Sigren et al., 1997).

Results from our pot experiment show the importance of Fe(III) regeneration during drainage on CH_4 emission in soil–rice systems. Similar to the effect of Fe(III) regeneration on CH_4 emission after aeration found in the slurry experiment, Fe amendment in the rice pots enhanced the level of reducible Fe(III) by 84% that was subject to regeneration during drainage, leading to effective reductions in CH_4 emission upon reflooding (Fig. 5). In the study by Furukawa and Inubushi (2002), the contribution of Fe(III) regeneration during drainage to reducing CH_4 emission was obvious only in some Fe amendment treatments, possibly due to the offsetting effect on CH_4 emission of carbon contained in amended Fe materials (Furukawa and Inubushi, 2004). The contribution could also be obscured when CH_4 emissions were greatly lowered for a prolonged time after drainage in all treatments (Furukawa and Inubushi, 2004). The significance and consistency of the contribution of Fe(III) regeneration during drainage to reducing CH_4 emission should be validated in the future on a range of other periodically flooded soils.

Also, the results from our pot experiment on CH_4 emissions after single and double drainage treatments (Fig. 5) showed the importance of Fe(III) regeneration in determination of suitable drainage durations required for reducing CH_4 emission in flooded rice soils. Short-term drainage is desirable if effective CH_4 mitigation is obtained. Long-term drainage, while effective in reducing CH_4 emission, may increase N_2O emission (Cai et al., 1999) and reduce rice yield (Yagi et al., 1997). Drainage could be shortened in reducible Fe-rich rice soils to effectively reduce CH_4 emission. Amendment of Fe materials could be an option in low reducible Fe rice soils to improve short-term drainage-based CH_4 mitigation.

5. Conclusions

Enhanced Fe(III) reduction by ferrihydrite amendment temporally stimulated N_2O production and effectively suppressed CH_4 emission in the anoxic soil slurry. The suppression on CH_4 emission remained after Fe(III) regeneration through aeration. Ferrihydrite amendment significantly increased N_2O emission in the rice pot in the early days after flooding. Ferrihydrite amendment effectively reduce CH_4 emission through increasing Fe(III) regeneration during drainage in the mid- and late-seasons, showing the importance of Fe(III) regeneration in short-term drainage-based options for effective CH_4 mitigation in flooded rice fields. The achieved results should be validated on a range of other periodically flooded soils in the future.

Acknowledgements

This research is supported by the USDA National Research Initiative Competitive Grants Program. This paper is in dedication to Dr. William H. Patrick, Jr. (1925–2004) who was the principle investigator of this project.

References

Aulakh, M.S., Bodenbender, J., Wassmann, R., Rennenberg, H., 2000. Methane transport capacity of rice plants. I. Influence of methane concentration and growth stage analyzed with an automated measuring system. Nutr. Cycl. Agroecosys. 58, 357–366.

Aulakh, M.S., Wassmann, R., Bueno, C., Kreuzwieser, J., Rennenberg, H., 2001. Characterization of root exudates at different growth stages of ten rice (*Oryza sativa* L.) cultivars. Plant Biol. 3, 139–148.

American Public Health Association, 1995. Nitrate electrode method 4500 D. In: Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (Eds.), Standard Methods for the Examination of Water and Wastewater, 19th ed. Washington, DC, pp. 86–87.

Brons, H.J., Hagen, W.R., Zehnder, A.J.B., 1991. Ferrous Fe dependent nitric-oxide production in NO_3^- reducing cultures of *Escherichia coli*. Arch. Microbiol. 155, 341–347.

Cai, Z.C., Xing, G.X., Shen, G.Y., Xu, H., Yan, X.Y., Tsuruta, H., Yagi, K., 1999. Measurements of CH_4 and N_2O emissions from rice paddies in Fengqiu. Chin. Soil Sci. Plant Nutr. 45, 1–13.

Cheng, W., Yagi, K., Akiyama, H., Nishimura, S., Sudo, S., Fumoto, T., Hasegawa, T., Hartley, A.E., Megonigal, J.P., 2007. An empirical model of soil chemical properties that regulate methane production in Japanese rice paddy soils. J. Environ. Qual. 36, 1920–1925.

Frenzel, P., Bosse, U., Janssen, P.H., 1999. Rice roots and methanogenesis in a paddy soil: ferric iron as an alternative electron acceptor in the rooted soil. Soil Biol. Biochem. 31, 421–430.

Furukawa, Y., Inubushi, K., 2002. Feasible suppression technique of methane emission from paddy soil by Fe amendment. Nutr. Cycl. Agroecosys. 64, 193–201.

Furukawa, Y., Inubushi, K., 2004. Effect of application of Fe materials on methane and nitrous oxide emissions from two types of paddy soils. Soil Sci. Plant Nutr. 50, 917–924.

Huang, Y., Jiao, Y., Zong, L.G., Zheng, X.H., Sass, R.L., Fisher, F.M., 2002. Quantitative dependence of methane emission on soil properties. Nutr. Cycl. Agroecosys. 64, 157–167.

Intergovernmental Panel on Climate Change, 2001. The Third Assessment Report, Climate Change. Cambridge University Press, Cambridge.

Jckel, U., Russo, S., Schnell, S., 2005. Enhanced Fe reduction by Fe supplement: a strategy to reduce methane emission from paddies. Soil Biol. Biochem. 37, 2150–2154.

Krüger, M., Eller, G., Conrad, R., Frenzel, P., 2002. Seasonal variation in pathways of CH_4 production and in CH_4 oxidation in rice fields determined by stable carbon isotopes and specific inhibitors. Glob. Change Biol. 8, 265–280.

Lovley, D.R., Phillips, E.J.P., 1986. Organic-matter mineralization with reduction of ferric iron in anaerobic sediments. Appl. Environ. Microbiol. 51, 683–689.

Lovley, D.R., Phillips, E.J.P., 1988. Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron or manganese. Appl. Environ. Microbiol. 54, 1472–1480.

Lovley, D.R., 1991. Dissimilatory Fe(III) and Mn(IV) reduction. Microbiol. Rev. 55, 259–287.

McLain, J.E.T., Ahmann, D.M., 2008. Increased moisture and methanogenesis contribute to reduced methane oxidation in elevated CO_2 soils. Biol. Fert. Soils 44, 623–631.

Neubauer, S.C., Toledo-Durán, G.E., Emerson, D., Megonigal, J.P., 2007. Returning to their roots: iron-oxidizing bacteria enhance short-term plaque formation in the wetland-plant rhizosphere. Geomicrobiol. J. 24, 65–73.

Neubauer, S.C., Emerson, D., Megonigal, J.P., 2008. Microbial oxidation and reduction of iron in the root zone and influences on metal mobility. In: Violante, A., Huang, P.M., Gadd, G.M. (Eds.), Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments. John Wiley and Sons, Hoboken, NJ, pp. 339–371.

Neue, H., 1993. Methane emission from rice fields. Bioscience 43, 466–474.

Patrick, W.H., Williams, B.G., Moraghan, J.T., 1973. Simple system for controlling redox potential and pH in soil suspensions. Soil Sci. Soc. Am. J. 37, 331–332.

Ratering, S., Conrad, R., 1998. Effects of short-term drainage and aeration on the production of methane in submerged rice soil. Glob. Change Biol. 4, 397–407.

Schwertmann, U., Cornell, R.M., 1991. Iron Oxides in the Laboratory: Preparation and Characterization. VCH Verlagsgesellschaft, Weinheim.

Sigren, L.K., Lewis, S.T., Fisher, F.M., Sass, R.L., 1997. Effects of field drainage on soil parameters related to methane production and emission from rice paddies. Glob. Biogeochem. Cycl. 11, 151–162.

van Bodegom, P., Stams, F., Mollema, L., Boeke, S., Leffelaar, P., 2001. Methane oxidation and the competition for oxygen in the rice rhizosphere. Appl. Environ. Microbiol. 67, 3586–3597.

van Bodegom, P.M., van Reeven, J., Denier, H.A.C., 2003. Prediction of reducible soil iron content from iron extraction data. Biogeochemistry 64, 231–245.

Wang, Z.P., Lindau, C.W., Delaune, R.D., Patrick, W.H., 1993. Methane emission and entrapment in flooded rice soils as affected by soil properties. Biol. Fert. Soils 16, 163–168.

Watanabe, A., Kimura, M., 1999. Influence of chemical properties of soils on methane emission from rice paddies. Commun. Soil Sci. Plant Anal. 30, 2449–2463.

Yagi, K., Tsuruta, H., Minami, K., 1997. Possible options for mitigating methane emission from rice cultivation. Nutr. Cycl. Agroecosys. 49, 213–220.

Yao, H., Conrad, R., Wassmann, R., Neue, H.U., 1999. Effect of soil characteristics on sequential reduction and methane production in sixteen rice paddy soils from China, the Philippines and Italy. Biogeochemistry 47, 269–295.

Yu, K., Patrick, W.H., 2003. Redox Range with minimum nitrous oxide and methane production in a rice soil under different pH. Soil Sci. Soc. Am. J. 67, 1952–1958.