

Effects of copper concentration on methane emission from rice soils

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Abstract

Outdoor pot experiments with various paddy soils representing five soil types were conducted at Nanjing Agricultural University during the 2000 and 2001 rice-growing seasons. Eighteen soils and ten out of the eighteen soils were involved in the 2000 and the 2001 experiment, respectively. Two treatments were designed as mineral fertilization (MF) and mineral fertilizer + wheat straw incorporation (MF + WS) for the 2001 experiment. Seasonal average rate of CH₄ emission from different soils ranged from 1.96 to 11.06 mg m⁻² h⁻¹ in the 2000 experiment, and from 0.89 to 5.92 mg m⁻² h⁻¹ for the MF treatment in the 2001 experiment, respectively. Incorporation of wheat straw enhanced considerably CH₄ emission with an average increment of 7.09 mg m⁻² h⁻¹. CH₄ emissions from the two-year experiment were negatively correlated to soil available and total copper concentration. A further investigation showed that CH₄ emission from the MF treatment was positively related to the dissolved organic carbon (DOC) in the soil ($r = 0.904$, $p < 0.001$), and that the DOC was negatively correlated to the concentrations of available copper ($r = -0.844$, $p < 0.01$) and total copper ($r = -0.833$, $p < 0.01$), respectively. Nevertheless, the incorporation of wheat straw did not enhance the soil DOC, and the relationship between CH₄ emission and soil DOC was not statistically significant ($r = 0.470$, $p < 0.20$). It was concluded that higher concentration of copper in the soils resulted in lower soil DOC and thus reduced CH₄ emission when there was no additional organic matter input. Incorporation of wheat straw did not affect soil DOC and available copper concentration but enhanced CH₄ emission.

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1. Introduction

The atmospheric concentration of methane (CH₄) has increased by 1060 ppb since 1750 and continues to increase, from about 1610 ppb in 1983 to 1745 ppb in

1998 (IPCC, 2001, <http://www.ipcc.ch>). Rodhe (1990) reported that CH₄ has some 15–30 times greater infrared absorbing capability than CO₂ on a mass basis and may account for 15% of anticipated global warming. Worldwide, irrigated rice cultivation is thought to be a major source of atmospheric CH₄ (Schütz et al., 1991; Neue et al., 1994) and may contribute 10–30% of the total emitted into the atmospheric methane pool (Cicerone and Oremland, 1988; Houghton et al., 1990). Projections based on population growth rates in countries where rice is the main food crop indicate that rice

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production must increase 65% by 2020 to meet the rice demand for the growing population, which will most likely be accompanied by an increase in methane emissions (Bouwman, 1991). Since soil properties control CH₄ production/emission in wetland ecosystems (Neue and Roger, 1993; Conrad, 1993) and up to now the soil factor has not been taken into account in the IPCC guidelines because data on harvested area by major soil type are not available from the standard activity data sources (IPCC, 2000), clarifying the role of soil properties in CH₄ emission is of great importance to quantify emission inventories.

Efforts have been expended over the past two decades to identify the soil parameters controlling methane emission from rice paddies. These parameters include soil types (Yagi and Minami, 1990), soil texture (Parashar et al., 1991; Sass et al., 1994), soil organic carbon (Neue and Roger, 1993; Neue et al., 1994) and organic nitrogen (Wassmann et al., 1998), and soil total inorganic electron donors and available organic carbon (Yao et al., 1999). Little knowledge is available for the effect of soil copper content on CH₄ emission from rice fields. Recent laboratory incubation studies showed that copper inhibited CH₄ production in three soils (Mishra et al., 1999) and stimulated CH₄ oxidation in two soils (Moharty et al., 2000). Though incubation studies provided very useful information of CH₄ production associated with soil copper content (e.g. Mishra et al., 1999), we believe that soil parameters controlling methane emission would be different when rice plants are involved. On the other hand, because methane fluxes cannot be measured continuously in all paddy soils, a practical method is required to evaluate the role soil parameters such as soil copper content play in methane emission.

In this paper, we report results of CH₄ emission from various rice paddy soils with different copper concentrations in a two-year outdoor pot experiment. The main objectives were to evaluate the effect of soil copper concentration on CH₄ emission and to understand the possible mechanism.

2. Material and methods

2.1. Pot experiment

Outdoor pot cultivation experiment was conducted at Nanjing Agricultural University, Nanjing, Jiangsu province of China during the 2000 and 2001 rice-growing seasons. Soils involved the experiment are mainly representative of five paddy soil types in China, including hydromorphic, percologenic, submergenic, gleyed and degleyed paddy soils. Acreage percentages of these five types to the total paddies in China were 52.2%, 18.9%, 13.2%, 8.5% and 3.5%, respectively (National Soil Sur-

vey Office, 1998). During the winter season in 1999, soil samples were collected from approximately 0–20 cm depths of rice paddies in the region of latitude between 31°20'N and 33°20'N, longitude between 118°50'E and 120°10'E, Jiangsu province.

Pots were made of pottery clay, 22 cm high with an inside diameter of 20 cm. The top edge of a pot has a groove for filling water to seal the rim of the gas-collecting chamber. Four kilograms of soil was placed in each pot, yielding an approximately 16 cm depth of soil. To reduce the potential unevenness of temperature distribution among pots, about 4/5 height of the pot was buried in soil. A *japonica* cultivar, #9516, was cultivated in the two-year experiment.

Eighteen soils were involved in the 2000 rice-growing season. Rice plants were transplanted with eight seedlings for each pot on June 29 and harvested on October 18. During the rice-growing season, all the pots were filled with passively dechlorinated tap water and remained flooded until 10 days before harvest. Chemical fertilizer was applied at the same rate as needed to all soils. No additional organic matter was incorporated to the soils. Three pots for each soil were employed as replicates.

Based on the 2000 experiment, ten of the eighteen soils were selected to further perform the pot experiment in the 2001 rice-growing season. Rice plants were transplanted on June 21 with the same seedling numbers as that in 2000 and harvested on October 20. Water management before heading was similar as that in 2000, and an intermittent irrigation was performed after heading. Two treatments were designed as mineral fertilizer (MF) and mineral fertilizer + wheat straw incorporation (MF + WS). Two pots for each soil and each treatment were employed as replicates.

Mineral fertilizer was applied at the same rate in the two-year experiment. Each pot received chemical fertilizers as urea 1.28 g, KH₂PO₄ 0.77 g and K₂SO₄ 0.89 g. For the MF + WS treatment in the 2001 rice-growing season, 10 g of wheat straw per pot was incorporated before rice transplanting.

2.2. Methane measurements

Methane measurements were taken once a week between local time 08:30 and 10:30, by taking samples of the headspace gas in an open-bottom cylindrical chamber. The chamber was 100 cm high and wrapped with a layer of sponge and aluminum foil to minimize temperature changes during the period of sampling. While taking gas samples, the chamber was placed over the vegetation with the rim of the chamber fitted into the groove of the pot. Methane mixing ratios were obtained by gas chromatography (Shimadzu, GC 14-A in 2000

and Agilent, HP 4890 in 2001, respectively) with a flame ionization detector. The emission was determined from the slope of the mixing ratio change in the five samples of 60 cm³ taken over a 20 min sampling period. Sample sets that did not yield a linear regression value of r^2 greater than 0.90 were rejected. Rates of methane emission were determined from an average of three replicates in 2000, and two replicates in 2001. Air temperature inside the chamber was recorded with each set of emission measurements.

2.3. Determination of soil physico-chemical properties

Physico-chemical properties of the soil samples were determined according to the Chinese Soil Society guidelines (Liu, 1996) for soil analysis (Table 1). An atomic absorption spectrometer was used to determine the amounts of total and available copper. Soils were sampled twice before rice transplanting and after harvesting to detect available copper content in 2001.

Water-soluble organic C (i.e., dissolved organic C; DOC) in the soil samples was measured by using a Total Organic Carbon Analyzer (MODEL TOC-5000A, SHIMADZU) during the 2001 rice-growing season. Fresh soil samples were taken on July 11, August 12 and September 7, respectively. Concentrations of total C (TC) and inorganic C (IC) in the prepared soil supernatant liquid were detected by the combustion/non-dispersive infrared gas analysis method. The DOC was then determined by subtracting the IC from the TC concentration.

3. Results

3.1. Variation in methane emission among soils

A wide variation in CH₄ emission was observed among the soils in the 2000 experiment. The average emission rate over the season was 6.42 mg m⁻² h⁻¹ for all 18 soils with a standard deviation of 2.70 mg m⁻² h⁻¹. The highest emission rate came from soil E3 with an average value of 11.06 mg m⁻² h⁻¹ and the lowest was from soil A3 with an average value of 1.96 mg m⁻² h⁻¹, approximately a 5.6-fold difference between the highest and the lowest.

Fig. 1 shows representative seasonal patterns of CH₄ emission from three soils typical of low, medium and high emission. As shown in Fig. 1, CH₄ emissions from the higher emission soil D2 increased rapidly, while that from the lower emission soil A3 increased slowly during the early growing season. Two emission peaks occurring in the developmental stages of panicle differentiation and heading were observed from soil D2. As rice growth and development proceeds, CH₄ emission from soil A3

remained lower in comparison with that from soils of C5 and D2. Emissions from soil D2 were considerable higher than those from soil A3 over the entire season. The comparable seasonal pattern of CH₄ emission (Fig. 1) suggests that soils emit more CH₄ throughout the season when high emission rates occur in the early season.

Similar seasonal pattern of CH₄ emission as that in 2000 was observed for the MF treatment in 2001 (Fig. 2(a)). Incorporation of wheat straw not only enhanced CH₄ emission but also changed the seasonal pattern (Fig. 2(b)), which confirmed results from Yagi and Minami (1990) who reported that identical amounts of straw incorporation may cause different timing and shapes of emission peaks in the initial phase.

CH₄ emissions were lower in 2000 than those in 2001 when no additional organic matter was incorporated (Fig. 3). One reason comes from the water management. The intermittent irrigation after heading in 2001 might result in CH₄ reduction (Fig. 2(a)). Soil conditions in the previous season might also affect the CH₄ emission. The soil samples were air-dried for about 5 months before the rice was transplanted in the 2000 experiment, while wheat crop was planted in the previous season in the 2001 experiment. Pot experiment by Xu et al. (2000) suggested that the non-rice growth season management might influence soil redox potential and methanogens substrates and eventually CH₄ emissions.

The average emission rate over the 2001 rice-growing season for all 10 soils was 3.53 mg m⁻² h⁻¹ for the MF treatment and 10.62 mg m⁻² h⁻¹ for the MF + WS treatment, respectively. Wheat straw incorporation enhanced CH₄ emission with an average increment of 7.09 mg m⁻² h⁻¹, ranging from 5.46 mg m⁻² h⁻¹ to 10.09 mg m⁻² h⁻¹ (Fig. 4). Correlation analysis indicated that the increment of CH₄ emission from different soils was not dependent on soil texture, pH, and the contents of carbon and nitrogen.

3.2. CH₄ emission and rice production

Above ground biomass of the rice crop was determined as dry weight at harvest. ANOVA test indicated that there was a significant difference in the above ground biomass among soils ($p < 0.001$) in the two-year experiment. However, no significant relationship was observed between the total CH₄ emission and the above ground biomass. The correlation coefficient (r) was 0.268 ($p = 0.282$) in 2000, 0.210 ($p = 0.560$) and 0.152 ($p = 0.676$) for the treatments of MF and MF + WS in 2001, respectively. Since the dependence of CH₄ emission on rice biomass production was only documented for the similar soils and cultivational practice (Sass

Table 1
Physico-chemical properties of air-dried paddy soil sample

Soil code	County/city	Village	Sub-class	Clay <0.002 mm (%)	Silt 0.002–0.05 mm (%)	Sand >0.05 mm (%)	pH	Organic carbon (g kg ⁻¹)
A1	Jiangning	Jiefang	Percogenic	46.6	31.1	22.3	7.5	19.2
A2	Jiangning	Gaogang	Gleyed	37.1	53.7	9.2	7.5	15.5
A3	Jiangning	Jincun	Hydromorphic	49.1	41.4	9.5	6.7	19.4
B1	Yixing	Minglin	Hydromorphic	4.3	41.8	53.9	5.9	16.1
B2	Yixing	Yanghui	Percogenic	12.4	81.5	6.1	7.0	9.8
B3	Yixing	Lidu	Degleyed	37.5	55.1	7.4	6.4	17.9
C1	Baoying	Gongcheng	Percogenic	37.1	30.2	32.7	8.6	9.9
C2	Baoying	Zhangzhuang	Hydromorphic	56.6	37.2	6.3	8.3	18.2
C3	Baoying	Madu	Degleyed	59.8	36.6	3.5	8.0	27.1
C4	Baoying	Luchao	Degleyed	27.6	50.1	22.3	5.6	39.4
C5	Baoying	Daizhuang	Gleyed	32.1	39.0	28.9	7.5	18.0
D1	Yizheng	Beishang	Submergenic	43.1	36.0	21.0	7.1	8.6
D2	Yizheng	Qinfeng	Percogenic	31.7	54.7	13.6	7.9	10.5
D3	Yizheng	Huafeng	Hydromorphic	5.5	24.2	70.3	6.7	11.4
D4	Yizheng	Heyun	Percogenic	26.2	35.9	37.9	7.4	5.2
E2	Luhe	Jiebei	Gleyed	36.0	53.0	10.9	7.7	10.8
E3	Luhe	Changcheng	Hydromorphic	60.6	28.6	10.8	7.6	16.3
E4	Luhe	Daying	Hydromorphic	25.7	35.3	38.9	7.1	18.1
Mean				34.9	42.5	22.5	7.3	16.2
CV (%)				47.7	32.0	81.6	10.8	48.2

2000 Growing season

2001 Growing season

	Total Cu ^a (g kg ⁻¹)	Available Cu ^a (mg kg ⁻¹)	Available Cu ^a (mg kg ⁻¹)	Available Cu ^b (mg kg ⁻¹)	Available Cu ^c (mg kg ⁻¹)	Average ^d (mg kg ⁻¹)	Average ^e (mg kg ⁻¹)
A1	0.050	2.8	3.92	5.22	5.50	4.57	4.71
A2	0.043	5.3					
A3	0.070	5.3	6.80	8.90	8.80	7.85	7.80
B1	0.025	1.9	2.14	2.74	2.80	2.44	2.47
B2	0.023	2.0					
B3	0.033	2.3	3.62	4.28	4.90	3.95	4.26
C1	0.024	1.5					
C2	0.037	2.5					
C3	0.035	3.4	3.00	7.04	6.98	5.02	4.99
C4	0.031	3.7					
C5	0.034	3.1	3.62	5.26	5.05	4.44	4.34
D1	0.035	4.6					
D2	0.020	1.5	1.58	2.04	1.72	1.81	1.65
D3	0.026	1.0	2.34	2.60	2.82	2.47	2.58
D4	0.034	3.9					
E2	0.030	2.9	2.48	3.30	3.44	2.89	2.96
E3	0.050	3.0					
E4	0.033	2.4	3.22	4.38	4.40	3.80	3.81
Mean	0.035	3.0					
CV (%)	34.2	46.3					

^a Measured before rice transplanting.

^b Measured after rice harvesting (MF treatment).

^c Measured after rice harvesting (MF + WS treatment).

^d Averaged the concentrations measured before rice transplanting and after harvesting (MF treatment).

^e Averaged the concentrations measured before rice transplanting and after harvesting (MF + WS treatment).

et al., 1990; Huang et al., 1997), it is not surprising that CH₄ emission is not determined by rice biomass

production when various soils were involved (Huang et al., 2002).

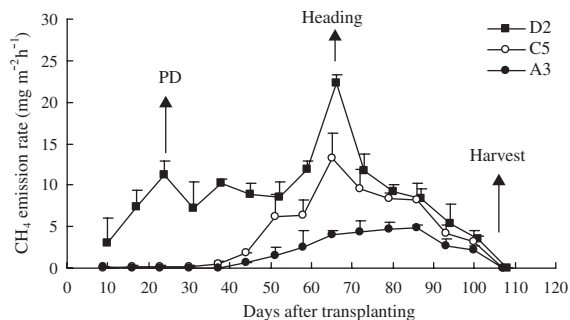


Fig. 1. Seasonal pattern of CH₄ emission from different soils in 2000.

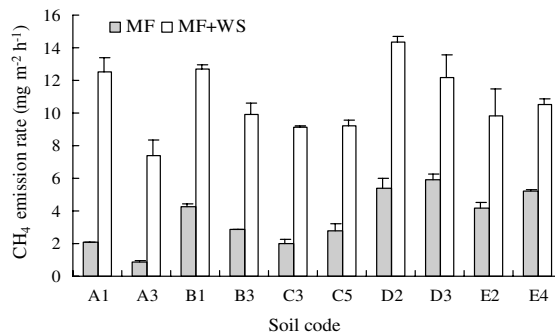


Fig. 4. Seasonal average rate of CH₄ emission from different soils with and without organic matter input in 2001.

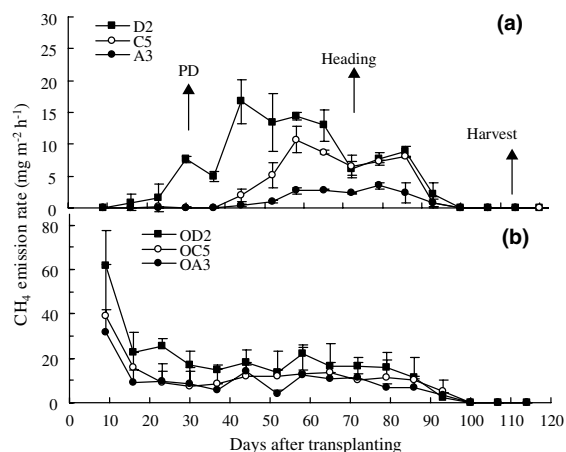


Fig. 2. Seasonal pattern of CH₄ emission from different soils for the treatments of MF (a) and MF + WS (b) in 2001.

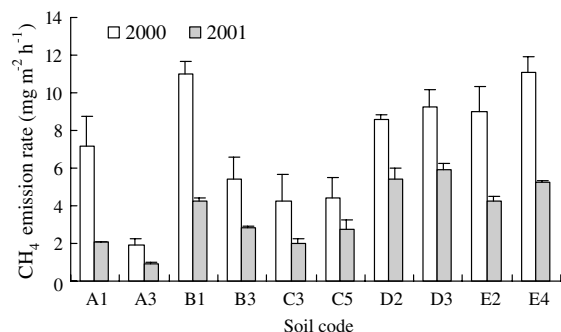


Fig. 3. Seasonal average rate of CH₄ emission from different soils without organic matter input in 2000 and 2001.

3.3. Dependence of CH₄ emission on soil copper and DOC

Average rates of CH₄ emission were negatively correlated with soil concentrations of available copper (Fig. 5)

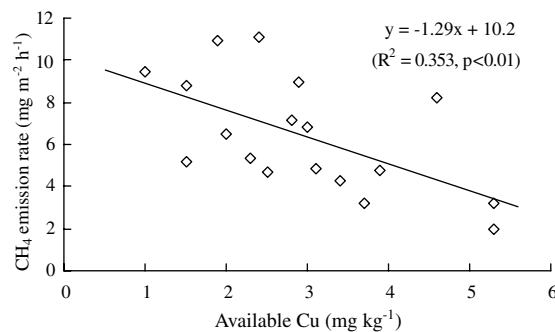


Fig. 5. Dependence of CH₄ emission on soil available Cu content in 2000.

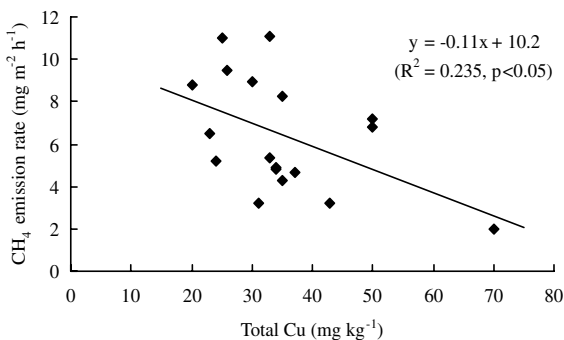


Fig. 6. Dependence of CH₄ emission on soil total Cu content in 2000.

and total copper (Fig. 6) in the 2000 rice-growing season, respectively. Over an entire rice-growing season in 2001, the concentration of available copper increased not only for the MF treatment but also for the MF + WS treatment (Table 1). We took an average value of the available copper concentrations measured before rice transplanting and after harvesting to evaluate its impact on CH₄ emission over the season. Very similar results as

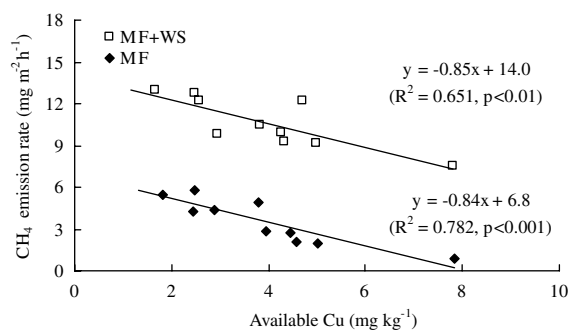


Fig. 7. Dependence of CH₄ emission on soil available Cu content in 2001.

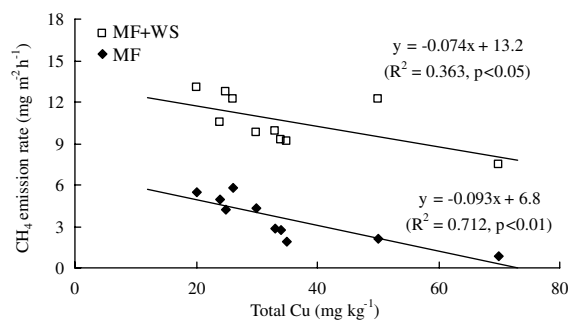


Fig. 8. Dependence of CH₄ emission on soil total Cu content in 2001.

in Figs. 5 and 6 were observed that CH₄ emission was dependent on the soil concentrations of available copper (Fig. 7) and total copper (Fig. 8) in 2001. In contrast with the correlations in Figs. 6 and 8, correlations in Figs. 5 and 7 are more significant and reasonable since the concentration of available copper is evenly distributed among the soils, suggesting that available copper

in soils might be a good indicator in addressing the effect of soil copper concentration on CH₄ emission.

Incorporation of wheat straw did not significantly change the soil available copper concentration (Table 1). Note that the slopes of CH₄ emission against the available copper were very close, while the intercepts were different for the treatments of MF and MF + WS (Fig. 7). The difference of 7.2 between two intercepts of the linear correlation in Fig. 7 is close to the average increment of CH₄ emission (7.09 mg m⁻² h⁻¹) due to the incorporation of wheat straw. Correlation of CH₄ emission against the total copper concentration (Fig. 8) gives the similar trend as that in Fig. 7.

Concentrations of soil DOC increased with plant growth for all soils (Table 2). Incorporation of wheat straw did not significantly change the soil DOC concentration (Table 2), suggesting that the DOC might not be induced by decomposition of the straw. Average value of the DOC for all 10 soils in the vegetative, reproductive and ripening stage was 12.9 mg kg⁻¹, 14.9 mg kg⁻¹ and 17.6 mg kg⁻¹ for the MF treatment, and 12.9 mg kg⁻¹, 15.0 mg kg⁻¹ and 18.8 mg kg⁻¹ for the MF + WS treatment, respectively. Concentrations of the DOC measured at tree developmental stages (Table 2) were averaged for each soil to assess its role in the CH₄ emission over an entire season. Plotting the seasonal average rate of CH₄ emission against the DOC, relationship between these two parameters is significant for the MF treatment but not for the MF + WS treatment (Fig. 9), suggesting that the plant-enriched DOC pool provided a carbon source for CH₄ production when no additional organic carbon was amended.

3.4. Correlation of DOC with copper concentration

Incubations conducted by Mishra et al. (1999) and Moharty et al. (2000) indicated that copper inhibited methane production but not oxidation. Our results

Table 2
Soil DOC concentration (mg kg⁻¹) in different rice growing stages in 2001

Soil code	Vegetative (July 15)		Reproductive (August 12)		Ripening (September 11)		Average	
	MF ^a	MF + WS ^b	MF	MF + WS	MF	MF + WS	MF	MF + WS
A1	13.5	11.7	12.9	16.3	12.6	13.8	13.0	13.9
A3	6.6	8.7	11.3	11.6	12.0	15.0	10.0	11.8
B1	13.4	13.4	12.5	10.6	29.2	27.4	18.4	17.1
B3	11.7	16.4	14.5	15.0	18.6	22.4	14.9	17.9
C3	13.9	13.9	15.3	18.9	10.2	13.7	13.2	15.5
C5	9.4	10.8	12.6	12.3	17.7	14.2	13.2	12.4
D2	15.8	10.2	19.0	16.1	16.7	17.3	17.2	14.5
D3	18.0	16.0	19.8	18.6	21.0	26.6	19.6	20.4
E2	10.0	13.9	12.7	12.4	19.0	15.1	13.9	13.8
E4	16.9	14.3	18.4	18.3	18.9	22.1	18.1	18.2

^a Mineral fertilizer treatment.

^b Mineral + wheat straw treatment.

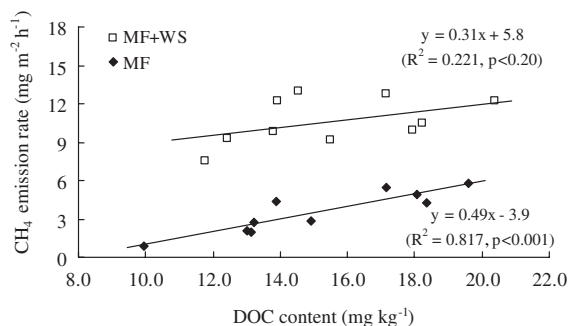


Fig. 9. Dependence of CH₄ emission on soil DOC content in 2001.

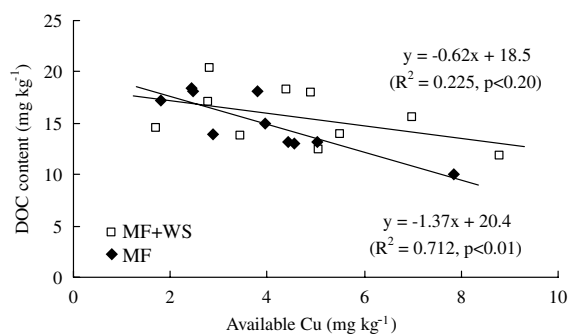


Fig. 10. Correlation of soil DOC content with available Cu in 2001.

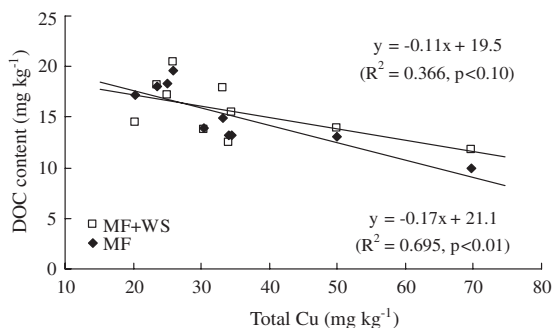


Fig. 11. Correlation of soil DOC content with total Cu in 2001.

indicated that the effect of soil copper on CH₄ emission was associated with soil DOC (Figs. 10 and 11). It is interesting that higher concentrations of copper resulted significantly in lower DOC when there were no additional organic matter inputs, while the relationship between CH₄ emission and DOC became indistinct when the wheat straw was added (Figs. 10 and 11). A possible interpretation is that soils with higher concentration of copper might chelate root secretion as DOC (Figs. 10 and 11), thus might yield a carbon–copper compound

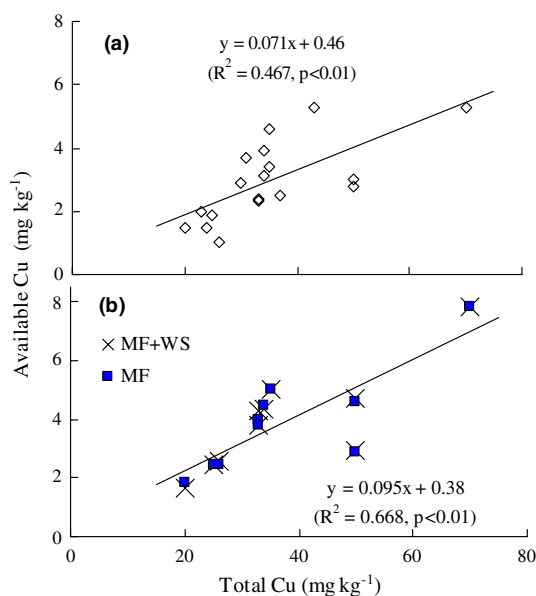


Fig. 12. Relationships between soil concentrations of available and total Cu in the 2000 experiment (a) and the 2001 experiment (b), respectively.

which reduced the availability of methanogenic substrate, and hence resulted in lower CH₄ emission (Figs. 5–8). We simply don't know if the organic compounds derived from the straw decomposition have the same feature as that exuded from rice roots, because the incorporation of wheat straw did not significantly change the soil DOC concentration (Table 2).

Higher concentration of available copper was in general associated with higher concentration of total copper in the soils (Fig. 12). The available copper might be a more likely candidate for the active mechanism involved in the relationship between CH₄ emission and soil copper (Figs. 5 and 7).

4. Discussion

It has been well recognized that soil properties controlled CH₄ production/emission in wetland ecosystems (Conrad, 1993; Neue and Roger, 1993). We previously reported that the key soil parameters affecting CH₄ emission included N status, concentration of available copper and sand percentage, while the soil parameters of organic carbon, C:N ratio, pH, Fe, Mn, Mg, S and P were not significantly correlated to CH₄ emission over an entire growing season (Huang et al., 2002).

Results from the 2001 experiment suggested that the dependence of CH₄ emission on soil copper concentration (Figs. 5 and 7) was associated with soil DOC (Figs. 9–11). In flooded rice soils, CH₄ production is

significantly affected by added organic manure (Yagi and Minami, 1990; Sass et al., 1997) and plant-released materials (Neue et al., 1997; Sass and Fisher, 1997; Lu et al., 1999). The organic carbon presented in various pools is not completely available to microorganisms. Several studies have implied that the amount of DOC is a measure of the readily available resource for microbial growth and biological decomposition, often being considered as a good index of carbon availability (Paul and Beauchamp, 1989; Liang et al., 1996; Jensen et al., 1997). The root zone DOC that is enriched by the plant borne carbon appears to be a main source for CH₄ production when there was no additional organic carbon input (Fig. 9), while decomposition of organic matter might provide another source of methanogenic substrates rather than DOC since incorporation of wheat straw did not significantly change the soil DOC concentration (Table 2).

Apparently, the plant-enriched DOC pool provided a carbon source for CH₄ production (Fig. 9). The facts that CH₄ emission is dependent on soil copper concentration (Figs. 5–8) and that lower DOC is linked by higher concentrations of soil copper (Figs. 10 and 11) open the question as to which forms of soil copper are more responsible for the reduction of DOC if the carbon–copper compound formed. It would be valuable to carry out an additional experiment by adding copper into the soil with different forms and quantities. With respect to the methanogenic substrates, constitutions of the DOC should be distinguished from the decomposition of organic matter to better understand the active mechanisms in CH₄ production.

5. Conclusion

Methane emission is significantly dependent on soil copper concentration. Higher concentration of copper in the soils resulted in lower soil DOC and thus reduced CH₄ emission when there was no additional organic matter input. Incorporation of wheat straw did not affect soil DOC and available copper concentration but enhanced CH₄ emission. A further investigation should focus on determining which forms of soil copper are more responsible for the CH₄ production/emission.

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