To understand which soil chemical properties are the best predictors of CH$_4$ production in rice paddy soils, a model was developed with empirical data from nine types of rice soils collected around Japan and anaerobically incubated at 30°C for 16 wk in laboratory conditions. After 1, 2, 4, 8, and 16 wk of incubation, CO$_2$, CH$_4$, and Fe(II) were measured to understand soil organic matter decomposition and iron (Fe) reduction. Available N (N$_{ava}$) was also measured at the end of incubation. The results showed that decomposable C and reducible Fe are two key parameters that regulate soil CH$_4$ production (P$_{CH4}$). There was a significant relationship between decomposable C and available N (N$_{ava}$) ($r^2 = 0.975^{**}$). Except for a sandy soil sample, a significant relationship between total Fe (Fetotal) and reducible Fe was found. From this experiment, a simple model of soil CH$_4$ production was developed: 

$$P_{CH4} = 1.593N_{ava} - 2.460F_{total}/1000 \text{ (each unit was mg kg}^{-1} \text{ soil}).$$

After simulated CH$_4$ production by two soil chemical properties as above, there was a significant consistency between model simulation and actual measurement ($r^2 = 0.831^{**}$).

An Empirical Model of Soil Chemical Properties that Regulate Methane Production in Japanese Rice Paddy Soils

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Atmospheric methane (CH$_4$) is one of the most important greenhouse gases because it is responsible for approximately 20% of the anthropogenic global warming effect. Most atmospheric CH$_4$ is produced by microbial activity in extremely anaerobic ecosystems, such as natural and cultivated wetlands, sediments, sewage, landfills, and the rumen of herbivorous animals. Rice paddies account for about 17% of the anthropogenic CH$_4$ sources (IPCC, 1995). The amount of CH$_4$ produced and emitted from flooded rice soil is primarily determined by the availability of methanogenic substrates and the influence of environmental factors. The environmental factors affecting soil CH$_4$ production include soil properties, climate, and agricultural practices (Mer and Roger, 2001).

Theoretically, CH$_4$ production in flooded rice soils begins when more energetically favorable terminal electron acceptors, such as NO$_3^-$, Mn(IV), Fe(III), and SO$_4^{2-}$, have been completely reduced as a result of organic matter decomposition, at which point the soil Eh has typically decreased to $-150$ mV (Inubushi et al., 1984; Wang et al., 1993). In the processes of microbial decomposition of soil organic matter, organic matter or its fermentation product H$_2$ are the electron donors, and NO$_3^-$, Mn(IV), Fe(III), and SO$_4^{2-}$ are inorganic electron acceptors (Takai, 1970; Inubushi et al., 1984). Because reducible Fe(III) is one of the most abundant electron acceptors in paddy soils, it plays a key role in the regulation of CH$_4$. An important role is also played by abundance of labile soil organic matter as the electron donor (Gaunt et al., 1997; Wasmann et al., 1998; Yao et al., 1999; Mer and Roger, 2001; Huang et al., 2002; Mitra et al., 2002; Van Bodegom et al., 2003).

Rice is harvested on 150 million ha globally, with about 90% grown in Asia (IRRI, 1993). Methane released from paddies is released through the rice plants, and net CH$_4$ emission is determined by the balance between CH$_4$ production and CH$_4$ oxidation in rice plant and paddy soil ecosystems (Mer and Roger, 2001). The ability to model CH$_4$ emissions from rice paddy soils is limited by an understanding of the interaction between soil properties and CH$_4$ production. To estimate CH$_4$ emission from different regions with different soil types and to evaluate mitigation options for CH$_4$ emis-

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sion from paddy soils, it is necessary to identify soil parameters that are predictive of \( \text{CH}_4 \) production. The objective of this study was to relate various soil chemical properties to \( \text{CH}_4 \) production in a wide variety of Japanese rice paddy soils.

**Material and Methods**

**Soil Collection**

Nine kinds of soils were collected from seven prefectures of Japan (Table 1, latitude from 35°01′ N to 39°41′ N and longitude from 135°37′ E to 141°00′ E). One soil was an Andisol, five were Inceptisols, and three were Entisols. The Andisols, Inceptisols, and Entisols represent 10, 37, and 31% of all Japanese paddy fields, respectively (Kyuma et al., 1984). Soils were collected from the plow layer (top 20 cm) of the rice fields before rice transplanting season. All soils were air-dried and sieved (2 mm) before the experiment.

**Soil Analysis and Pre-incubation**

Air-dried soils were used to measure total C and N, soil bulk density, pH, available Fe, and total Fe and Mn by standard methods according to soil normal analysis methods (JSSSPN, 1986). Total C and N were analyzed by a CN-900 Analyzer (Sumika Chemical Analysis Service). Available Fe was analyzed by the methods of Asami and Kumada (1959).

Total Fe and Mn were extracted by treatment with HF and \( \text{HClO}_4 \), and analyzed by inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Varian VISTA-PRO).

All soils were air-dried and sieved (2 mm) before the experiment.

**Anaerobic Incubation Experiment**

Each soil sample (5 g on an oven-dried basis) that was pre-incubated at 40% WFPS for 2 wk was weighed into a 68-mL serum bottle and amended with 10 mL distilled water. All bottles were capped with a butyl rubber stopper and the air replaced with pure \( \text{N}_2 \) gas by vacuum and gas replaceable equipment (Freezemobile and Unitop HL, Virtis Company, New York). All bottles were incubated at 30°C. After 1, 2, 4, 8, and 16 wk of incubation, three replicate bottles for each soil sample were taken from the incubator, first for measuring headspace concentrations of \( \text{CO}_2 \) and \( \text{CH}_4 \). Iron(II) production in submerged soil samples with 10 mL submerged water was determined after extraction with 40 mL

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**Table 1. Collection sites and characteristics of nine kinds of Japanese paddy soil samples.**

<table>
<thead>
<tr>
<th>No.</th>
<th>Soil classification</th>
<th>Management</th>
<th>Collection site</th>
<th>Latitude, longitude</th>
<th>Bulk density</th>
<th>Total C (mg kg(^{-1}))</th>
<th>Total N (mg kg(^{-1}))</th>
<th>C/N</th>
<th>pH (H(_2)O)</th>
<th>Total Fe (mg kg(^{-1}))</th>
<th>Total Mn (mg kg(^{-1}))</th>
<th>Available Fe (mg kg(^{-1}))</th>
<th>NH(_4)–N (mg N kg(^{-1}))</th>
<th>NO(_3)–N (mg N kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Andisols</td>
<td>Conventional</td>
<td>Iwate, Japan</td>
<td>39°40′N, 137°25′E</td>
<td>0.649</td>
<td>80.3</td>
<td>5.33</td>
<td>15.08</td>
<td>39.5</td>
<td>0.6</td>
<td>8.83</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Inceptisols</td>
<td>Conventional</td>
<td>Yamagata, Japan</td>
<td>38°16′N, 140°19′E</td>
<td>0.933</td>
<td>21.6</td>
<td>1.70</td>
<td>12.69</td>
<td>5.91</td>
<td>1.0</td>
<td>10.11</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Inceptisols</td>
<td>Manure appl.</td>
<td>Yamagata, Japan</td>
<td>38°14′N, 140°19′E</td>
<td>0.937</td>
<td>25.8</td>
<td>1.96</td>
<td>13.21</td>
<td>5.36</td>
<td>0.9</td>
<td>10.58</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Entisols</td>
<td>Conventional</td>
<td>Niigata, Japan</td>
<td>37°26′N, 138°53′E</td>
<td>0.893</td>
<td>18.9</td>
<td>1.69</td>
<td>11.18</td>
<td>5.75</td>
<td>0.6</td>
<td>5.63</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Entisols</td>
<td>Conventional</td>
<td>Niigata, Japan</td>
<td>37°26′N, 138°53′E</td>
<td>0.773</td>
<td>27.1</td>
<td>2.43</td>
<td>11.14</td>
<td>5.20</td>
<td>0.5</td>
<td>5.84</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Inceptisols</td>
<td>Conventional</td>
<td>Fukushima, Japan</td>
<td>37°24′N, 138°53′E</td>
<td>0.773</td>
<td>17.7</td>
<td>1.56</td>
<td>11.37</td>
<td>6.61</td>
<td>0.6</td>
<td>5.94</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Inceptisols</td>
<td>Conventional</td>
<td>Chiba, Japan</td>
<td>35°33′N, 138°53′E</td>
<td>0.989</td>
<td>17.7</td>
<td>1.56</td>
<td>11.37</td>
<td>6.61</td>
<td>0.6</td>
<td>5.94</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Inceptisols</td>
<td>Conventional</td>
<td>Kyoto, Japan</td>
<td>35°01′N, 138°53′E</td>
<td>1.251</td>
<td>26.6</td>
<td>2.15</td>
<td>11.64</td>
<td>6.29</td>
<td>0.8</td>
<td>5.87</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Inceptisols</td>
<td>Conventional</td>
<td>Kyoto, Japan</td>
<td>35°01′N, 138°53′E</td>
<td>1.033</td>
<td>26.6</td>
<td>2.15</td>
<td>11.64</td>
<td>6.29</td>
<td>0.8</td>
<td>5.87</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.939</td>
<td>26.6</td>
<td>2.15</td>
<td>11.64</td>
<td>6.29</td>
<td>0.8</td>
<td>5.87</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Number was according to the collection sites listed from north to south of Japan; soils were named as U.S. Soil Taxonomy.
‡ The different management for No. 3, 9, and 4 indicate a soil sample from paddy fields with cattle manure application and drainage equipment.
§ Mean and CV (coefficient of variation) were for all nine kinds of soils.
acetic acid solution (1.25 mol L$^{-1}$ pH 2.8). The last three replicates for each of the soil samples were extracted with 10% KCl solution for 30 min to measure NH$_4^+$ production after 16 wk of incubation.

Carbon dioxide and CH$_4$ concentrations were determined on a gas chromatograph (GC-7A; Shimadzu) equipped with thermal conductivity and flame ionization detectors, respectively (Cheng et al., 2005).

**Calculations**

Carbon dioxide and CH$_4$ concentrations in the headspace were used to calculate CO$_2$ and CH$_4$ production after correcting for gaseous dissolution in the incubation water by Bunzen’s law (Cheng et al., 2005). Methane consumption was assumed to be negligible in the highly anaerobic incubations; therefore, CH$_4$ fluxes were described as CH$_4$ production throughout this study. Decomposed carbon was calculated as CO$_2$–C and CH$_4$–C during the 16-wk incubation. We defined Fe(II) produced after the 16-wk incubation as reducible Fe and NH$_4^+$ produced after the 16-wk incubation (corrected for the pre-incubation [NH$_4^+$]) as available N.

**Results and Discussion**

**Properties of Nine Japanese Agricultural Soils**

The properties of the nine kinds of soils from seven prefectures of Japan varied widely (Table 1). The Andisols had the highest total C (80.3 g kg$^{-1}$) and the lowest bulk density, while one Entisol (a sand paddy with a suborder name of Psamments) had the lowest total C (8.1 g kg$^{-1}$) and the highest bulk density. As expected, total C and N were closely related ($r^2 = 0.984^{**}$). Mean soil pH (in water) was 6.29 with a coefficient of variation (CV) of 10.1%, showing that all soils were neutral or acidic. The mean contents of total Fe and total Mn were 39.7 and 0.8 g kg$^{-1}$ soil with CV of 21.7 and 28.1%, respectively. Mean available Fe was 7.57 g kg$^{-1}$ soil with a CV of 32.7%. Mean NO$_3^-$–N was 42.2 mg kg$^{-1}$ soil with a CV of 105.2%.

Among these compounds, NO$_3^-$, Mn(IV), and Fe(III) are used as terminal electron acceptors for microbial respiration (Takai, 1970; Inubushi et al., 1984). Concentration data would suggest that Fe is the most important of these electron acceptors, because the amount of total Fe is larger than total Mn by a factor of 50 and NO$_3^-$ by a factor of 1000 (Table 1).

**Iron(II), Carbon Dioxide, and Methane Production during Anaerobic Incubation**

Cumulative increases in Fe(II) and CO$_2$ (Fig. 1a and b) indicated that production rates declined over the course of the 16-wk incubations. Headspace CO$_2$ accumulated rapidly in soils 1, 4, and 5, and more slowly in soils 7 and 8. This pattern in CO$_2$ production among the nine soils was similar to the pattern of Fe(II) produced by the respiration of Fe(III)-reducing bacteria. Initial rates of Fe(II) production were highest in soil 5. In soils 1, 4, 5, and 9, Fe(II) production ceased after 8 wk of incubation; in soil 5 production ceased after 4 wk of incubation (Fig. 1a). High rates of CH$_4$ production coincided with the cessation of Fe(III) reduction in soils 1, 4, 5, and 9 (Fig. 1a and c). Also, the CO$_2$ and CH$_4$ production ratio (in molar units) began to trend toward 1:1 after Fe(III) was completely reduced (data not shown).
Carbon and Nitrogen Mineralization after 16 wk of Anaerobic Incubation

Carbon dioxide and \( \text{CH}_4 \) originate from the decomposition and fermentation of soil organic carbon. After the 16-wk incubation, the total decomposed C (\( \text{CO}_2-C + \text{CH}_4-C \)) was significantly different among the soils (\( P < 0.01 \)). There was not a significant relationship between total decomposed C and total C (\( r^2 = 0.328 \)). Mean mineralized N averaged 123.62 units with a CV of 59.9%. The mean ratio of total decomposed C to mineralized N was 5.62 with a low CV of 19.1%, which is comparable to Redfield ratio (\( C/N = 5.67 \)) and soil microbial biomass C and N ratio in rice paddies reported by Shibahara and Inubushi (1995). Compared to the mean total C/N (11.64, Table 1), the ratio of decomposed C to mineralized N in rice soil was lower than that of the bulk soil organic matter pool, which indicated that the easily decomposed organic matter was from soil microbial biomass and humified organic matter in the soils. Also, the relationship between total decomposed C and mineralized N was significant (Fig. 2, \( r^2 = 0.975** \)).

Relationships among Total Iron, Available Iron, and Reducible Iron

Relationships among total Fe, available Fe, and reducible Fe were shown in Fig. 3. Available Fe measured by the method of Asami and Kumada (1959) was almost equal to reducible Fe in soils 4 and 5, two Entisols samples (Table 1). There was a strong linear relationship between total Fe and reducible Fe that held for all the soils except soil 7 (\( r^2 = 0.837** \) without soil 7). We cannot fully explain this result because the total Fe content was similar to the other soils, but soil 7 was a sand paddy with the lowest organic matter content in the group (8.1 mg kg\(^{-1}\), Table 1). Because soil organic matter can stabilize Fe minerals in a poorly crystalline (i.e., reducible) form (D’Angelo, 2005), the low soil organic matter content of soil 7 could have allowed iron minerals to crystallize more completely than in the other soils. Additionally, sand paddy occupies a very small area in Japan for cultivated rice compared with the other soil types.

Parameterized Soil Chemical Properties for Evaluating Soil Methane Production

The goal of this study was to develop predictive relationships between soil \( \text{CH}_4 \) production and the soil characteristics we measured. Based on our results, we reasoned that \( \text{CH}_4 \) production would occur only when the amount of labile organic carbon (i.e., electron donor) exceeded the amount of reducible Fe(III) (i.e., the primary terminal electron acceptor). We used a ratio of 1 mole carbon mineralized to 4 moles of Fe reduced to convert Fe(III) to carbon units. A significant relationship was found between \( \text{CH}_4 \) production and difference of decomposed C and Fe(II) production (Fig. 4a, \( r^2 = 0.888** \)) and is expressed as a simple equation below:

\[
P_{\text{CH}_4} = 0.302 (C_{\text{edc}} - 1/4 F_{\text{ered}}) \text{ (in mol units)} \quad [1]
\]

Available N can be referred to from the database in Japan, while the easily decomposable C cannot. Easily decomposable C had the following simple zero-order relationship with available N (Fig. 2):

\[
C_{\text{edc}} = 5.28 N_{\text{ava}} \text{ (in mass units)} \quad [2]
\]

where \( N_{\text{ava}} \) is mineralized or available soil N. So we use \( N_{\text{ava}} \) to substitute \( C_{\text{edc}} \) in Eq. [1]. Usually, the total Fe is reported in soil databases, while available Fe is not. Therefore, total Fe should be a more useful parameter than available Fe for estimating \( \text{CH}_4 \) production at a landscape scale. Reducible Fe also can be predicted with a simple zero-order equation (Fig. 3) as:

\[
F_{\text{ered}} = 0.152 F_{\text{etotal}} \text{ (in mass units)} \quad [3]
\]

where \( F_{\text{etotal}} \) is total Fe of the soil. Combining Eq. [2] and [3], \( \text{CH}_4 \) production can be expressed as:

\[
P_{\text{CH}_4} = 1.593 N_{\text{ava}} - 2.460 F_{\text{etotal}}/1000 \text{ (units of mg kg}\text{^{-1})} \quad [4]
\]
Acknowledgments

We thank the Ministry of the Environment, Japan, for financial support through the Global Environment Research Fund and the Eco-Frontier Fellowship Program. We also thank many colleagues in Iwate, Yamagata, Niigata, Tokushima, Ibaraki, Chiba, and Kyoto prefectures for providing soil samples and Dr. T. Ohkura of NIAES for financial support through the Global Environment Research Fund and the Eco-Frontier Fellowship Program.

Conclusions

Several previous studies have related soil properties to CH₄ production for the purpose of simulating CH₄ production and emission from rice fields (Wassmann et al., 1998; Huang et al., 1998; Yao et al., 1999; Mitra et al., 2002, Yan et al., 2003; Li et al., 2004). However, many of the soil properties that have been measured, such as redox potential, reducible Fe and Mn, and decomposable C, are not easily extrapolated to the landscape scale because they are not reported in soil databases. The purpose of our laboratory incubation experiment was to relate CH₄ production to soil parameters that are more readily available in such databases. The results showed that CH₄ production is positively related to available N and reducible Fe in a group of nine Japanese soils that collectively represent most of the paddy soils in Japan. Reducible Fe was significantly related to total Fe. From this experiment, a simple CH₄ production model was proposed (Eq. [4]).

It should be noted that our results were from a simple laboratory experiment without rice plants. The only source of decomposable C was from the soil organic matter, while in rice paddies, most decomposable C comes from rice plant residues and root exudates. Therefore, a field-based model should be developed based on the parameterization of soil chemical properties.

References


