Published online June 29, 2007

Major Biogeochemical Processes in Soils—A Microcosm Incubation from Reducing to Oxidizing Conditions

Kewei Yu*
Wetland Biogeochemistry Institute
School of the Coast and Environment
Louisiana State Univ.
Baton Rouge, LA 70803

And:
Institute of Applied Ecology
Chinese Academy of Sciences
Shenyang 110016
China

Frank Böhme
Helmholtz Centre for
Environmental Research–UFZ
Dep. of Soil Chemistry
Theodor-Lieser-Str. 4
06120 Halle/Saale
Germany

Current Address:
KataLeuna GmbH Catalysts
Am Haupttor
06237 Leuna
Germany

Jörg Rinklebe
Helmholtz Centre for
Environmental Research–UFZ
Dep. of Soil Chemistry
Theodor-Lieser-Str. 4
06120 Halle/Saale
Germany

Current Address:
Univ. of Wuppertal
Dep. D, Soil and Groundwater Management
Pauluskirchstraße 7
42285 Wuppertal
Germany

Heinz-Ulrich Neue
Helmholtz Centre for
Environmental Research–UFZ
Dep. of Soil Chemistry
Theodor-Lieser-Str. 4
06120 Halle/Saale
Germany

Ronald D. DeLaune
Wetland Biogeochemistry Institute
School of the Coast and Environment
Louisiana State Univ.
Baton Rouge, LA 70803

Six soils used for rice (*Oryza sativa* L.) production were incubated using an automatic microcosm system. Production of trace gases (CO_2, CH_4, and N_2O) and transformation of N, S, and metals (Fe and Mn) were studied in soil suspensions incubated from reducing to oxidizing conditions. Results show that soil pH variation was inversely correlated to soil redox potential (E_H) change ($P < 0.01$). Soil CO_2 production exponentially increased with soil E_H increase. In contrast, soil CH_4 production and DOC showed an exponential decrease with soil E_H increase. Without the presence of soil oxidants, methanogenesis occurred across the entire E_H range, with probable H_2–supported methanogenesis at higher soil E_H conditions constituting up to 20% of total CH_4 production. The CH_4 compensation point, where CH_4 concentration became constant due to equilibrium between CH_4 production and consumption, exponentially decreased with soil E_H increase. At pH 7, the critical E_H above which soils consumed atmospheric CH_4 varied among the soils, but was generally >400 mV. Significant N_2O production was observed between 200 and 500 mV. Nitrification could also contribute to N_2O production when E_H is >500 mV, a possible critical E_H for the initiation of nitrification. The critical E_H for substantial immobilization of Fe and Mn was estimated to be around 50 and 250 mV, respectively. The intermediate E_H range (approximately −150 to 180 mV) provided optimum conditions for minimizing cumulative global warming potential resulting from CO_2, CH_4, and N_2O production in soils. Our results have implications in interpreting the overall benefits of soil C sequestration efforts.

Abbreviations: DOC, dissolved organic carbon; E_H, redox potential; GC, gas chromatograph; OM, organic matter.

Oxidation and reduction reactions regulate many biogeochemical reactions in Earth surface environments. The intensity of soil reduction can be rapidly characterized by soil oxidation–reduction (redox) potential (E_H), which allows the prediction of the stability and availability of various nutrients and metal elements in soils and sediments. Soils tend to undergo a series of sequential redox reactions in a homogenous environment when soil redox status changes from aerobic (high E_H) to anaerobic (low E_H) conditions. Major reactions include, in order of E_H from high to low, nitrification, denitrification, Mn(IV) reduction, Fe(III) reduction, SO_4^{2-} reduction, and methanogenesis (Patrick and DeLaune, 1972; Ponnamperuma, 1972; Smith and DeLaune, 1984; Reddy et al., 1989; Patrick and Jugsujinda, 1992). Meanwhile, soil respiration going from aerobic to anaerobic conditions results in CO_2 production across the entire E_H range. Although the reduction reactions proceed in a thermodynamic order (Ponnamperuma, 1972; Patrick and Reddy, 1978), the given oxidation–reduction system is only partially applicable to field conditions, because the mineral phases present in soils are mixed and often unknown. Changes in pH and activities of reactants and products can also alter the order of redox reactions. As a consequence, reduction potentials of a given redox reaction can span a wide range along the redox scale. Chemical reactions that are favored thermodynamically are not necessarily favored kinetically. The lack of effective coupling and the slowness of redox reactions mean that catalysis is required if equilibrium is to be attained. In soils, the catalysis of redox reactions is mediated by microorganisms. Equilibrium

Soil Sci. Soc. Am. J. 71:1406–1417
doi:10.2136/sssaj2006.0155
Received 12 Apr. 2006.
*Corresponding author (kyu1@lsu.edu).

depends entirely on the growth and ecological behavior of the soil microbial population and the degree to which the reactants and products can diffuse and mix. Most of the information on soil redox processes has been obtained from flooded rice systems, but applies to natural wetland soils, and probably upland soils as well (Yu et al., 2001).

Wetland rice ecosystems are a unique aerobic and anaerobic environment. In wetland rice soils, two distinct aerobic–anaerobic interfaces have been identified: (i) the water–soil interface that receives sufficient O_2 from the floodwater (Patrick and DeLaune, 1972)—the thickness of the layer may range from several millimeters to several centimeters depending on perturbation by soil fauna and the percolation rate of water; and (ii) the plant rhizosphere maintained by O_2 diffusing through the aerenchyma of rice plants (Reddy et al., 1989). Redox processes play an important role in soil nutrient availability, biogeochemical cycling of elements, and ecological functions of rice ecosystems. Carbon dioxide, CH_4, and N_2O are the most important atmospheric trace gases that contribute to the global greenhouse effect. Biological N_2O can be produced from nitrification under aerobic conditions, and denitrification under moderately reducing conditions where the reducing condition is not intense enough to completely reduce NO_3^- to N_2 gas. Denitrification is the final step of the N cycle by which atmospheric N_2 fixed in the biosphere returns to the N_2 pool. Significant CH_4 formation (methanogenesis) in soils generally occurs under strictly reducing conditions when soil redox potential decreases below a critical point. Rice fields have been the most studied methanogenic ecosystem because of their economical importance and high potential as an atmospheric CH_4 source. Culturable microorganisms associated with CH_4 and N_2O dynamics were found to be strongly related with key edaphic soil properties (i.e., pH, C/N ratio) in soils (Kravchenko and Yu, 2006). Transformation of Mn, Fe, and S between their oxidized and reduced forms can significantly affect N_2O and CH_4 dynamics in soils (Yu and Patrick, 2004).

Almost all reported information on major redox processes has been obtained by incubating soils in a direction going from oxidizing to reducing conditions. This is analogous to flooding a thoroughly drained soil where all soil redox-active components are in their oxidized forms. During the incubation, however, soil microbial communities and enzyme activities for anaerobic processes may develop progressively, which ultimately influences the dynamics of various redox reactions. For example, N_2O production is significantly affected by the development of denitrifying enzymes during the incubation, especially the N_2O reduction enzyme that controls the N_2O/N_2 ratio (Rudaz et al., 1991; Dendooven and Anderson, 1995). In this study, the soil incubation was initiated under oxidizing conditions, continuing until reducing conditions (Phase I) developed, which allowed anaerobic microbial activities to fully function and soil redox-active components to be transformed to their reduced forms. In the subsequent reducing to oxidizing phase of the incubation (Phase II), major soil biogeochemical processes were analyzed at different soil redox conditions, including nitrification, denitrification, methanogenesis, methanotrophy, and transformation of Fe, Mn, and S. This was an analog to draining a long-flooded rice field, with the results complementing the previous information obtained by incubating soils from oxidizing to reducing conditions.

MATERIALS AND METHODS

Soil Sampling

Six soils (surface 20 cm) were collected from four major rice-cultivating states in the USA (Arkansas, California, Louisiana, and Texas), and from two Asian regions: Hangzhou (China) and Java (Indonesia). The soils were air dried, sieved (1-mm sieves), thoroughly mixed, and stored at room temperature (20°C) before the experiment. Major soil characteristics were analyzed and are provided in Table 1.

Description of the Soil Microcosm System

Soils were incubated using an advanced microcosm system, which allows continuous monitoring and control of soil E_H, pH, and temperature in soil suspensions (Fig. 1). Soil E_H was maintained within a specific range by adding N_2 (to lower E_H) and O_2 (to raise E_H) through an automatic-valve gas regulation system. All microcosm systems were connected to a gas chromatograph (GC) via a computer-operated valve–pipe system. Thus, gas concentration in the headspace of each microcosm was automatically quantified.

Soil Incubation and Measurement

In total, 12 microcosm systems were used, allowing for two replicates of each soil except for the Louisiana and China soils (not replicated due to limited amounts of soil sample). Soil suspension was established by adding 200 g dry soil to a 2.88-L microcosm vessel with 1.6 L of deionized water. To each soil suspension, 5 g

Table 1. Selected physical and chemical characteristics of soils used in a microcosm incubation study.

Soil	Classification†	pH	OM‡	Total N	Sand	Silt	Clay	Fe§	Mn§	S§	Na§	K§
			mg kg^{-1}		g kg^{-1}			mg kg^{-1}				
Arkansas	Alfisols	6.0	14.6	0.7	41	809	150	134	105	13	88	142
California	Entisols	6.7	40.8	1.6	33	366	601	224	107	45	431	305
Louisiana	Alfisols	7.3	16.7	0.7	143	731	126	68	19	11	185	104
Texas	Alfisols	5.1	25.4	1.1	75	284	641	115	35	38	140	291
China	Ultisols	5.6	46.4	2.7	31	635	334	190	102	66	ND¶	ND
Indonesia	Andisols	5.3	23.7	1.0	122	470	408	211	280	65	ND	ND

† U.S. Soil Taxonomy classification: the Arkansas soil is a Stuttgart soil (fine, smectitic, thermic Albaquultic Hapludalf); the California soil is a Willows clay (fine, smectitic, thermic Sodic Endoaquert); the Louisiana soil is a Crowley silt loam (fine, smectitic, thermic Typic Albaqualf); the Texas soil is a Beaumont clay (fine, smectitic, hyperthermic Chromic Dystraquert). No classification information is available for the Chinese and Indonesian soils.

‡ Organic matter.

§ Mn, Fe, S, K, and Na contents were analyzed after extracting the soils with diethylene triamine pentaacetic acid (DTPA) solution.

¶ Not determined.

ground rice straw (388.0 g kg^{-1} C, 7.2 g kg^{-1} N, and C/N ratio 53.8) was added as an additional source of organic matter (OM). The original oxidized soils were incubated by continuously flushing the microcosm with N_2 until stable reducing conditions with an E_H below −200 mV (corresponding value at pH 7) were established. In this oxidizing to reducing phase (Phase I) of the incubation, only soil E_H and pH were monitored and recorded every 15 min. A single Pt electrode with a Ag–AgCl reference electrode was used for the E_H measurement. Original soil NO_3^- was completely denitrified during this earlier phase of the incubation. In the subsequent reducing to oxidizing phase (Phase II) of the incubation, soil E_H was stepwise elevated to a specific E_H value by providing O_2 to the microcosms. Soil E_H and pH were continuously monitored and recorded. To provide a N source for denitrification, 6 mL of 0.1 *M* NO_3–N as KNO_3 was added to each microcosm when soil E_H reached moderately reducing conditions (E_H approximately 0 mV at pH 7). Nitrate was added only once because it can significantly buffer soil redox conditions. Concentrations of CO_2, CH_4, and N_2O in the microcosm headspace were quantified every 2 h. At selected E_H levels, soil suspension was withdrawn (20 mL each time) from each microcosm, and was immediately filtered in an N_2 atmosphere through a 0.45-µm Millipore membrane (Whatman Inc., Florham Park, NJ) into two 10-mL test tubes. One subsample was used immediately to monitor concentrations of dissolved organic carbon (DOC), NO_3^-, and NH_4^+. For the other subsample, three drops of 2 *M* HNO_3 was added to preserve the solution for later analysis of Na^+, K^+, soluble Mn^{2+}, Fe^{2+}, and S (mainly in form of SO_4^{2-}). The microcosm was flushed with N_2 after a series of gas measurements and after sampling the soil suspensions. Changes in soil mass, water, and headspace volume in the microcosm were considered in calculations while soil/water ratio remained the same in the microcosms.

Sample Analysis

Initial soil pH was measured in a soil/water (1:1) slurry. Soil OM was measured colorimetrically after oxidizing with $K_2Cr_2O_7$ and concentrated H_2SO_4. Soil total N was analyzed in dry combustion by a Leco N analyzer (Leco Corp., St. Joseph, MI). Initial soil Mn, Fe, S, K, and Na contents were analyzed by inductively coupled plasma (ICP) after extracting with diethylene triamine pentaacetic acid (DTPA) solution. All metal elements and S concentrations in the soil solution were analyzed directly on ICP–mass spectrometry using an ELAN 5000 (PerkinElmer, Wellesley, MA). Nitrate and NH_4^+ were colorimetrically measured using a FIAstar 5000 Analyzer (FOSS Analytical, Hillerød, Denmark). Dissolved organic C was analyzed after combustion of the finely sprayed solution with a micro N/C analyzer (Analytik Jena AG, Jena, Germany). Gas concentrations were analyzed using a Shimadzu GC-14BPFE (Shimadzu Corp., Kyoto, Japan) with an electron capture detector (for N_2O), a flame ionization detector (FID, for CH_4), and another FID detector (for CO_2) coupled with a methanizer for transformation of CO_2 into CH_4. The GC columns were filled with HayeSep Q (80/100 mesh).

Calculation and Statistical Analysis

The experiment was conducted at room temperature (20 ± 1°C). Gas production rate was calculated by linear regression of three consecutive analyses with time after flushing the microcosm with N_2. The amount of gas dissolved in the liquid phase was determined by using the mole fraction solubility of 5.07×10^{-4} for N_2O, 2.81×10^{-5} for CH_4, and 7.07×10^{-4} for CO_2 (Lide, 1991). Soil E_H was adjusted to the standard H_2 electrode by adding 210 mV (correction factor for the Ag–AgCl electrode) to the recorded instrument reading. All E_H data were reported as their corresponding values at pH 7 that were calculated according to the inverse relationship of E_H and pH as described by the Nernst equation. Redox potential change per pH unit may vary from 59 to 177 mV, depending on redox couples and kinetics of the reaction (Bohn, 1971). Since E_H values represent mixed potentials, a simple correction of 59 mV per pH unit (assuming equal numbers of protons and electrons involved in the reactions) was used.

Statistical analysis was conducted using SAS 9.1 (SAS Institute, Cary, NC). Simple linear regressions using PROC REG were conducted. Multiple regressions were conducted when more than one variable was considered in the model, with stepwise analysis to identify the most significant factor(s). Variables were considered statistically significant at $P \leq 0.05$ ($\alpha = 0.05$).

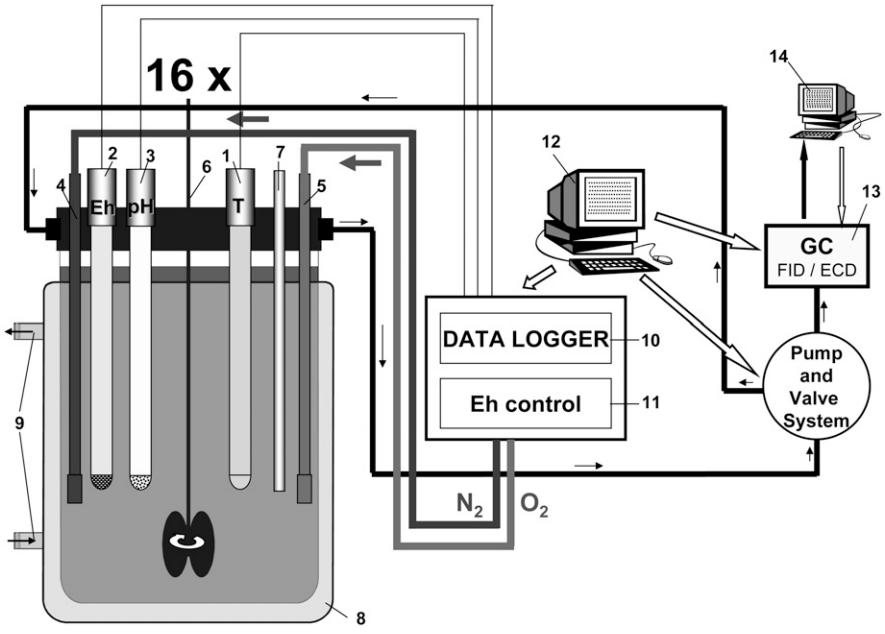

Fig. 1. Components of the soil microcosm system used in an incubation study with six soils: (1) thermometer; (2) redox potential (E_H) electrode; (3) pH electrode; (4) dispersion tube for N_2; (5) dispersion tube for O_2; (6) stirrer; (7) sampling tube; (8) microcosm vessel; (9) temperature control by a thermostat and water circulation; (10) data logger for E_H, pH, and temperature; (11) automatic redox regulation by N_2 and O_2 valves; (12) control computer for data logger, pump, and valve system (gas sampling), and gas chromatograph (start signal); (13) gas chromatograph (GC) with flame ionization detector/electron capture detector for trace gas measurements (CO_2, CH_4, and N_2O); and (14) computer for GC control and GC data storage.

RESULTS AND DISCUSSION

Relationship between Soil Redox Potential and pH

The measured E_H in soils generally represented a composite value that reflects

Table 2. Variations of soil pH and redox potential (E_H), and their linear regression analysis in a microcosm incubation study with six soils†.

Soil	pH			E_H at pH 7			Linear regression of pH and E_H (V) at pH 7‡	
	Mean	Median	Range	Mean	Median	Range	Equation	r^2 (n)
				mV				
Arkansas-1	6.2	5.9	4.3–7.4	162	195	–225 to 619	pH = –2.65 E_H + 6.72	0.75 (8114)
Arkansas-2	6.5	6.5	5.4–7.6	221	277	–206 to 584	pH = –2.87 E_H + 7.09	0.95 (9679)
California-1	6.9	6.9	6.0–7.6	75	9	–264 to 580	pH = –1.20 E_H + 6.96	0.65 (9580)
California-2	6.6	6.4	5.5–7.6	69	105	–271 to 481	pH = –1.02 E_H + 6.63	0.19 (9580)
Louisiana	7.2	7.4	5.9–8.4	124	62	–237 to 498	pH = –2.27 E_H + 7.46	0.73 (9679)
Texas-1	5.9	6.0	5.1–7.0	167	222	–136 to 619	pH = –1.49 E_H + 6.42	0.31 (7618)
Texas-2	5.9	5.9	5.1–6.9	193	132	–7 to 462	pH = –3.54 E_H + 6.57	0.88 (9679)
China	6.1	5.9	5.4–7.0	93	30	–192 to 499	pH = –1.13 E_H + 6.16	0.43 (9679)
Indonesia-1	6.2	6.2	4.9–7.3	115	67	–229 to 518	pH = –2.76 E_H + 6.55	0.91 (9679)
Indonesia-2	5.9	5.8	4.8–7.3	208	186	–167 to 583	pH = –3.03 E_H + 6.57	0.95 (9679)

† Measurements from both Phase I (from oxidizing to reducing conditions) and Phase II (from reducing to oxidizing conditions) were used.

‡ All regressions showed a significant relationship ($P < 0.01$).

a weighted average contributed by all redox couples present. In aerobic soils where the O_2–H_2O redox couple functions, the E_H range is between 300 and 700 mV. Soil E_H and pH were recorded in both the earlier oxidizing to reducing (Phase I) and later reverse (Phase II) phases of the incubation. The soil E_H generally ranged from −200 to 600 mV in this study, a typical E_H range that occurs in wetland soils under natural conditions. At the extreme two ends of this E_H range, nitrification occurs under oxidizing conditions (high E_H) and methanogenesis under strictly reducing conditions (low E_H). Soil pH fluctuated with changes in soil E_H conditions. All major soil redox reactions (such as denitrification, and reduction of Mn, Fe, and SO_4^{2-}) increase soil pH. The pH increase, however, is limited by the precipitation of Fe(II) and Mn(II) carbonates occurring at about pH 7, and production of CO_2 and organic acids from decomposing OM. Under reducing conditions, all soils tend to reach near-neutral pH values for either originally acidic or alkaline soils (Ponnamperuma, 1972). Dynamics of the soil E_H and pH measurement are summarized in Table 2. Statistical analysis showed a significant ($P < 0.01$) negative correlation between the soil E_H and pH. The activities of many biogeochemical processes will be significantly altered due to such pH shifts with redox fluctuations.

Carbon Dioxide Production

All major reduction reactions of soil oxidants generate CO_2 (soil respiration), with OM as the electron donor. Soil oxidants [mainly Mn(IV), Fe(III), and SO_4^{2-}] can be regenerated by introducing O_2 into a reducing system, as was the case in Phase II in this study. Thus, aerobic respiration by soil microbes using O_2 as an electron acceptor also probably contributed to CO_2 production in this study.

Dissolved organic C, as an active soil electron donor, was measured by sampling soil suspensions at different stages of the Phase II incubation, because of its direct relationship with soil CO_2 and CH_4 production. Carbon dioxide production rates, for all studied soils, increased with soil E_H. The same tendency has been reported in incubations from oxidizing to reducing conditions (Yu and Patrick, 2003, 2004). In this study, only CO_2 production rates at times of DOC measurements are included in Fig. 2. Higher CO_2 production rates were found at higher redox conditions, despite decreasing DOC content in the soil microcosms with increasing E_H (Fig. 3-i). The DOC content decrease found at higher redox conditions indicates that formation of DOC from soil OM could not balance mineralization to CO_2 during the incubation. Multiple regression analysis of all soils (n = 52) indicated that both the soil E_H and DOC were positively correlated with the logarithm of CO_2 production rates (r^2 = 0.42, $P < 0.01$). Stepwise regression analysis indicated that the soil E_H was more highly related to CO_2 production (for E_H analysis: r^2 = 0.41, $P <$ 0.01; for DOC analysis: r^2 = 0.06, P = 0.08). For each microcosm, DOC-adjusted CO_2 production rates were calculated by assuming the CO_2 production rate is proportional with DOC content (DOC-adjusted CO_2 production rate = measured CO_2 production rate × DOC content). With this adjustment, the calculated CO_2 production rates are independent of DOC content in each microcosm. The CO_2 production rates and corresponding DOC measurements are summarized in Table 3. Without DOC interference of CO_2 production rates (after adjustment), CO_2 production rates tended to increase exponentially with the soil E_H. For all soils, regression of the CO_2 production rates (after adjustment) with the soil E_H showed a significant relationship (r^2 = 0.57, $P < 0.01$).

Soil CO_2 production rates are generally low during anaerobic respiration, with less energy yield for soil microorganisms. Such inefficient respiration is a principle mechanism for soil C sequestration, as found in wetland ecosystems (Smith et al., 1983) and no-till agroecosystems (Kessavalou et al., 1998). Conversely, significant increases in respiration rates after flooding were reported in paddy soils (Bossio and Scow, 1995) and floodplain soils (Rinklebe and Langer, 2006), possibly due to an unspecific stress to aerobic microorganisms. The overall benefit of C sequestration, however, deserves careful evaluation. Some of the C sequestration benefit may be offset, in terms of contribution of total soil radiative forcing, by enhanced soil N_2O production (Batjes, 1998), and especially by significant CH_4 production (Roulet, 2000; Yu et al., 2006).

Methane Production

Dissolved organic C is a relatively mobile and labile form of soil C. In flooded soils, DOC may serve as a C source for CH_4 production. Methane emission rates have been found to be positively correlated with the dynamics of DOC in the rice root zone (Lu et al., 2000). Significant CH_4 production was found under relatively low E_H conditions in this study (Fig. 3-ii). As a substrate for methanogenesis, soil DOC is directly responsible for the observed CH_4 production. Following the same assumption as for CO_2 production, CH_4 production rates were adjusted with the corresponding DOC content in each microcosm. After adjusting the CH_4 production rates with the measured DOC, the results showed similar CH_4 production patterns under different E_H conditions (Fig. 3-iii). Increasing soil E_H by supplying O_2, however, may exert a toxic effect on the methanogenic bacteria along with increasing the soil redox status. In fact, experiments with cultures of methanogenic bacteria showed that O_2 had a greater adverse effect on methanogenic activity than high redox potentials, and that methanogens were able to initiate CH_4 production at E_H values up to 420 mV (Fetzer and Conrad, 1993). Other studies in which soils were not treated with O_2 showed initiation of CH_4 production at E_H values around 0 to 100 mV (Peters and Conrad, 1996; Ratering and Conrad, 1998). Nevertheless, soil redox potential is generally a good indicator for the onset of soil methanogenesis, but should be combined with careful characterization of the soil and its CH_4 production behavior.

Statistical analysis (n = 37) indicated that there was no significant correlation between the CH_4 production rates (both before and after DOC adjustment) and DOC contents (P > 0.05) in the studied soils. Methane production tended to exponentially increase with decreasing soil E_H (r^2 = 0.27, P < 0.01). After adjusting the CH_4 production rates by the soil DOC contents, the correlation between the CH_4 production rates and soil E_H remained significant (r^2 = 0.15, P < 0.01).

The results of this incubation study from reducing to oxidizing conditions suggest that soil redox potential may not be a good indicator for the cessation of ongoing soil methanogenesis. The relative poor relationship (low r^2 values) between the CH_4 production rates and soil E_H may be due to two mechanisms involved in CH_4 production. Past studies have shown that, when soil incubations were initiated under oxidizing conditions, small amounts of CH_4 production were observed at the beginning of the incubation with high E_H (Fetzer and Conrad, 1993; Roy et al., 1997; Yao and Conrad, 1999; Yu and Patrick, 2003). Such initial methanogenesis was H_2 dependent and was generally insignificant (2–6% of total CH_4 production) compared with the vigorous acetate-dependent methanogenesis under strictly anaerobic conditions (Yu and Patrick, 2003). Under conditions where soil goes from oxidizing to reducing, redox-active soil oxidants, such as NO_3^-, Mn(IV), Fe(III), and SO_4^{2-}, can significantly reduce H_2 production, limiting early CH_4 production. Significant CH_4 production can only take place when these oxidants are reduced into their reduced forms. At the same time, soil oxidants can contribute to oxidation of the existing CH_4 in the system without using O_2 (Iversen et al., 1987; Miura et al., 1992; Kumaraswamy et al., 2001). The critical E_H for significant CH_4 production has been determined to be about −150 mV or less in most studies (Neue et al., 1995; Yu et al., 2001; Yu and Patrick, 2003). In this study, measurement of CH_4 production started under strictly reducing conditions when all soil redox-active oxidants had been transformed into their reducing forms. There was no limitation for methanogenesis in such a reducing environment. In transition from reducing to oxidizing conditions, inhibition

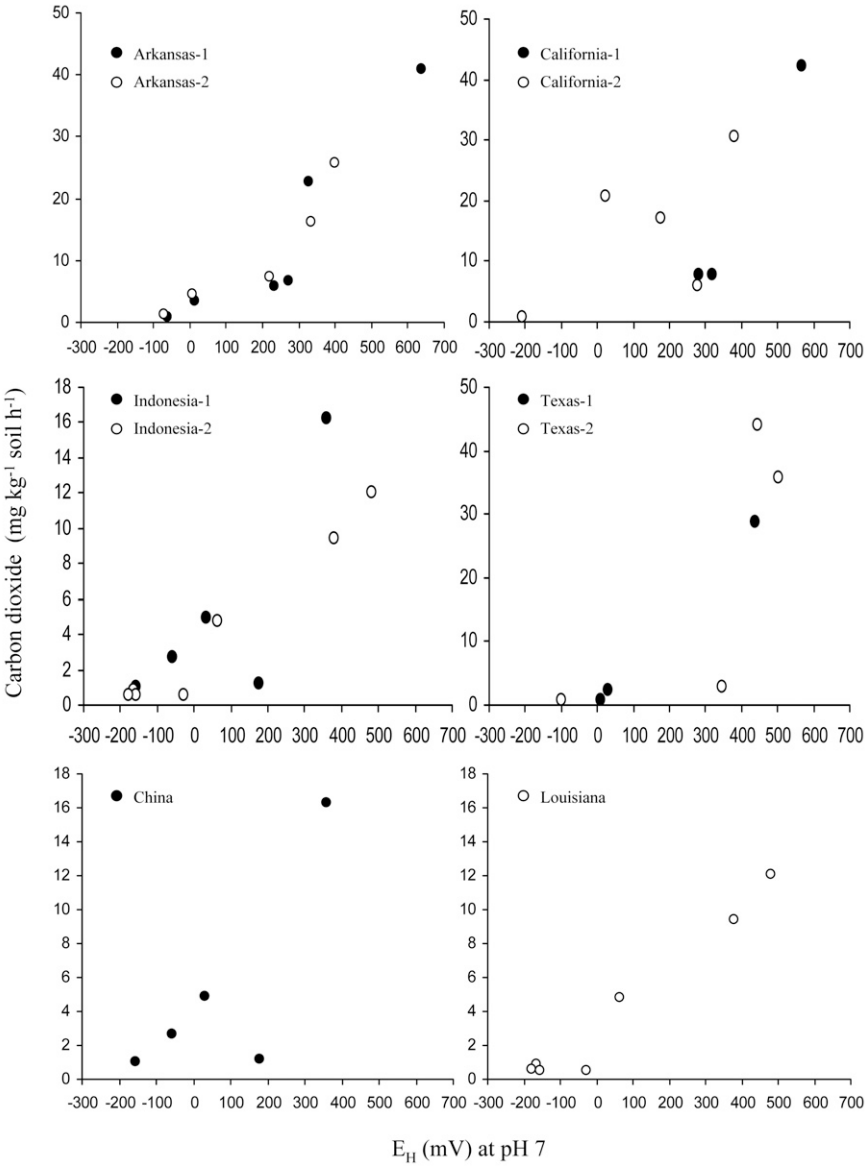

Fig. 2. Carbon dioxide production rates under different redox potential (E_H) conditions in a microcosm incubation study with six soils. Only results when soil dissolved organic carbon (DOC) measurements were conducted are included.

mechanisms for methanogenesis (by redox-active soil oxidants, and even increase of O_2 partial pressure) developed gradually. No clear E_H boundary could be found for the two phases of methanogenesis in this study. With less competition of various soil oxidants for H_2, CH_4 production under higher E_H conditions was significant (up to 20% of total CH_4 production), compared with the CH_4 production under strictly reducing conditions. A reported field study concluded that H_2–dependent methanogenesis contributed about 25 to 30% of the CH_4 produced in soils (Conrad and Klose, 1999a, 1999b). Methane production tended to terminate only when soil E_H was >400 mV in this study. Measurement of CH_4 production under different redox conditions provides valuable guidance for managing rice fields to mitigate CH_4 emission and also helps to understand CH_4 dynamics in natural wetlands under different hydrological conditions.

Methane Compensation Point under Different Redox Potential Conditions

Compensation occurs when consumption is balanced by simultaneous production. Trace gas consumption generally increases with ambient trace gas concentration. Trace gas production, however, is normally independent of the product concentration. Therefore, there exists a concentration level for a specific gas at which its production equals consumption, the so-called *compensation point* (Conrad, 1994). In this study, no compensation point could be determined for CO_2 due to lack of consumption activity in the system, or for N_2O due to the limited number of measurements.

Mechanisms of CH_4 production have been discussed above. The major soil CH_4 consumption mechanism is aerobic oxidation using O_2. The significance of anaerobic CH_4 oxidation has not been quantified, but the occurrence has been reported in marine sediments and in saline inland waters (Iversen and Joergensen, 1985; Iversen et al., 1987), and also in soils coinciding with reduction of Fe(III) (Kimura et al., 1992; Miura et al., 1992). Compensation points for CH_4 have so far not been determined in either field or laboratory conditions. The automatic microcosm system used in this study made detailed monitoring of CH_4 concentration in the microcosm possible. In such a closed system, two approaches for measuring CH_4 compensation point were implemented. One was to monitor CH_4 concentration increasing in the headspace of microcosms until it reached a steady state (Fig. 4-i), and the second was to monitor CH_4 concentration decreasing to a steady state (Fig. 4-ii). Under low- E_H conditions, a high CH_4 compensation point was found due to strong CH_4 production and weak CH_4 oxidation capacity. The CH_4 compensation point was low under high-E_H conditions due to strong methanotrophic activity and weak methanogenesis activity. This analysis was applied to each soil across the entire E_H range studied, and the results

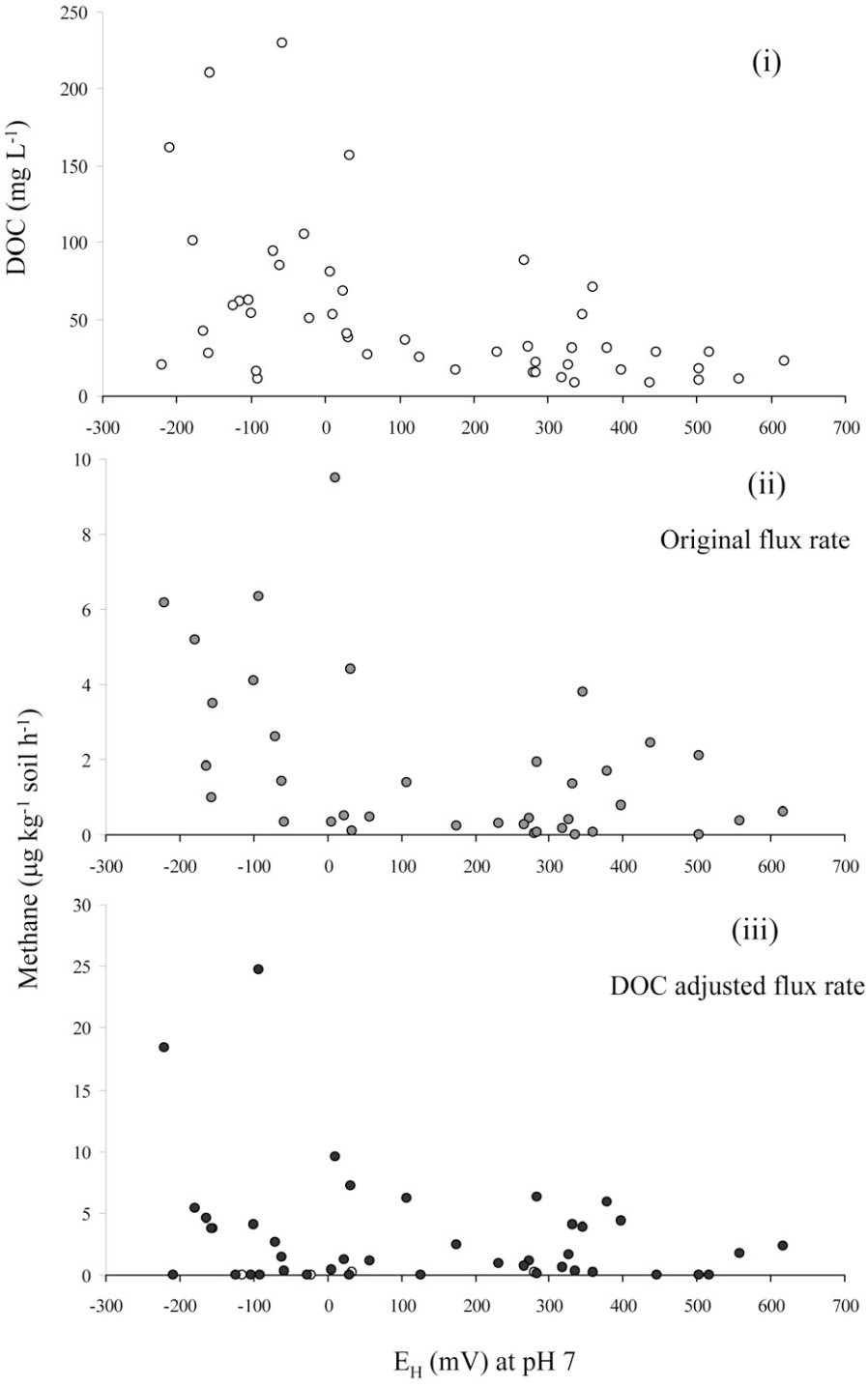

Fig. 3. Soil CH_4 production rates and dissolved organic carbon (DOC) concentrations in soil suspensions under different redox potential (E_H) conditions in a microcosm incubation study with six soils: (i) DOC measurement; (ii) original CH_4 flux rate; and (iii) DOC adjusted CH_4 flux rate. Only results when soil DOC measurements were conducted are included. Adjusted CH_4 flux rates were calculated by: DOC adjusted CH_4 flux rate = measured CH_4 flux rate × DOC content.

Table 3. Variations of CO_2 production rates and associated dissolved organic carbon (DOC) contents, and exponential regression analysis of DOC-adjusted CO_2 production rates with soil redox potential (E_H) in a microcosm incubation study with six soils.

Soil	DOC range	CO_2 range		Relation of CO_2 (DOC adjusted) and E_H (V) at pH 7		
		Original	DOC adjusted†	Equation	r^2	P (n)
	mg L^{-1}	mg kg^{-1} h^{-1}				
Arkansas-1	16.7–94.5	1.3–5.3	1.3–25.7	$Log_{10}\ CO_2 = 2.4\ E_H + 0.42$	0.92	0.01 (5)
Arkansas-2	13.0–85.3	0.9–6.2	0.9–40.9	$Log_{10}\ CO_2 = 2.2\ E_H + 0.31$	0.88	<0.01 (6)
California-1	10.5–161.3	0.5–8.7	0.7–30.5	$Log_{10}\ CO_2 = 2.1\ E_H + 0.66$	0.56	0.15 (5)
California-2	11.1–15.4	1.9–9.3	7.7–42.3	$Log_{10}\ CO_2 = 2.7\ E_H + 0.07$	0.98	0.08 (3)
Louisiana	23.2–105.5	0.1–2.7	0.5–12.1	$Log_{10}\ CO_2 = 2.1\ E_H + 0.15$	0.86	<0.01 (7)
Texas-1	9.9–53.8	0.8–23.7	0.8–44.1	$Log_{10}\ CO_2 = 2.8\ E_H + 0.05$	0.79	0.11 (4)
Texas-2	8.3–53.4	0.9–4.4	0.9–28.7	$Log_{10}\ CO_2 = 3.2\ E_H + 0.08$	0.94	0.15 (3)
China	70.6–230.0	0.5–5.0	1.1–16.3	$Log_{10}\ CO_2 = 1.6\ E_H + 0.37$	0.47	0.20 (5)
Indonesia-1	13.7–61.4	0.8–6.8	0.8–9.8	$Log_{10}\ CO_2 = 0.6\ E_H + 0.53$	0.12	0.51 (6)
Indonesia-2	7.7–62.0	0.7–6.7	0.7–53.8	$Log_{10}\ CO_2 = 2.0\ E_H + 0.62$	0.59	0.03 (8)

† DOC-adjusted CO_2 production rate = measured CO_2 production rate × DOC content.

showed that the CH_4 compensation point decreased exponentially with increasing soil E_H (Table 4). For all studied soils, Fig. 4-iii clearly shows the reverse relationship between the CH_4 compensation concentration and soil E_H. The critical E_H where the CH_4 compensation point equals the ambient atmospheric CH_4 concentration, above which soils start to consume atmospheric CH_4, is important. Such critical E_H values varied among the different soils studied. Regression analysis indicated that the critical E_H value was 414 mV for all soils combined, above which the soils functioned as a sink of atmospheric CH_4 (Table 4).

The CH_4 compensation point largely depends on the CH_4 oxidation capacity. In rice fields, variations in CH_4 emission have been primarily attributed to variations in methanotrophic activities (Sass et al., 1990; Schütz et al., 1989). Similar results have been reported in a Florida swamp where the CH_4 emission increase associated with a decrease in environmental oxidation was not due to stimulation of methanogenesis but due to a decrease in the methanotrophic activity (King et al., 1990). Therefore, CH_4 oxidation strength determines not only the potential of soils to act as a sink of atmospheric CH_4, but also the CH_4 emission strength of soils.

Nitrous Oxide Production and Associated Ammonium and Nitrate Content

With no addition of NO_3^- at the beginning of the incubations (Phase I), NO_3^- was essentially depleted when soils reached strongly reducing conditions (data not shown). During the reducing to oxidizing phase of the incubation, the soils occasionally reached higher E_H conditions when excess O_2 was introduced, and N_2O formation was detected when the soil E_H reached 500 mV or higher (Fig. 5). Without external NO_3^- addition, soil nutrient analysis showed an elevated level of NO_3^- in soil suspensions under such higher E_H conditions. Nitrification was the probable cause of NO_3^- formation. Nitrous oxide production was attributed to nitrification itself or to the subsequent denitrification, the so-called *coupled nitrification–denitrification process*. No information on the critical E_H for nitrification has been previously reported. Based on the results from this study, an E_H value of approximate 500 mV is the likely critical E_H threshold for nitrification activity to occur. Ammonium concentration in soil suspensions tended to decrease with increasing E_H. Both immobilization by soil microorganisms and nitrification activity could contribute to the disappearance of soil NH_4^+. Considering that NH_4^+ was generated from soil organic matter mineralization, nitrification could play an important role in the consumption or depletion of the soil NH_4^+.

Nitrate was only applied when soil E_H was >0 mV. Significant N_2O production was observed in the E_H range of 200 to 500 mV. Complete denitrification with N_2 as the end product occurred when soil E_H was <200 mV. The results agreed well with previous studies where soil incubations were conducted from oxidizing to reducing conditions (Yu and Patrick, 2003, 2004). When soil E_H was <300 mV, strong denitrification activity rapidly consumed the NO_3^-, resulting in only trace amount of NO_3^- in the soil microcosms. Elevated levels of NO_3^- in the soil suspensions were found when the soil E_H was in a higher range (>300 mV), especially when >500 mV. This could be attributed to a redox condition too high for denitrification but favorable for nitrification. Ammonium content remained low under such oxidizing conditions of the incubation. Initiation of nitrification at E_H >500 mV was evidenced by NO_3^- concentration elevation during the Phase I incubation without adding NO_3^- (Fig. 5). The prolonged soil incubation under high- E_H conditions in this study provides corroborating data for previous incubation studies where soil E_H remained above 500 mV for just a few hours (Yu and Patrick, 2003, 2004).

Following a soil E_H increase during the incubation, there was a parallel and substantial pH decrease in soil suspensions (Table 2). Microorganisms involve in soil N transformations generally function optimally under near-neutral pH conditions (Paul and Clark, 1996); however, nitrification can proceed rapidly at low pH. Significant net nitrification rates at pH 5 have been observed in a tropical forest soil (Neill et al., 1995). Nitrous oxide production depends mainly on denitrification intensity and the N_2O/N_2 ratio (higher under acidic conditions) in denitrification products. Small pH shifts may have little effect on total $N_2 + N_2O$ produced, but the relative effect of pH on N_2O reductase may regulate the N_2O/N_2 ratio (Burford and Bremner, 1975; Firestone et al., 1980; Klemedtsson et al., 1997).

Relation between Metals and Sulfur Transformation and Soil Redox Potential Conditions

When soils reached strongly reducing conditions (E_H < −200 mV), all soil redox-active species were transformed into their reducing forms, Fe(III) to Fe(II), Mn(IV) to Mn(II), and SO_4^{2-} to S^{2-}, resulting in observed higher soluble Fe and Mn concentrations in soil solutions (Fig. 6-i and 6-ii). Elevating soil redox status from reducing to oxidizing conditions in this study generated a reverse order of Fe and Mn immobilization (Fe earlier than Mn), compared with the reported order of Fe and Mn mobilization (Mn earlier than Fe) when soil was incubated from oxidizing to reducing conditions (Patrick and Jugsujinda, 1992). In this study, the critical E_H value for substantial immobilization of Fe and Mn was estimated to be about 50 and 250 mV, respectively. Previous studies showed that 100 mV at pH 7 was the critical value for Fe reduction and consequent dissolution (Gotoh and Patrick, 1974). Another study showed that, at pH between 6 and 8, most of the Mn conversion was found to take place at E_H of 200 to 300 mV (Gotoh and Patrick, 1972). Variations of critical E_H values for Fe and Mn transformations exist among different soils and different studies, due to the composite nature of redox reactions in the system. With drying in fields (soil pH will decrease), Fe and Mn carbonates will dissolve and oxidize to form oxides, amorphous oxides, and hydroxides that slowly recrystallize to stable Fe(III) oxides. Not much is known about this transformation, but pure $Fe(OH)_3$ and MnO_2 are not likely to form. At E_H values between that typically found in flooded soils and that of well-aerated soils, the stable form of Fe is $Fe_3(OH)_8$ (Schwab and Lindsay, 1983). At higher E_H, $Fe_3(OH)_8$ is not stable, although some $Fe_3(OH)_8$ may persist during short, dry fallows in rice fields. Under aerobic conditions, ferrihydrite may also be formed (Neue, 1991).

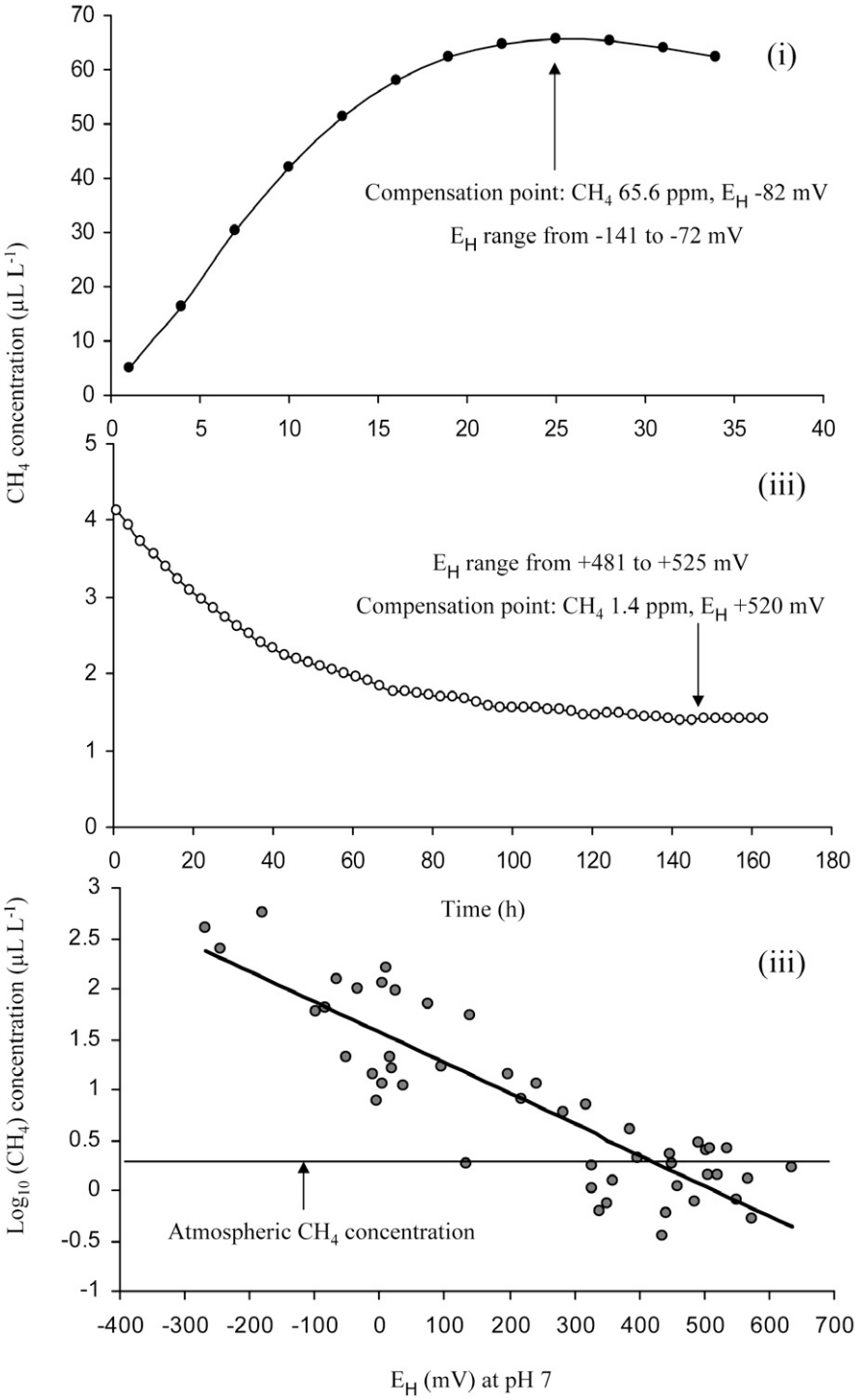

Fig. 4. Determination of CH_4 compensation point under different redox potential (E_H) conditions, and exponential regression analysis of CH_4 compensation point and soil E_H in a microcosm incubation study with six soils: (i) CH_4 concentration increases to a steady point; (ii) CH_4 concentration decreases to a steady point; and (iii) relationship between CH_4 compensation points and soil E_H conditions from analysis of all six soils. Examples in determining CH_4 compensation point are given from analysis of the Indonesian soil.

The most common form of soluble S in soils is SO_4^{2-}. Since most S in soils occurs in the organic state, reactions are closely associated with organic matter transformations and the activity of microorganisms. Upon flooding, sulfates are reduced to sulfides, and proteins are dissimilated after hydrolysis to H_2S, mercaptans, S_2^{2-}, NH_3, and fatty acids (Neue and Mamaril, 1985). No clear relation between soluble S (mostly in the form of SO_4^{2-}) content and soil E_H (r^2 = 0.004, P = 0.59, n = 84) could be found in this study (Fig. 6-iii). Precipitation of certain metal ions as sulfides in flooded soils or sediments is an important mechanism regulating the solution concentrations of toxic S^{2-} and metal ions (Fe^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, and Hg^{2+}). For the metal ions involved, the toxicity to plants is inversely related to the solubility of their sulfide salts, with Hg^{2+} being the most toxic and Fe^{2+} the least toxic (Engler

Table 4. Exponential regression analysis of CH_4 compensation point and soil redox potential (E_H) in a microcosm incubation study with six soils.

Soil	Relation between CH_4 (μL L^{-1}) compensation point and E_H (V)			Critical E_H †
	Equation	r^2	*P* (*n*)	
				mV
Arkansas	$Log_{10}\ CH_4 = -1.55\ E_H + 1.18$	0.90	<0.01 (7)	606
California	$Log_{10}\ CH_4 = -4.06\ E_H + 1.73$	0.90	<0.01 (14)	367
China	$Log_{10}\ CH_4 = -1.82\ E_H + 1.06$	0.83	0.27 (3)	451
Indonesia	$Log_{10}\ CH_4 = -2.68\ E_H + 1.49$	0.80	<0.01 (14)	466
Louisiana	$Log_{10}\ CH_4 = -2.83\ E_H + 1.74$	0.78	0.05 (5)	530
Texas	$Log_{10}\ CH_4 = -4.03\ E_H + 1.96$	0.94	<0.01 (5)	427
All soils	$Log_{10}\ CH_4 = -3.02\ E_H + 1.56$	0.77	<0.01 (48)	437

† E_H above which soils would consume atmospheric CH_4 was calculated from the regression equation taking CH_4 concentration as 1.75 μL L^{-1}. Lack of statistical significance was found only in the Chinese soil due to the limited number of measurements (*n*).

and Patrick, 1975; Patrick and Reddy, 1978). When a flooded soil or sediment is drained and subsequently aerated, sulfides are transformed to more soluble SO_4^{2-}, while the metal ions become insoluble oxidized forms. For acid soils, a further increase in soil acidity may dissolve these metal oxides by chemical reactions.

Ponnamperuma (1972) reported that the specific conductance of the soil solution first increases after flooding by 1 to 2 dS m^{-1} as a result of production of NH_4^+, HCO_3^-, $RCOO^-$, Mn^{2+}, and Fe^{2+}, followed by displacement of Na^+, K^+, Ca^{2+}, and Mg^{2+} from soil colloids. The subsequent decrease in conductance is the result of HCO_3^- removal, degradation and transformation of organic constituents, changes in the pH-dependent charges, and precipitation. In this study, the non-redox-active metal species, such as Na and K, showed no relation with soil E_H. Concentrations of Na^+ and K^+ in soil microcosms tended to strongly correlate with the duration of incubation. For all soils, Na^+ and K^+ concentration significantly increased during the incubation, probably due to both dissolution and ion exchange mechanisms (Table 5). During the study period, Na^+ and K^+ concentrations apparently did not reach saturation status. Breaking down the soil mineral structure under fluctuating redox conditions due to ferrolysis (Brinkman, 1979) may enhance the dissolution processes. Exchange reactions may also be important in regulating the behavior of water-soluble Fe and Mn (Gotoh and Patrick, 1972).

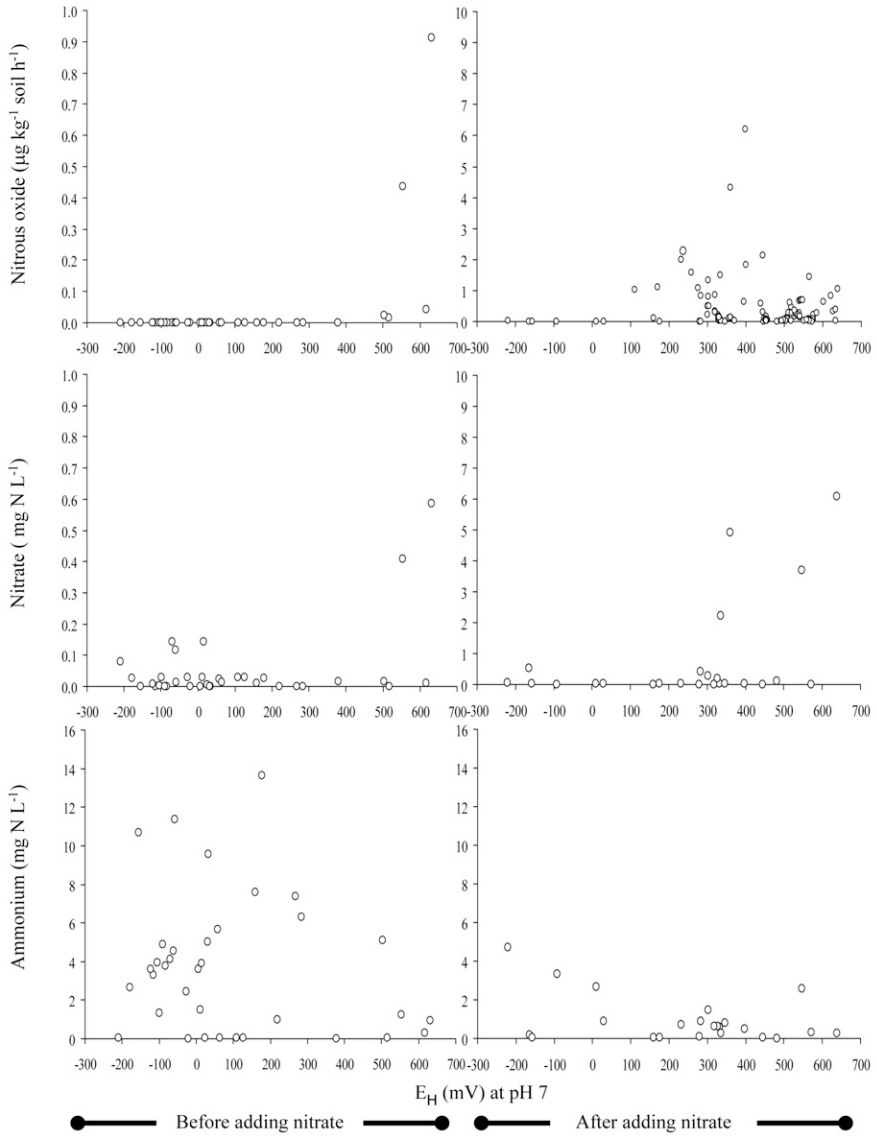

Fig. 5. Soil N_2O production rates and NH_4^+ and NO_3^- concentrations in soil suspensions under different redox potential (E_H) conditions in a microcosm incubation study with six soils. Additional NO_3^- was amended when E_H > 0 mV. Soil E_H occasionally fluctuated beyond the desired level, especially during the period before NO_3^- was added, where measurements were also conducted.

CONCLUSIONS

The microcosm incubation and measurement of changes in soil biogeochemical processes under reducing to oxidizing conditions has several advantages: (i) it allows all possible microbial communities and enzymes to be fully developed during the preincubation from oxidizing to reducing conditions, (ii) all soil redox-active oxidants are converted into their reduced forms, creating an environment representing prolonged flooded soils and sediments, (iii) the information obtained on trace gas dynamics and nutrient transformation by elevating soil redox status is more similar to conditions occurring in draining flooded fields, and (iv) it provides an extended period of aerobic conditions by elevating soil E_H with O_2.

The E_H range of −150 to 180 mV (corresponding value at pH 7) represents optimum soil conditions for minimizing the cumulative global warming poten-

tial from CO_2, CH_4, and N_2O (Fig. 2, 3, and 5), which is in good agreement with previous studies (Yu and Patrick, 2003, 2004). The results have a significant implication in evaluating the overall benefits of soil C sequestration efforts, because part of the C captured in soils may be substantially offset by enhanced soil CH_4 production at lower E_H conditions (Roulet, 2000), and enhanced N_2O emission under higher E_H conditions (Li et al., 2005). Optimum E_H conditions for minimizing soil global warming potential are mainly due to three factors: (i) the reduction potential in this E_H range is favorable for complete denitrification, with N_2 as the end product, but is still not strong enough to initiate significant CH_4 production, (ii) a slightly acidic pH condition limits methanogenesis, and the N_2O/N_2 ratio of denitrification is relatively smaller than more acidic conditions (E_H > 180 mV), and (iii) soil oxidants (mainly Fe and Mn) significantly lower the CH_4 compensation point by competing with H_2 produced from OM decomposition, and possibly by anaerobically oxidizing CH_4.

The comprehensive analysis of soil nutrient and metal transformations and trace gas dynamics in this study integrates the main environmental factors regulating major biogeochemical processes in soils. Fluctuation in soil E_H status represents changes occurring in aerobic and anaerobic environments on scales as small as soil aggregates (Tiedje et al., 1984) to as large as riparian zones and wetland ecosystems (Yu et al., 2006). The achieved quantification of the CH_4 compensation point under different E_H conditions provides a better understanding of the role of soils as a source or sink of atmospheric CH_4. Biological CH_4 oxidation is an important mechanism in controlling the CH_4 emissions from anoxic soils and sediments, because up to 90% of the produced CH_4 is consumed before being released to the atmosphere (Frenzel et al., 1992). A prolonged period of incubation under high soil E_H conditions provides some evidence of soil nitrification activity, which is normally studied in a soil slurry system. Our analysis indicates that 500 mV is probably a critical E_H value for soil nitrification to take place, where NO_3^- (also possibly part of N_2O) is formed from the oxidizing NH_4^+.

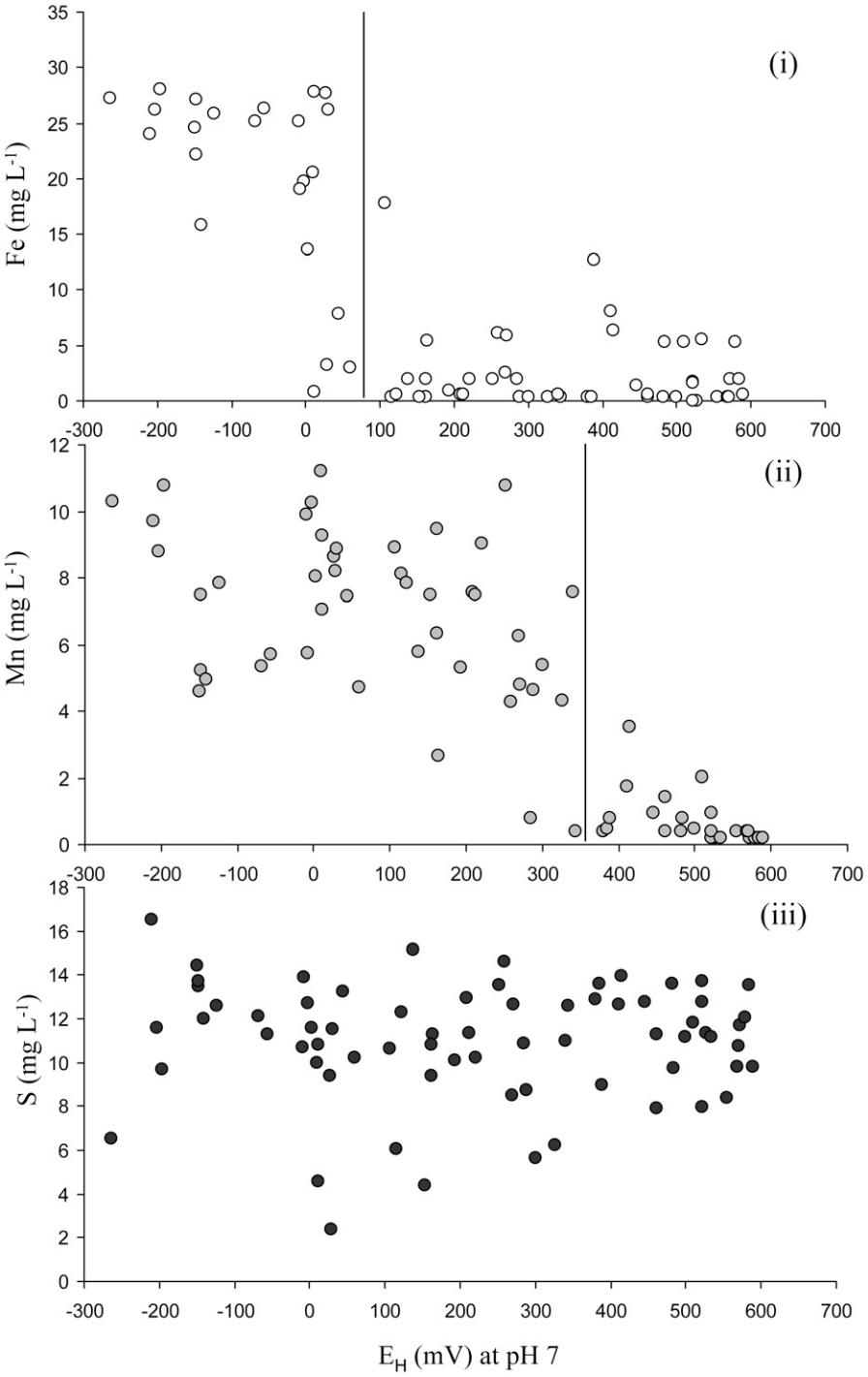

Fig. 6. Soluble (i) Fe, (ii) Mn, and (iii) S concentrations in soil suspensions under different redox potential (E_H) conditions in a microcosm incubation study with six soils. Data represent the cumulative results from all six soils. The vertical lines represent the approximate E_H conditions at which (i) Fe and (ii) Mn become immobilized when E_H further increases. To use the same scale for the *y* axis, values of each analyte are standardized by multiplying by a standardized factor. For Fe concentration (soil × standardized factor): Arkansas × 10, California × 1.67, Louisiana × 10, Texas × 1, China × 1.5, Indonesia × 3. For Mn concentration (soil × standardized factor): Arkansas × 1, California × 2, Louisiana × 4, Texas × 4.8, China × 2.4, Indonesia × 1. For S concentration (soil × standardized factor): Arkansas × 3.56, California × 1.33, Louisiana × 3.56, Texas × 1.78, China × 1, Indonesia × 1.

ACKNOWLEDGMENTS

This paper is dedicated to Dr. William H. Patrick, Jr., (1925–2004) who participated in collecting soil samples and planning for this collaborative study.

Table 5. Variations of Na and K concentrations in soil suspensions, and their liner regression analysis with incubation time in a microcosm incubation study with six soils.

Soil	Day	Na				K			
		Range	Equation	r^2	*P* (*n*)	Range	Equation	r^2	*P* (*n*)
		mg L^{-1}				mg L^{-1}			
Arkansas-1	68	14.8–27.4	Na = 0.16Day + 13.0	0.71	<0.01 (8)	51.2–186.5	K = 1.84Day + 52.9	0.99	<0.01 (8)
Arkansas-2	68	14.5–29.6	Na = 0.17Day + 13.0	0.67	0.24 (7)	65.9–266.5	K = 2.86Day + 69.6	1.00	<0.01 (7)
California-1	71	49.7–72.7	Na = 0.32Day + 46.1	0.83	<0.01 (8)	41.04–150.0	K = 1.39Day + 42.7	0.89	<0.01 (8)
California-2	71	50.7–71.3	Na = 0.31Day + 47.8	0.92	<0.01 (10)	40.4–152.1	K = 1.49Day + 42.1	0.96	<0.01 (10)
Louisiana	68	19.7–33.6	Na = 0.17Day + 19.0	0.77	<0.01 (7)	73.0–239.2	K = 2.41Day + 89.3	0.96	<0.01 (7)
Texas-1	54	14.7–26.8	Na = 0.24Day + 14.7	0.96	<0.01 (6)	27.5–96.8	K = 1.09Day + 30.3	0.93	<0.01 (6)
Texas-2	44	15.9–26.0	Na = 0.22Day + 15.6	0.99	<0.01 (4)	35.2–91.6	K = 1.06Day + 40.4	0.93	0.03 (4)
China	68	11.6–28.2	Na = 0.20Day + 10.0	0.61	0.04 (7)	57.2–176.3	K = 1.50Day + 59.0	0.95	<0.01 (7)
Indonesia-1	63	17.8–30.6	Na = 0.19Day + 16.7	0.75	<0.01 (8)	33.9–155.7	K = 1.84Day + 37.9	0.99	<0.01 (8)
Indonesia-2	68	18.0–33.0	Na = 0.19Day + 16.4	0.69	0.01 (8)	37.8–188.6	K = 2.06Day + 41.0	0.98	<0.01 (8)

REFERENCES

Batjes, N.H. 1998. Mitigation of atmospheric CO_2 concentrations by increased carbon sequestration in the soil. Biol. Fertil. Soils 27:230–235.

Bohn, H.L. 1971. Redox potentials. Soil Sci. 112:39–45.

Bossio, D.A., and K.M. Scow. 1995. Impact of carbon and flooding on the metabolic diversity of microbial communities in soils. Appl. Environ. Microbiol. 61:4043–4050.

Brinkman, R. 1979. Ferrolysis, a soil-forming process in hydromorphic conditions. WAU Diss. no. 756. Wageningen Univ., Wageningen, the Netherlands.

Burford, J.R., and J.M. Bremner. 1975. Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. Soil Biol. Biochem. 7:389–394.

Conrad, R. 1994. Compensation concentration as critical variable for regulating the flux of trace gases between soil and atmosphere. Biogeochemistry 27:155–170.

Conrad, R., and M. Klose. 1999a. Anaerobic conversion of carbon dioxide to methane, acetate and propionate on washed rice roots. FEMS Microbiol. Ecol. 30:147–155.

Conrad, R., and M. Klose. 1999b. How specific is the inhibition by methyl fluoride of acetoclastic methanogenesis in anoxic ricefield soil? FEMS Microbiol. Ecol. 30:47–56.

Dendooven, L., and J.M. Anderson. 1995. Maintenance of denitrification potential in pasture soil following anaerobic events. Soil Biol. Biochem. 27:1251–1260.

Engler, R.M., and W.H. Patrick. 1975. Stability of sulfides of manganese, iron, zinc, copper, and mercury in flooded and nonflooded soils. Soil Sci. 119:217–221.

Fetzer, S., and R. Conrad. 1993. Effect of redox potential on methanogenesis by *Methanosarcina bakeri*. Arch. Microbiol. 160:108–113.

Firestone, M.K., R.B. Firestone, and J.M. Tiedje. 1980. Nitrous oxide from soil denitrification—factors controlling its biological production. Science 208:749–751.

Frenzel, P., F. Rothfuss, and R. Conrad. 1992. Oxygen profiles and methane turnover in a flooded microcosm. Biol. Fertil. Soils 14:84–89.

Gotoh, S., and W.H. Patrick. 1972. Transformation of manganese in a waterlogged soil as affected by redox potential and pH. Soil Sci. Soc. Am. Proc. 36:737–742.

Gotoh, S., and W.H. Patrick. 1974. Transformation of iron in a waterlogged soil as influenced by redox potential and pH. Soil Sci. Soc. Am. Proc. 38:66–71.

Iversen, N., and B.B. Joergensen. 1985. Anaerobic methane oxidation rates at the sulfate–methane transition in marine sediments from Kattegat and Skagerrak (Denmark). Limnol. Oceanogr. 30:944–955.

Iversen, N., R.S. Oremland, and M.S. Klug. 1987. Pelagic methanogenesis and anaerobic methane oxidation. Limnol. Oceanogr. 32:804–814.

Kessavalou, A., A.R. Mosier, J.W. Doran, R.A. Drijber, D.J. Lyon, and O. Heinemeyer. 1998. Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat–fallow tillage management. J. Environ. Qual. 27:1094–1104.

Kimura, M., Y. Miura, A. Watanabe, J. Murase, and S. Kuwatsuka. 1992. Effects of rice straw application and percolation rate on the leaching of methane and other soil components into the subsoil. Soil Sci. Plant Nutr. 38:665–672.

King, G.M., P. Roselev, and H. Skovgaard. 1990. Distribution and rate of methane oxidation in sediments of the Florida Everglades. Appl. Environ. Microbiol. 56:2902–2911.

Klemedtsson, L., A.K. Klemedtsson, F. Moldan, and P. Weslien. 1997. Nitrous oxide emissions from Swedish forest soils in relation to liming and simulated increased N-deposition. Biol. Fertil. Soils 25:290–295.

Kravchenko, I.K., and K.W. Yu. 2006. Relationship between major soil properties and culturable microorganisms affecting CH_4 and N_2O dynamics in rice soils. Arch. Agron Soil Sci. 52:607–615.

Kumaraswamy, S., B. Ramakrishnan, and N. Sethunathan. 2001. Methane production and oxidation in an anoxic rice soil as influenced by inorganic redox species. J. Environ. Qual. 30:2195–2201.

Li, C.S., S. Frolking, and K. Butterbach-Bahl. 2005. Carbon sequestration in arable soils is likely to increase nitrous oxide emissions, offsetting reductions in climate radiative forcing. Clim. Change 72:321–338.

Lide, D.R. (ed.) 1991. Handbook of chemistry and physics. 72nd ed. CRC Press, Boca Raton, FL.

Lu, Y.H., R. Wassmann, H.U. Neue, and C.Y. Huang. 2000. Dynamics of dissolved organic carbon and methane emissions in a flooded rice soil. Soil Sci. Soc. Am. J. 64:2011–2017.

Miura, Y., A. Watanabe, J. Murase, and M. Kimura. 1992. Oxidation of methane and its coupled ferric oxide reduction in the subsoil. Soil Sci. Plant Nutr. 38:673–679.

Neill, C., M.C. Piccolo, P.A. Steudler, J.M. Melillo, B.J. Feigl, and C.C. Cerri. 1995. Nitrogen dynamics in soils of forests and active pastures in the western Brazilian Amazon Basin. Soil Biol. Biochem. 27:1167–1175.

Neue, H.U. 1991. Holistic view of chemistry of flooded soil. p. 5–32. *In* Soil management for sustainable rice production in the tropics. IBSRAM Monogr. 2. Int. Board for Soil Res. and Manage., Bangkok.

Neue, H.U., and C.P. Mamaril. 1985. Zinc, sulphur and other micronutrients in wetland soils. p. 307–320. *In* Wetland soils: Characterization, classification and utilization. Int. Rice Res. Inst., Manila, Philippines.

Neue H.U., L.H. Ziska, R.B. Matthews, and Q. Dai. 1995. Reducing global warming—The role of rice. Geojournal 35:351–362.

Patrick, W.H., and R.D. DeLaune. 1972. Characterization of the oxidized and reduced zones in flooded soil. Soil Sci. Soc. Am. Proc. 36:573–576.

Patrick, W.H., and A. Jugsujinda. 1992. Sequential reduction and oxidation of inorganic nitrogen, manganese, and iron in flooded soil. Soil Sci. Soc. Am. J. 56:1071–1073.

Patrick, W.H., and C.N. Reddy. 1978. Chemical changes in rice soils. p. 361–380. *In* Soils and rice. Int. Rice Res. Inst., Manila, Philippines.

Paul, E.A., and F.E. Clark. 1996. Soil microbiology and biochemistry. 2nd ed. Academic Press, San Diego.

Peters, V., and R. Conrad. 1996. Sequential reduction processes and initiation of CH_4 production upon flooding of oxic upland soils. Soil Biol. Biochem. 28:371–382.

Ponnamperuma, F.N. 1972. The chemistry of submerged soils. Adv. Agron. 24:29–96.

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

Reddy, K.R., W.H. Patrick, and C.W. Lindau. 1989. Nitrification–denitrification at the plant root–sediment interface in wetlands. Limnol. Oceanogr. 34:1004–1013.

Rinklebe, J., and U. Langer. 2006. Microbial diversity in three floodplain soils at the Elbe River (Germany). Soil Biol. Biochem. 38:2144–2151.

Roulet, N.T. 2000. Peatlands, carbon storage, greenhouse gases, and the Kyoto Protocol: Prospects and significance for Canada. Wetlands 20:605–615.

Roy, R., H.D. Kluber, and R. Conrad. 1997. Early initiation of methane production in anoxic rice soil despite the presence of oxidants. FEMS Microbiol. Ecol. 24:311–320.

Rudaz, A.O., E.A. Davidson, and M.K. Firestone. 1991. Sources of nitrous oxide production following wetting of dry soil. FEMS Microbiol. Ecol. 85:117–124.

Sass, R.L., F.M. Fisher, A. Ding, and Y. Huang. 1990. Methane production and emission in a Texas ricefield. Global Biogeochem. Cycles 4:47–68.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler. 1989. A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy field. J. Geophys. Res. 94:16405–16416.

Schwab, A.P., and W.L. Lindsay. 1983. The effect of redox on the solubility and availability of iron. Soil Sci. Soc. Am. J. 47:201–205.

Smith, C.J., and R.D. DeLaune. 1984. Effect of rice plants on nitrification–denitrification loss of nitrogen under greenhouse conditions. Plant Soil 79:287–290.

Smith, C.J., R.D. DeLaune, and W.H. Patrick. 1983. Carbon dioxide emission and carbon accumulation in coastal wetlands. Estuarine Coastal Shelf Sci. 17:21–29.

Tiedje, J.M., A.J. Sexstone, T.B. Parkin, N.P. Revsbech, and D.R. Shelton. 1984. Anaerobic processes in soil. Plant Soil 76:197–212.

Yao, H., and R. Conrad. 1999. Thermodynamics of methane production in different rice paddy soils from China, the Philippines and Italy. Soil Biol. Biochem. 31:463–473.

Yu, K.W., S.P. Faulkner, and W.H. Patrick. 2006. Redox potential characterization and soil greenhouse gas concentration across a hydrological gradient in a Gulf Coast forest. Chemosphere 62:905–914.

Yu, K.W., and W.H. Patrick. 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.

Yu, K.W., and W.H. Patrick. 2004. Redox window with minimum global warming potential contribution from rice soils. Soil Sci. Soc. Am. J. 68:2086–2091.

Yu, K.W., Z.P. Wang, A. Vermoesen, W.H. Patrick, and O. Van Cleemput. 2001. Nitrous oxide and methane emissions from different soil suspensions: Effect of soil redox status. Biol. Fertil. Soils 34:25–30.