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Localization of iron-reducing activity in paddy soil by profile studies

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Abstract. Profiles of iron speciations (porewater Fe(II) and Fe(III), solid-phase Fe(II) and Fe(III)) have been studied to localize both iron reduction and oxidation in flooded paddy soil. Sulfate and nitrate were determined to analyze interactions of redox reactions involved in the iron cycle with those of the sulfur and nitrogen cycle. The development of the iron(II) and iron(III) profiles was observed in microscale over a time period of 11 weeks. After 11 weeks the profiles were stable and showed lowest concentrations of solid-phase iron(II) on the soil surface with increasing concentrations to a soil depth of 10 mm ($\approx$ 100 μmol/cm^3). Profiles of iron(III) showed a maximum of iron(III) at a depth of 2 to 4 mm ($\approx$ 100–200 μmol/cm^3). Porewater iron(II) concentrations were three orders of magnitude lower than extracted iron(II) and indicated that most iron(II) was adsorbed to the solid-phase or immobilized as siderite and vivianite. Diffusive loss of iron from the soil was indicated by iron recovery (0.3 μmol gdw^{-1}) in the flooding water after 12 weeks. The organic content of the soil influenced the concentrations of solid-phase iron(II) in deeper soil layers ($>$ 6 mm); higher Fe(II) concentrations in soil with limiting amounts of electron donors may indicate lower consumption of CO_2 by methanogenic bacteria and therefore a higher siderite precipitation. Soil planted with rice showed similar iron(II) profiles of fresh paddy soil cores. However, maximal iron(III) concentrations ($\approx$ 350 μmol/cm^3) were present in planted soil at a depth of 1 to 2.5 mm where oxygen is provided by a mat of fine roots. Sulfate and nitrate concentrations in the porewater were highest on the soil surface (10 μM NO_3^-, 40 μM SO_4^{2-}) and decreased with depth. Similar profiles were detected for malate, acetate, lactate, and propionate, the concentrations decreased gradually from the surface to a depth of 4 mm. Profiles of oxygen showed highest concentrations at the surface due to photosynthetic production and a depletion of oxygen below 3 mm depth. Methane production rates measured from soil layers incubated separately in closed vessels were zero at the soil surface and increased with depth. In soil depths below 4 mm where iron(III) concentrations decreased higher methane production rates were found.

Introduction

Rice soil is subjected to periodic changes of oxic and anoxic conditions. After flooding of the fields a major part of the soil becomes anoxic and the electron acceptors are reduced sequential in the following order: NO_3^-, Mn(IV), Fe(III), SO_4^{2-}, and CO_2 (Ponnamperuma 1972; Patrick & Reddy 1978). Before the rice is harvested the fields are drained and reduced compounds like NH_4^+, Fe(II), and HS^- are oxidized with oxygen. Beside this seasonal reoxidation event a steady reoxidation of reduced compounds occurs during the flooded stage. On the soil surface dissolved oxygen from the flooding water is consumed by chemical and microbial oxidation of reduced inorganic compounds (Frenzel et al. 1992) and aerobic degradation of organic matter. Oxygen is also available for oxidation processes (Ando et al. 1983; Trolldenier 1988; Begg et al. 1994; Kirk & Bajita 1995; Green & Etherington 1977) in the close proximity of rice roots due to the diffusive transport via the aerenchym (Nouchi et al. 1990; Lee et al. 1981). The penetration depth of oxygen in the soil surface and in the rhizophere depends on the diffusive O_2-influx and the O_2-consumption of both, the soil organisms and chemical oxidation. Depletion of O_2 generates a redox stratification (Zehnder & Stumm 1988) with theoretically defined niches for different physiological groups of bacteria. Theoretically the different niches are ordered in the same sequence as the reduction processes after flooding (Zehnder & Stumm 1988; Nealson & Saffarini 1994). The cycles of nitrogen (e.g. Arth et al. 1998; Reddy et al. 1989), sulfur (e.g. Wind & Conrad 1995, 1997; Freney et al. 1982), and methane (e.g. Conrad 1993; Schütz et al. 1989; Frenzel et al. 1992; Gilbert & Frenzel 1995, 1998) have been studied in rice fields. Similar oxidation/reduction cycles are expected for iron in paddy fields.

The role of ferric iron as an important electron acceptor in anoxic environments became more and more recognized, since the first dissimilatoric iron-reducing bacteria were isolated (Balashova & Zavarzin 1980; Lovley & Phillips 1988; Myers & Nealson 1988a). Studies in freshwater (Roden & Wetzel 1996) and in marine sediments (Canfield et al. 1993; Thamdrup & Canfield 1996) showed that iron reduction accounted for up to 50% of the total carbon metabolism. Experiments with paddy soil in closed vessels showed similar results although these experiments did not allow reoxidation as occurring in natural rice paddies (Yao et al. 1999; Jäckel & Schnell 1999). Canfield et al. (1993) demonstrated in marine sediments with bioturbation that one iron atom is reduced and oxidized 100 to 300 times before it is finally buried in the sediment. Iron(II) is oxidized chemically by oxygen at neutral conditions (Stumm & Morgan 1996) as well as microbially by neutrophilic (Emerson & Moyer 1997; Emerson & Revsbech 1994a, b; Hanert 1991) and

acidophilic bacteria (Blake et al. 1993). In the absence of oxygen iron(II) can also be oxidized chemically by manganese(IV) oxide (Postma 1985; Myers & Nealson 1988b), nitrous oxide (Hansen et al. 1994), or nitrite (Moraghan & Buresh 1977). Moreover an anaerobic microbial iron(II) oxidation was demonstrated with phototrophic bacteria (Widdel et al. 1993; Ehrenreich & Widdel 1994) and nitrate-reducing bacteria (Straub et al. 1996; Benz et al. 1998; Hafenbradl et al. 1998).

Vertical stratification of iron has been studied in marine sediments in detail. Profiles obtained in cores from pelagic sediments of the eastern equatorial Atlantic (Froelich et al. 1979) reveal that oxidants are reduced sequentially (O_2 > manganese oxide $\geq$ nitrate > iron oxides > sulfate). Dissolved iron profiles suggested the reduction of the solid-oxide-phases and an upward fluxes of dissolved metals. Sørensen and Jørgensen (1987) found in coastal sediments in contrast to the pelagical sediment a less distinct vertical separation of Mn^{2+} and Fe^{2+}. In continental margin sediments Thamdrup and Canfield (1996) showed the general importance of Fe reduction in C oxidation. For the submarine basins in the Gulf of Maine Hines et al. (1991) showed that metal oxide reduction could be a significant process.

Saltmarsh studies (Kostaka & Luther 1995) presented evidence that the redox cycle of solid iron is controlled by sulfate reduction and sediment oxidation which respond to both, annual cycles and to short term, episodic effects such as weather and tides. Microbial iron reduction can play a minor role in the carbon turnover in those environments (Jacobson 1994), because the majority of the reduced iron is a result from chemical reduction mediated by hydrogen sulfide.

Howler and Bouldin (1971) measured iron species in flooded soil and found that ferric iron showed maximal concentrations in the oxic layer and ferrous iron concentrations were maximal in the reduced layer. The depth of the oxic layer depended on the oxygen concentration in the flooding water. In freshwater sediments Lovley and Phillips (1986a) showed highest iron reduction rates in the first 4 cm of the sediments. In these zones iron reduction and methane production were of similar importance for anaerobic degradation. Like Froehlich et al. (1979) Patrick and DeLaune (1972) showed vertical sequential distribution of the redox processes for a flooded silt loam soil as well as Wersin et al. (1991) in a perialpine freshwater lake. However, iron reduction played a minor role as indicated by very slow transformation of iron oxides of 30 μmol dm^{-2} yr^{-1} and low precipitation rates of siderite from 3 μg gdw^{-1} yr^{-1} (Wersin et al. 1991). Siderite is reported to be the dominate speciation of Fe(II) in natural waters with carbonate alkalinity greater than 1 mM (King 1998).

In the present study iron-reducing and iron-oxidizing activities were localized in the rice soil by profile measurement of solid-phase Fe(III) and Fe(II). Three depth zones of different redox reaction involving iron, oxygen, nitrate, and organic compounds were identified in the soil.

Material and methods

The paddy soil was obtained in November 1995 from a rice field located in the Po river valley near Arborio, Italy. The soil was air-dried and stored in polyethylene containers. The dry soil lumps were crushed using a mechanical grinder and sieved through a 1 mm mesh size. The organic carbon content was 1.61% (w/w) determined according to a standard protocol (Schlichting & Blume 1966).

Unplanted soil cores were prepared by mixing soil with demineralized water (2:1). The soil water mixture was filled in polyvinyl chloride core tubes with a diameter of 6 or 10 cm, left to settled and incubated waterlogged in a greenhouse for 4, 6, and 11 weeks. Evaporated water was refilled with demineralized water and weed seedlings were removed.

In the fertilized soil cores rice straw was mixed into the dry soil at an amount of 4 mg straw gdw^{-1} soil before the core tubes were prepared. The straw had been cut in pieces smaller than 0.5 cm. Rice soil for soil cores with low C-content was prepared as followed: Fresh soil was preincubated waterlogged in the greenhouse for more than 11 weeks. The oxic layer was then removed to exclude a mat of photosynthetic organism and the anoxic soil part was air-dried to reoxidize the reduced compounds and stored until it was used to prepare soil cores with low C-content. The organic carbon content was 1.55% (w/w).

For the sterile soil cores water and soil was mixed 1:1 and the slurry was then autoclaved in an Erlenmeyer flask for 40 min two subsequent times. The soil was filled in sterile core tubes which were closed with sterile glass petridishes and incubated for 6 weeks in the greenhouse.

Profiles of planted soil were taken from a planted container (35 cm $*$ 27 cm $*$ 18 cm) with rice *Oryza sativa* var. Roma type japonica. Rice seeds were germinated on water-soaked cotton wool and 16 plants were transplanted when the young plants had reached a length of 30–50 mm. After 11 weeks the soil cores were cut out between the plants.

After freezing the soil cores (6 cm diameter) at –80 °C under N_2-atmosphere, profiles were taken by slicing the cores in 100 μm layers using a microtom-kryostat (Microm, Walldorf, Germany). The frozen soil cores were frozen onto a holding device with a special freezing agent (Microm, Walldorf, Germany) and sliced at a constant temperature of –18 °C. The disposable

blade was changed after every 10 to 20 cuts. For iron(III) and iron(II) determination the frozen slices were extracted immediately with 0.5 M HCl to prevent oxidation while thawing. Total iron profiles were measured from 9 weeks old soil cores using 100 μm soil layers that were freeze-dried and then extracted with concentrated HCl. Dissolved iron profiles were taken using every tenth 100 μm layer. The layers were kept frozen until 200 μl anaerobic water was added in an anaerobic chamber (Megaplex, Switzerland). After immediate mixing and centrifugation (640 g, 5 min) in the anaerobic chamber the porewater was diluted 1:1 with 1 M HCl to stabilize iron(II). All acidic extractions were incubated at least 24 h at room temperature. Iron was measured per ion chromatography (Schnell et al. 1998). Every layer of planted soil cores was analyzed as well as every second layer of unplanted soil. Iron concentrations were calculated in μmol/cm^3 soil including the values for density and porosity. Sediment bulk density was determined by measuring the weight of 1 mm core segments of known volumes. Porosity was calculated from the porewater content of 1 mm core segments and the volume of the segment.

For the determination of nitrate, sulfate, and fatty acid concentrations 11 weeks old soil cores (10 cm diameter) were sliced into 1 mm layers in the anaerobic chamber. The samples were centrifuged (640 g, 5 min) and the porewater was filtered through a 0.2 μm regenerated cellulose membrane (Minisart Regenerated Cellulose; Sartorius, Göttingen, Germany) and stored frozen (–20 °C) until analysis. Nitrate and sulfate were analyzed by ion chromatography (Bak et al. 1991) and fatty acids were analyzed per HPLC (Krumböck & Conrad 1991).

Methane production rates were determined of 11 weeks old cores by slicing the soil into 1 mm layers and transferring them into 50 ml serum bottles. The bottles were closed with latex stoppers and screw-caps in the anaerobic chamber. During the next 6 days gas samples (1 ml) were taken and analyzed for CH_4 by gas chromatography (Conrad et al. 1987). Rates were calculated for each layer from the linear slope of 7 to 8 concentrations measurements.

Profiles of oxygen were measured with a commercial clark type microelectrode (Tip $<$ 100 μm) from Mas-Com (Bremen, Germany). The microelectrode was mounted on a micromanipulator under the same type of lamp as the soil cores were incubated in the greenhouse. The soil core was incubated for 7 weeks in the greenhouse and measured waterlogged in a plastic beaker. Three different spots in the middle area of the core were chosen for the measurements. Measurements were taken with a current-to-voltage converter with an integrated voltage source in combination with a digital multimeter

(model 199, Keithly, U.S.A.). Calibration were done in air (250 μM) and N_2-saturated water (0 μM) at a water and room temperature of 23 °C.

Diffusion of iron from the soil into the flooding water was measured using cores with equal amounts of soil, which were waterlogged in 2 l plastic beaker and incubated in the greenhouse. After 12 weeks the flooding water was evaporated by increasing temperature to 105 °C. The residues were extracted for 24 h with 10 ml 0.5 M HCl and the iron content of the extracts was measured with ion chromatography. The soil cores were dried separetely and the dry weights were determined. As a control 5 l demineralized water was evaporated by 105 °C, extracted and analyzed for iron.

All experiments were carried out in triplicate with exception of nitrate, sulfate and sterile profile these were taken in quadruplicate and the methane production rates in duplicate.

Results

Development of iron profiles

In unplanted soil cores iron(II) and iron(III) profiles were stable after 11 weeks. All cores (4, 6 or 11 weeks) had the lowest iron(II) concentrations at the surface (Figure 1(A–C)). The iron(II) concentrations increased upto a depth of 10 mm reaching a maximum of 90 ± 12 μmol/cm^3 in 11 weeks old cores. Iron(III) concentrations showed a maximum peak in a depth of 2 to 4 mm in 6 and 11 weeks old cores (Figure 1(B, C)). In the 4 weeks old cores the maximum concentrations of iron(III) were slightly lower and closer to the soil surface (1–3 mm). In the first millimeter the iron(III) concentration ranged between 7 ± 7 and 36 ± 14 μmol/cm^3 and increased to a maximum of ≈ 150 μmol/cm^3 at a depth of 2 to 4 mm in 11 weeks old cores (Figure 1(C)). From 4 to 8 mm the iron(III) concentrations decreased to values smaller than 15 μmol/cm^3. In cores of autoclaved soil which were incubated sterile for 6 weeks in the greenhouse the iron(II) and iron(III) concentrations were more or less constant over soil depth (Figure 2).

Iron profiles in soil of various carbon content

In 11 weeks old cores with low carbon content the iron profiles (Figure 3(A)) were slightly different than in the 11 weeks old fresh soil cores. The iron(II) concentration increased steeply over the whole 10 mm to values of 168 ± 12 μmol/cm^3. Like in fresh soil cores the iron(III) profile showed similar high concentrations (134 ± 16 μmol/cm^3) at a depth of 2 to 4 mm.

Soil fertilized with straw (Figure 3(B)) showed a similar iron(II) profile as untreated soil. Iron(II) concentrations increased from 5 ± 5 μmol/cm^3 at the

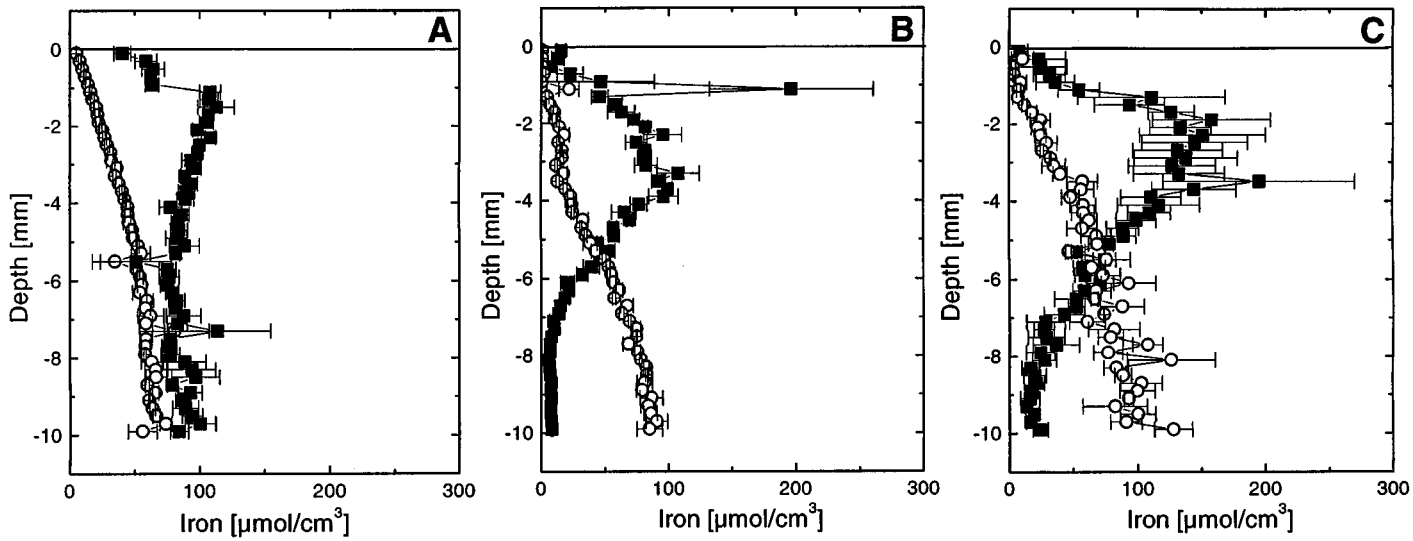

Figure 1. Depth profiles of iron(II) (–○–) and iron (III) (–■–) concentrations of unplanted soil after 0.5 HCl extraction. (A) Cores were incubated 4 weeks in the greenhouse, (B) cores were incubated 6 weeks in the greenhouse, and (C) cores were incubated 11 weeks in the greenhouse. Data are means of triplicates; error bars are ±1 standard error.

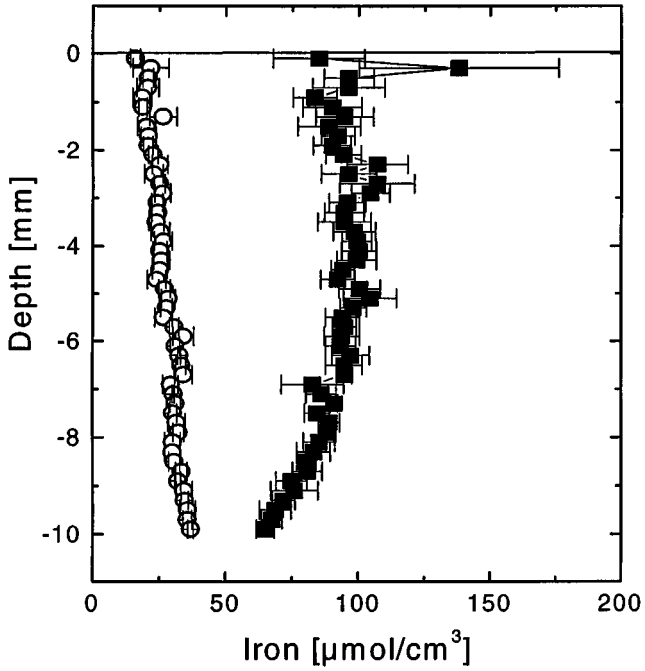

Figure 2. Depth profiles of iron(II) (–○–) and iron(III) (–■–) concentrations of soil cores incubated 6 weeks in the greenhouse under sterile conditions. The soil was autoclaved twice before the incubation was started. Data are means of quadruplicates; error bars are ±1 standard error.

surface to values of 85 μmol/cm^3 at a depth of 10 mm. In comparison to the untreated soil cores the iron(III) concentrations (Figure 3(B)) were relative high at the surface of straw treated soil (55 μmol/cm^3). The highest iron(III) concentrations (around 120 μmol/cm^3) were found at a depth of 2 mm.

Iron profiles in planted paddy soil

In planted paddy soil the iron(III) profile (Figure 3(C)) showed a narrow peak beneath the soil surface in the depth of 0.5 mm to 2.5 mm with iron concentrations up to 386 $\pm$ 128 μmol/cm^3. The concentrations decreased in sections between 2.5 and 6 mm to values below 15 μmol/cm^3. The iron(II) profile (Figure 3(C)) was similar to profiles of unplanted soil cores with slightly higher values for the mean and higher standard-errors. Below 4 mm the iron(II) concentrations ranged around $\approx$ 110 μmol/cm^3.

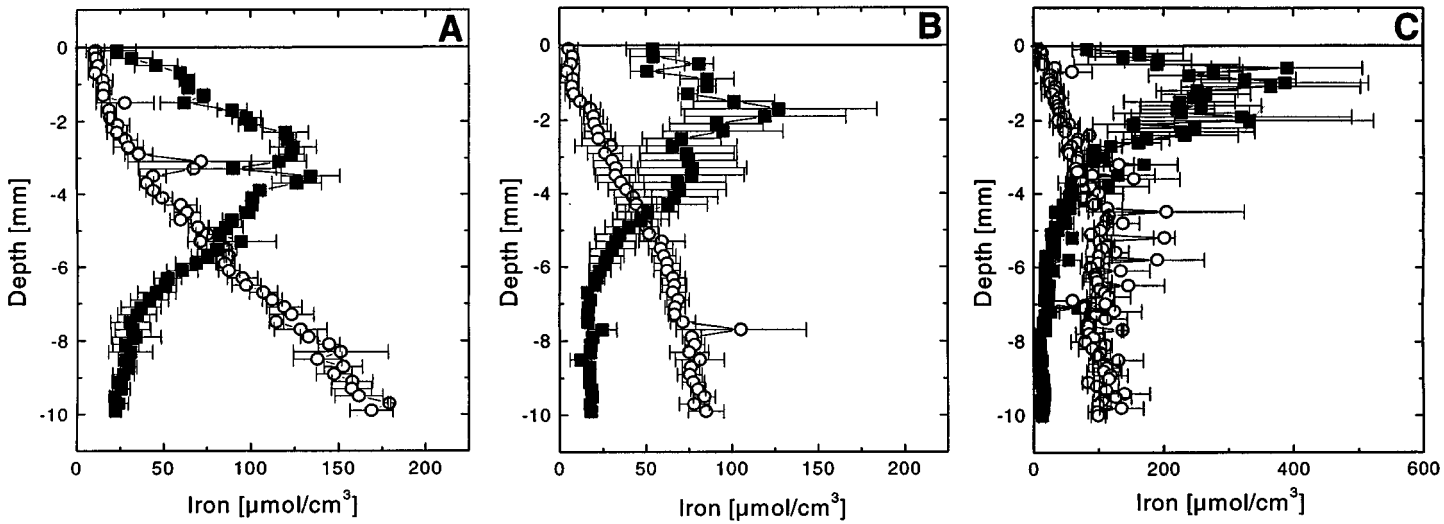

Figure 3. Depth profiles of iron(II) (–○–) and iron(III) (–■–) concentrations of soil cores incubated 11 weeks in the greenhouse. (A) Unplanted soil with a low organic content, (B) unplanted soil fertilized with straw, and (C) soil planted with rice. Data are means of triplicates; error bars are ±1 standard error.

Dissolved and total iron profiles

Porewater concentrations (Figure 4(A)) were measured in the porewater of 100 μm layers. The first soil millimeter showed the highest concentration of iron(II) (66 μM); below this soil layer the concentrations varied around 40 μM. The porewater iron(III) profile (Figure 4(A)) showed highest concentrations in the upper mm (37 to 51 μM) with a decrease to concentrations around 20 μM in a soil depth between 8 and 10 mm. Diffusion of iron out of the system was measured with soil cores incubated for 12 weeks in the greenhouse. The amount of iron diffused out of the cores was 0.29 ± 0.11 μmol gdw^{-1}. Total iron (Figure 4(B)) was extracted with concentrated HCl over 24 hours of incubation. The total iron concentrations showed high variation in the upper 1.7 mm of the profile with concentrations between 167 ± 13 and 243 ± 4 μmol/cm^3. From 1.7 mm to 2.9 mm depth the total iron content increased to 344 ± 21 μmol/cm^3. Below 2 mm the iron concentration varied slightly around 370 μmol/cm^3.

Profiles of nitrate, sulfate, and fatty acids

Anoxic porewater samples of 1 mm thick soil layers were analyzed for nitrate, sulfate, and fatty acids. Profiles of sulfate and nitrate (Figure 5) in untreated 11 weeks old cores showed highest concentrations at the surface. The nitrate concentration decreased from 16 ± 7 μM to values below the detection limit (4 μM) in a depth of 4 mm. The sulfate profile was similar with decreasing concentrations of 49 ± 10 μM at the surface to values below the detection limit (10 μM) in a depth of 6 mm. Various organic acids were found in highest concentrations at the surface and decreased with depth (Figure 6).

Methane production rates

One mm layers of soil cores were incubated separately under anoxic conditions for the measurements of methane production rates (Figure 7). No methane production was detected in the first mm of the surface soil. Between 2 mm and 6 mm the rates increased and were relative constant in layers between 6 mm and 10 mm. The highest rate (1.81 μmol d^{-1} g^{-1} wet weight) was found at 11 mm depth. Due to the transfer of the soil in the bottles and the disruption of the soil structure the conditions in the soil had changed. Therefore methane production rates might be overestimated.

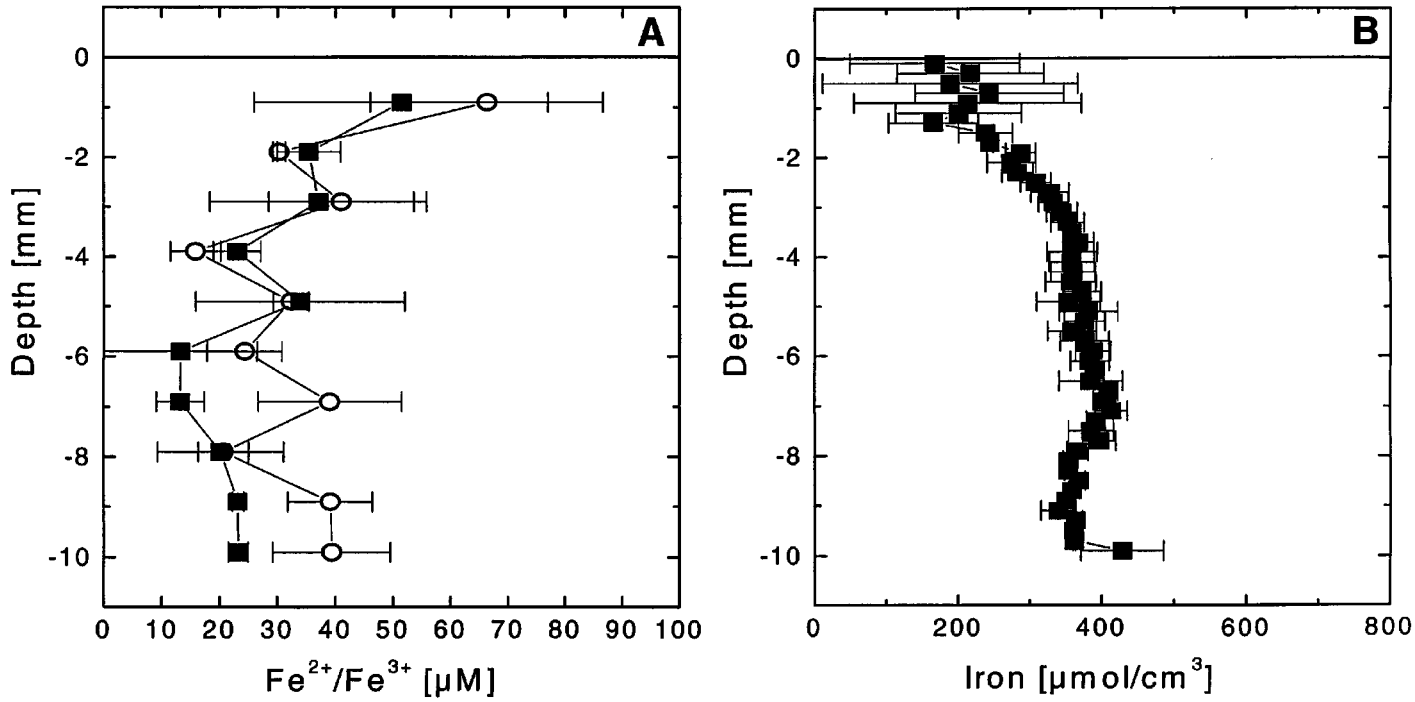

Figure 4. (A) Concentrations of porewater iron(II) (–○–) and porewater iron(III) (–■–) of unplanted soil incubated 11 weeks in the greenhouse. (B) Depth profiles of total iron (–■–) from 9 weeks old unplanted rice soil extracted with 12 M HCl. Data are means of triplicates; error bars are ±1 standard error.

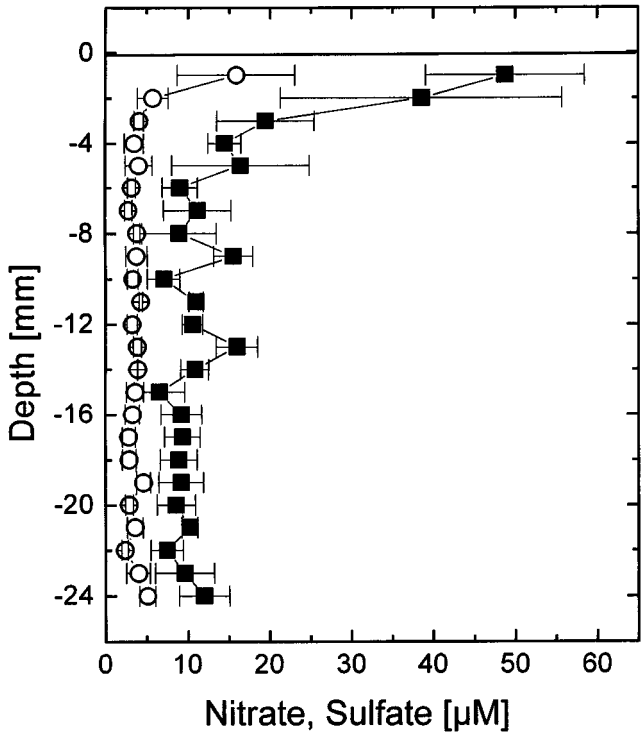

Figure 5. Depth profiles of nitrate (–○–) and sulfate (–■–) porewater concentrations measured in 1 mm layers of 11 weeks old unplanted paddy soil incubated in the greenhouse. Data are means of quadruplicates; error bars are ±1 standard error.

Oxygen profiles

In seven weeks old soil cores O_2 profiles were measured (Figure 8) with a clark type microelectrode. At the surface a maximum concentration of O_2 ($\approx$ 260 μM) was found due to photosynthetic production in an algal and cyanobacterial layer. Below the surface the O_2 concentration decreased constantly and was depleted in a depth of 3 mm.

Discussion

Zonation of iron(II) and iron(III) profiles

Depth profiles of iron(II) and iron(III) were studied to localize redox reactions of iron mediated by both, microbial and chemical activities. The iron concentrations were constant with depth at the start of the experiment. Stable

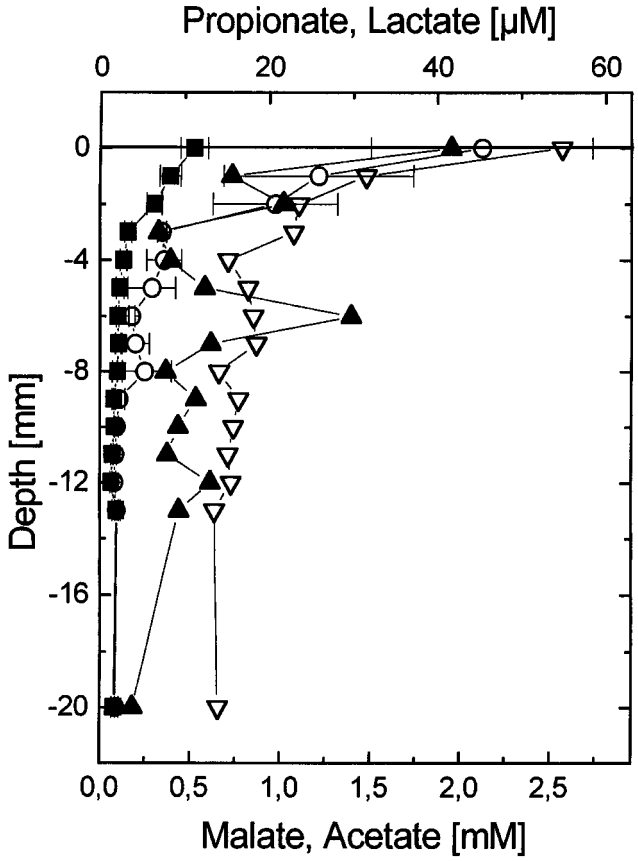

Figure 6. Depth profiles of propionate (–▽–), lactate (–▲–), malate (–○–), and acetate (–■–) porewater concentrations measured in 1 mm layers of 11 weeks old unplanted paddy soil incubated in the greenhouse. Data are means of quadruplicates; error bars are ±1 standard error.

and distinct profiles of iron(II) and iron(III) were developed during 11 weeks of incubation (Figure 1). In autoclaved soil the concentrations of iron(II) and iron(III) in the profile remained constant during 6 weeks of sterile incubation in the greenhouse (Figure 2). Therefore the development of the iron profiles in fresh paddy soil cores is driven by biological activities. The profiles show three characteristic zones; (i) low concentration of iron(II) and iron(III) at the soil surface, (ii) maximum iron(III) concentrations at a depth of 2 to 4 mm, and (iii) decreasing iron(III) concentrations between 4 and 8 mm soil depth and increasing iron(II) concentrations in this depth interval.

(i) The surface zone with low concentrations of iron(II) and iron(III) can be explained with a diffusive loss of iron. Porewater iron(II) concen-

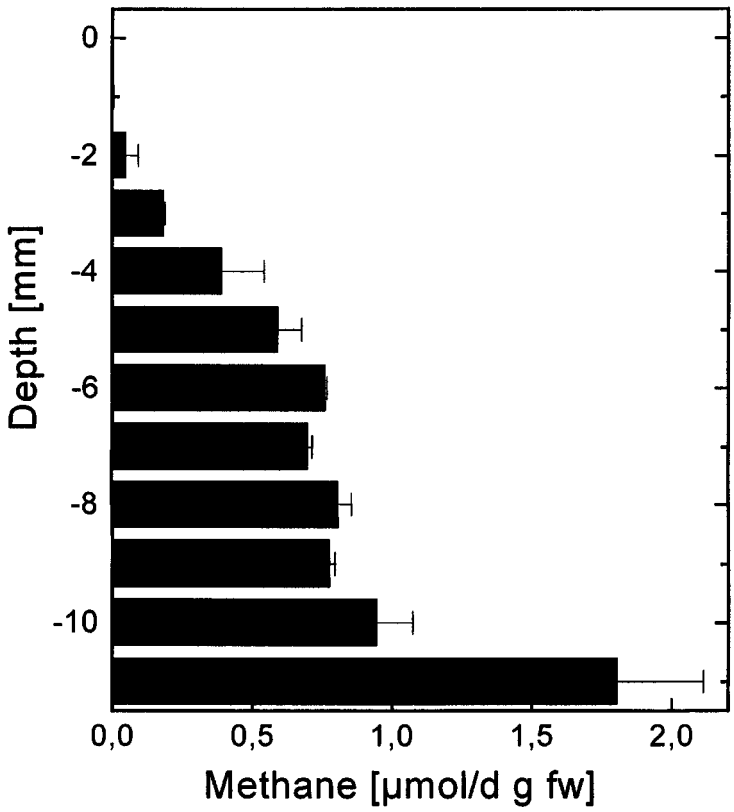

Figure 7. Depth profiles of potential methane production rates of unplanted soil after 11 weeks of incubation in the greenhouse. One mm slices were incubated anaerobically and methane production rates were determined. Data are means of duplicates; error bars show the range of the values.

trations were highest in the surface soil layer supporting the mobility of porewater iron(II) by diffusive transport from the soil into the flooding water (Figure 4(A)). This is also shown in the amount of iron (0.29 ± 0.11 μmol gdw^{-1}) found in the flooding water after 12 weeks of incubation. The mobility of iron(III) is assumed to be very low due to its extremely low solubility in water. In the presence of complexing agents like organic acids the concentration of porewater iron(III) is enhanced. Depth profiles of organic acids detected in the porewater showed highest concentrations in the surface soil layer (Figure 6) suggesting a higher mobility of iron(III) at the soil surface substantiated by organic complexing. The concentration of iron(III) in the porewater was in fact higher at the soil surface than in a depth of a few mm (Figure 4(A)). In salt marsh porewater containing organic compounds also porewater iron(III) was also found (Luther et al. 1996). Photoreduction of

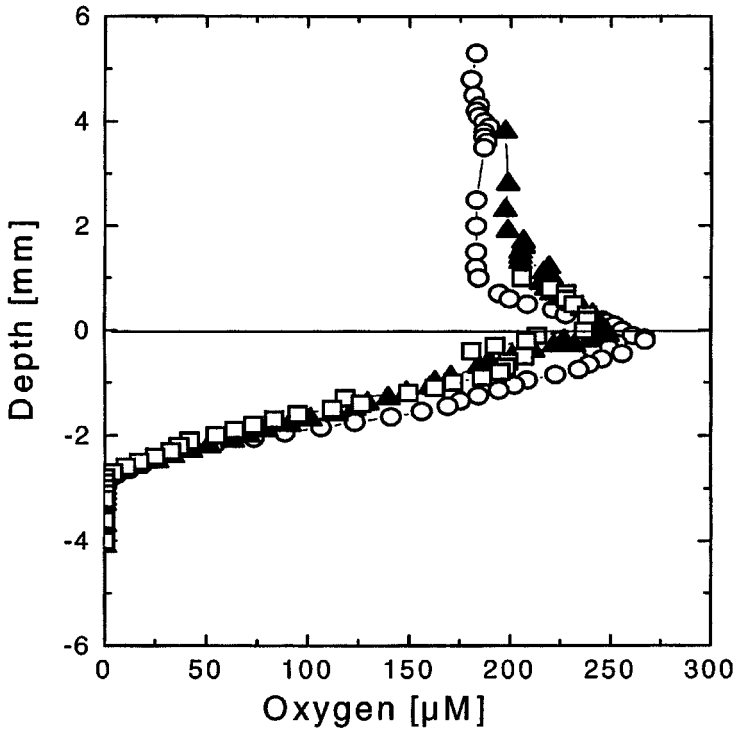

Figure 8. Depth profiles of oxygen concentrations measured with a clark typ microelectrode. Every profile was measured on an different spot at the soil core.

iron(III) has been observed in different freshwater environments (e.g. Collienne 1983; McKnight et al. 1988; Voelker et al. 1997; Madsen et al. 1986) and atmospheric water (Pehkonen et al. 1993). All studies however, showed photoreduction only in the surface water. The availability of organic ligands like carbonic acids greatly enhanced photoreduction (Stumm & Sulzberger 1991). Organic compounds can also stabilize porewater iron(II) before it precipitates as vivanite, siderite, pyrite and prevent oxidation to iron(III) oxide (Stumm & Morgan 1996; Luther et al. 1996) and therefore increase its mobility. The loss of iron on the soil surface is also indicated by depth profiles of total iron showing lower concentrations at the soil surface (167 μmol/cm^3) than at a depth below 2 mm (370 μmol/cm^3) (Figure 4(B)). Both dissolution of iron(III) by complexation and subsequent photoreduction could explain low iron(III) concentrations at the soil surface.

(ii) A maximum iron(III) concentration was observed in a depth of 2 to 4 mm. In contrast the highest concentrations of nitrate and sulfate were observed at the soil surface (Figure 5). Due to the presence of oxygen in the surface soil layer (Figure 8) ammonium, nitrite, and sulfide can be oxid-

ized by aerobic nitrifying and sulfur-oxidizing bacteria producing nitrate and sulfate. Similarly an oxygen mediated reoxidation of iron(II) is expected at the soil surface leading to accumulation of iron(III) (Howler & Bouldin 1971). Accumulation of iron(III) however, was observed not at the soil surface but beneath. The low iron(II) concentration at the surface might limit iron oxidation. At greater depths where iron(II) concentrations are higher, oxygen becomes limiting. Production of iron(II) below 4 mm and the diffusion of porewater iron(II) upwards to layers of iron(II)-oxidation could explain the accumulation of iron(III) at the depth between 2 and 4 mm of paddy soil. Below a depth of 3 mm no oxygen is present (Figure 8). Therefore the high iron(III) concentrations between 2 and 3 mm could be a result of oxygen-dependent iron(II) oxidation. Due to the lack of oxygen below 3 mm the high iron(III) concentration between 3 and 4 mm can not be the result of aerobic iron(II) oxidation. Thus, a microbial oxidation of iron(II) by nitrate-reducing bacteria (Straub et al. 1996; Benz et al. 1998) is likely. Moreover in anoxic slurry experiments with rice soil Klüber & Conrad (1998) found a reoxidation of iron(II) after addition of anoxic nitrate solution which also indicates a nitrate-dependent iron oxidation. Although nitrate (Figure 4) was not detected below 3 mm soil depth it could still be present due to the technical limitation of a 1 mm resolution. Iron(III) profiles which were measured in a 1 mm resolution showed decreasing iron(III) concentration below 3 mm (Schnell et al. 1998) whereas at high resolution the iron(III) concentrations decreased below 4 mm. The amount of NO_3^- may limit the nitrate-dependent iron oxidation although the diffusion of nitrate is much higher than that of iron(II). Nitrate can also be produced in the oxic layer by nitrification from ammonium diffusing out of the anoxic zone (Patrick & Delaune 1972). Additional ammonium could be produced by N_2-fixation and ammonium release of cyanobacteria in the biofilm. A chemical iron(II) oxidation with MnO_4 (Postma 1985; Myers & Nealson 1988b) is unlikely because very small concentrations of Mn(II) (0.9 ± 0.7 μmol/cm^3) were detected in the anoxic part of the cores. Also Yao et al. (1999) reported small amount of 10.8 μmol/g of total free manganese (Mn(II) + Mn(IV)) in an Italian rice soil. A chemical oxidation of iron(II) by nitrite (Moraghan & Buresh 1977) is unlikely because of very low NO_2^- concentrations (< 2 μM). Similar profiles were found in agarose tubes with gradients of iron(II) and oxygen inoculated with a pure culture of an iron-oxidizing nitrate reducer (Benz et al. 1998). Howeler and Bouldin (1971) shown that the thickness of iron(III) maximum peaks correlated with the oxygen concentration in the surface water and the soil organic content. Also Roden and Wetzel (1996) observed in unvegetated sediment of freshwater wetland a maximum peak of iron(III). The iron oxide in the layer of maximal iron(III) concentrations is most likely ferrihydrite.

Ferrihydrite is completely dissolved at the extraction conditions used and it was shown to be the final product of anaerobic iron oxidation (Straub et al. 1996; Widdel et al. 1993).

(iii) The depth between 4 and 8 mm is characterized by iron-reducing activity. Concentrations of iron(III) decreased with depth while concentrations of iron(II) increased. Conversion of iron(III) to iron(II) in a similar way was found in riverine sediments (Lovley & Phillips 1986a) and freshwater wetland sediments (Roden & Wetzel 1996). Iron reduction can occur through microbial and chemical reactions. In marine environments with high sulfur pool sulfide-linked Fe(III) reduction can indeed be the predominate process (Jacobson 1994; Kostaka & Luther 1994). In paddy soil a chemical reduction by reduced sulfur compounds (sulfide or organic thiole) only plays a minor role because of the small pool of total sulfur (8.4 μmol gdw^{-1}). Thus, the microbial reduction of iron(III) is responsible for the increase of iron(II) at depths below 4 mm. Below a depth of 8 mm the iron(III) concentration remained 15 μmol/cm^3 (Figure 1(B)). The residual iron(III) obviously consisted of iron minerals that were not accessible for microbial reduction. Residual iron(III) was also found in slurry experiments with paddy soil (Klüber & Conrad 1998).

Ferric iron

The iron(III) concentrations given in the depth profiles reflect the iron oxides that can be dissolved with 0.5 M hydrochloric acid. Ferrihydrite and parts of lepidocrocite are dissolved with the same extraction procedure (Raiswell et al. 1994). These iron oxides are much better available for microbial reduction than the more crystalline oxides goethite and hematite (Lovley & Phillips 1986b, 1988). The surface area (Roden & Zachara 1996) and the crystallinity (Munch & Ottow 1980; Phillips et al. 1993) of iron(III) oxides seemed to influence the reducibility of the oxides. Lepidocrocite is an iron oxide with a higher crystallinity than ferrihydrite. It was found in hydromorphic soils like rice paddies (Schwertman & Taylor 1989) and is formed as oxidation product on rice roots (Chen et al. 1980; Bacha & Hossner 1977).

Extraction with 12 M HCl (Figure 4(B)) showed a total extractable iron concentration of 400 μmol/cm^3 in the soil. Canfield (1988) showed that ferrihydrite, lepidocrocite, hematite, goethite were dissolved to 100% with concentrated HCl (6 M) within 12 hours as well as parts of iron silicates. The fraction of iron soluble in concentrated HCl but insoluble in 0.5 M HCl consists most likely of crystalline iron oxides like goethite. Goethite formation has also been observed in paddy fields (Karim 1984).

Ferrous iron

Solid-phase iron(II) is also extracted with 0.5 M HCl. A comparison of porewater iron(II) concentrations with iron(II) concentrations determined after acidic extraction showed that the fraction of iron(II) present as precipitate or adsorbed to the solid-phase is 4500 fold higher than the porewater iron(II) concentration. The most dominat iron(II) precipitate in soils with carbonate alkanity of 1 mM is siderite ($FeCO_3$) (King 1998). Wind and Conrad (1997) have shown that in depth profiles of acid volatile sulfide (H_2S + FeS) and chromium reducible sulfide (FeS_2 + S°) in an Italian paddy soil the highest concentration was only 0.15 μmol/cm^3 and 1.7 μmol/cm^3, respectively. These low concentrations suggests that iron sulfides play a minor role. Since the pool of phosphorus in paddy soil is low iron phosphate ($FePO_4$) therefore plays a minor role. The absolute porewater iron(II) and iron(III) concentrations could be overestimated somewhat by the sampling technique. The addition of water might have changed the ion-exchange equilibria and might have induced desorption of iron(II) and iron(III) from the solid-phase thus overestimating the values for porewater concentrations.

Effect of organic content

Different amounts of organic carbon lead to slightly different iron profiles. Soil cores fertilized with straw (Figure 3(B)) showed similar iron(II) profiles and a slightly smaller iron(III) peak as untreated soil. The smaller iron(III) peak may indicate higher microbial respiration due to the higher organic content leading to oxygen depletion at a lower depth (Howler & Bouldin 1971). In soil with low carbon content (Figure 3(A)) the iron(II) concentrations in the lower zone were twice as high as in the untreated soil cores. Higher iron(II) concentration in the anoxic zone (> 6 mm) of the soil cores must be interpreted as higher precipitation and/or higher adsorption of iron(II) during the incubation time. The thermodynamic theory predicts that the electron acceptor with a higher redox potential is reduced first (Zehnder & Stumm 1988). The bacteria reducing manganese(IV), iron(III), sulfate, and producing methane compete for electron donors. At the beginning of the experiment organic matter in rice soil is first oxidized to CO_2 by nitrate-, iron(III)- and sulfate-reducing bacteria. At low C-content the total amount of electrons transferred is smaller (Jäckel & Schnell 1999) and less substrates are available for methanogenic degradation. The methane production is lower compared to soil with higher C-content. In slurry experiments with rice soil the CO_2 and iron(II) production is highest during the first two weeks while the consumption of CO_2 is low. If we assume a similar situation in soil cores with low organic content we would expect similar CO_2 and iron(II) production as

in untreated soil, however a low methane production as the most important process of CO_2 consumption. This would lead to high levels of siderite precipitation in deeper soil layers. This is confirmed by high levels of solid iron(II) ($\approx$ 200 μmol/cm^3) in 10 mm depth of 2 weeks old cores (data not shown) compared with fresh soil ($\approx$ 100 μmol/cm^3). During methane production CO_2 is consumed and with limitation of free CO_2 precipitated siderite is dissolved after the equation $FeCO_3$ (solid) + $2H^+ \Leftrightarrow Fe^{2+}$ (porewater) + CO_2 + H_2O (Bruno et al. 1992) until an equilibrium of CO_2 consumption and production/solution is reached. The porewater iron(II) can diffused into the flooding water. In the soil with low C-content the CO_2 consumption in the methanogenic zone is smaller leading to higher concentration of siderite and reduced iron(II) diffusion in the flooding water.

Electron donors

The high concentrations of organic acids found in the upper soil layer (Figure 6) can be explained by organic biomass production of photosynthetic organisms on the soil surface. Photosynthetic activity is indicated by oxygen production at the soil surface (Figure 8). The high concentration of acetate, propionate, and lactate suggest that there is no limitation of electron donors for microbial iron reduction (Figure 6). These three organic acids are known substrates of iron-reducing bacteria (Lovley 1995). High concentration of acetate, propionate, and lactate in the first mm were unexpected because these typical products of anaerobic fermentation processes would normally be consumed fast under oxic conditions. One explanation for the accumulation of these organic acids could be the presence of anaerobic niches in the oxic part of the soil. In the surface zone the production rates of organic acids is assumed to be greater than the consumption rates leading to accumulation.

Other electron acceptors

The shape of oxygen profile indicated that oxygen consumption for both microbial and chemical oxidations is localized between 2–3 mm soil depth. An oxygen production zone was observed at the soil surface. The zone below the surface is mainly characterized by linear oxygen diffusion. Nitrate reduction and sulfate reduction occur in the same zone (3–6 mm) as iron reduction. The availability of common electron donors allows simultaneous operation of various reduction processes of different redox potentials (Lovley & Goodwin 1988; Achtnich et al. 1995; Lovley 1995; Westerman & Ahring 1987). Methane production rates increased with increasing soil depth (Figure 7). Due to the presence of oxygen in the first 2 mm of the surface soil (Figure 8) methanogenesis was inhibited. In the zone between 2 mm and 8 mm where nitrate,

iron(III), and sulfate reduction was active the rates of methane production were low indicating some competition for substrates. Below 8 mm soil depth only some residual iron(III) is present and no nitrate and sulfate. In agreement with the thermodynamic theory methanogenesis was the predominate process below 8 mm. This localization of methane-producing activity was confirmed by measurements with a gas diffusion probe in flooded paddy soil (Rothfuss & Conrad 1994) that showed maximal methane concentration below a depth of 10 mm.

Planted soil

In rice plants oxygen diffuses via the aerenchym from the leaves to the roots. Oxygen release of the rice roots into the rhizosphere soil depends on the root age. The fine mat roots directly on the soil surface correspond to maximum values of root biomass found in the top soil layer and to much higher oxygen concentration (over saturation) than in unplanted soil especially under illumination (Frenzel et al. 1992). High oxygen concentrations in the root mat at the soil surface allow effective iron(II) oxidation resulting in an accumulation of iron(III) and less diffusive loss of iron(II) into the surface water. Below the mat roots ordinary roots are present in lower density and the oxic zone around these roots might not cause a dramatic change in the iron(III) concentration. Microbial nitrate dependent iron(II)-oxidation might play a less important role in planted soil because of the effective nitrate consumption by the plants. This results in a narrow zone of high iron(III) concentrations close to the soil surface where solely oxygen is responsible for reoxidation of iron(II).

Conclusions

Soil of flooded rice paddies is stratified in various zones of different redox reactions of iron. Directly at the soil surface solid-phase iron(II) concentrations were low due to diffusive loss of porewater iron(II) into the flooding water. High concentrations of organic acids in this soil layer complexed iron(III) and enhanced diffusion thus preventing accumulation. The soil layer between 2 and 4 mm is characterized by iron(III) accumulation resulting from diffusive transport of porewater iron(II) from deeper soil layers and iron(II) oxidation by oxygen and nitrate. Iron-reducing activity was localized in a depth of 4 to 8 mm. Below this depth methanogenesis is the predominant process due to the lack of alternative electron acceptors. In planted rice paddies the oxygen release of roots stimmulated both iron(II) oxidation and iron(III) reduction.

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