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A methane-driven microbial food web in a rice field soil

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Abstract

Biological methane oxidation in wetland soils is a key process in the methane cycle, preventing large amounts of this greenhouse gas from escaping into the atmosphere. While methanotrophs are only a group of bacteria capable to oxidise and assimilate methane-C under aerobic conditions, the fate of assimilated methanotrophic biomass is largely unknown. We conducted a microcosm experiment, in which a thin layer of rice field soil was incubated under opposing gradients of oxygen and ^{13}C-labelled methane. ^{13}C-enriched "heavy" RNA could be affiliated not only to methanotrophs, but also to protozoan grazers including amoebae, ciliates, and flagellates, demonstrating a microbial food web driven by methane. The impact of protozoan grazing on methanotrophs was studied by another microcosm experiment, in which natural assemblages of bacterial community including methanotrophs retrieved from a rice field soil were re-inoculated to sterilised soils with or without protozoan isolates. Microarray analysis of *pmoA* gene showed that a group of type I methanotrophs became dramatically prominent when protozoa were absent. Protozoa isolated from the soil demonstrated selective grazing on type I methanotrophs. A series of our studies demonstrates that protozoan grazing with selectivity may have a crucial impact on the methanotrophic community in a wetland rice field soil.

Key Words

Food chain, molecular analysis, paddy field soil, predation, protists, stable isotope probing.

Introduction

Biological methane oxidation at the oxic-anoxic interface in wetland soils and sediments is a key process in methane cycling, preventing large amounts of this greenhouse gas escaping into the atmosphere (Conrad 1996). Methanotrophs are only a group of bacteria capable to oxidise and assimilate methane-C under aerobic conditions (Bowman 2000). However, methane-derived carbon may be utilised by other organisms in indirect ways. Predation on soil microbes by protozoan predators is a well-known feature (Clarholm 1994; Ekelund and Ronn 1994), but their impact on methanotrophic populations has never been studied. In this study, we report on a microbial food web driven by methane in a rice field soil. We adopted the RNA–stable isotope probing (SIP) approach (Manefield *et al.* 2002) using ^{13}C-labelled methane and universal primers for the domains Bacteria and Eukarya to follow the incorporation of methane carbon into microorganisms. The effect of protozoan grazing on methanotrophic populations was also studied through culture-dependent and independent experiments. The results demonstrate the crucial impact of selective grazing of protozoa on the methanotrophic community in the rice field soil.

Methods

Incorporation of methane carbon by prokaryotic and eukaryotic microorganisms revealed by RNA-SIP (Murase and Frenzel 2007)

Soil taken from a rice field of the Istituto Sperimentale della Risicoltura (Vercelli, Italy) in the spring of 2000 before flooding was used in this study. Microcosms made from a thin layer of water-saturated rice field soil were supported by a gas permeable membrane and supplemented with ^{13}C-methane (at 20 %[v/v] in N_2) from below and air from above, thus reproducing the oxic-anoxic interface (Figure 1A). After 20 days of incubation, RNA was extracted from soil and subjected to isopycnic centrifugation. T-RFLP (Terminal Restriction Lengths Polymorphism) and DGGE (Denaturating Gradient Gel Electrophoresis) analysis were conducted for fractionated RNA samples to study bacteria and eukarya that incorporated methane carbon.

Impact of protozoan grazing on the community composition of methanotrophs

Natural assemblages of bacterial community including methanotrophs were retrieved from the soil incubated under methane and re-inoculated to sterilised soils with or without a mixture of protozoa (1 ciliate, 3 flagellates and 4 naked amoeba) that had been isolated from the same soil. The soil was incubated in the microcosm described above. Incorporation of methane carbon into inoculated protozoa were followed by

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RNA-SIP. Community composition of methanotrophs were analysed by microarray targeting *pmoA* gene (Bodrossy *et al.* 2003).

Selectivity of protozoan grazing on methanotrophs
The number of methanotrophs-feeding protozoa in an air-dried rice field soil was estimated by determining the MPN using methanotrophs as food bacteria (Murase and Frenzel 2008). Protozoa were isolated from the positive wells inoculated with higher dilutions and their growths on different methanotrophs were tested by a cultivation method.

Results

Incorporation of methane carbon by prokaryotic and eukaryotic microorganisms
PCR-products were obtained from the 'heavy' RNA (up to the buoyant density of 1.801 g/mL) from the $^{13}CH_4$-applied microcosm and T-RFLP patterns differed between the 'light' and 'heavy' fractions. This is well contrasted with the normal CH_4-applied microcosm, which gave PCR products only from the 'light' RNA (up to the buoyant density of 1.784 g/mL) and nearly identical T-RFLP patterns over the density gradient. A clone library of ^{13}C-labelled 'heavy' 16S rRNA included methanotroph-related sequences as a dominant group (Figure 1B) confirming the incorporation of methane-C into methanotrophic biomass. *Methylocyctis*-, *Methylobacter*- and *Micromicrobium*-related sequences were dominated in the clones from the 'heavy' RNA. The most dominant sequences next to methanotrophs could be affiliated to Myxococcales. As the case of bacterial RNA, we obtained PCR-products from the ^{13}C-labelled 18S rRNA at high buoyant densities (up to the buoyant density of 1.801 g/mL). At the same densities, we failed to obtain any product in the control treated with normal CH_4. DGGE fingerprints of the 'heavy' fractions showed distinctly different patterns from those of the 'light' fractions, indicating that a subset of the eukaryotic community had assimilated methane-C (Figure 1C). Sequences retrieved from the DGGE bands of the 'heavy' RNA fractions could be affiliated to Colpodea (Ciliophora, band A), Cercozoa (band O), Amoebozoa (bands E, L and P), and Heterolobosea (band M), suggesting that these protists grazed on methanotrophs that assimilated $^{13}CH_4$.

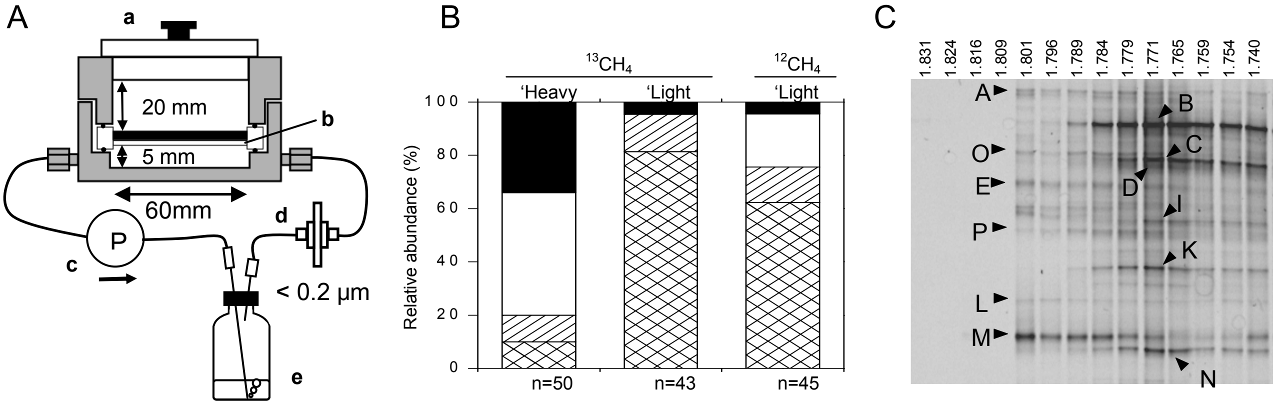

Figure 1. The gradient microcosm for the RNA-SIP experiment using ^{13}C-labelled methane. (A) A schematic drawing of the microcosm. (B) Phylogenetic affiliation and relative abundance of bacterial 16S rRNA clones from 'heavy' and 'light' RNA fractions of ^{13}C-labelled methane-treated microcosm ($^{13}CH_4$) compared to clones from the 'light' RNA fraction of the normal methane-treated microcosm ($^{12}CH_4$). Black: MOB (α-Proteobacteria); white: MOB (γ-Proteobacteria); hatched: Myxococcales; cross-hatched: others. (C) Eukaryotic DGGE fingerprints over the density-range of a fractionated rRNA centrifugation gradient for the microcosm applied with ^{13}C-labelled methane. Buoyant densities of the fractions (g/mL) are given on the lanes. Sequences retrieved from DGGE bands could be affiliated to the following taxa: bands A and B, Colpodea (Ciliophora); bands C, E, K, I, L, P, and G, Amoebozoa; bands D and O, Cercozoa; bands M and N, Heterolobosea. Redrawn from Murase and Frenzel (2007).

Impact of protozoan grazing on the community composition of methanotrophs
Inoculation of soil with protozoa enhanced methane oxidation in the initial period of incubation (up to 10 days). After 20 days of incubation, DNA and RNA were extracted from the soil to analyse the community structure of protozoa and methanotrophs. RNA-SIP (stable isotope probing) approach revealed that some of inoculated protozoa incorporated methane-^{13}C, indicating the grazing of the protozoa on methanotrophic biomass. 18S rRNA of the same protozoa were detected from the ultracentrifuged fractions with a wide range of buoyant density, suggesting that the same protozoa can have different grazing preference at the

individual level; some individuals more preferably grazed on methanotrophs and some on non-methanotrophs. Microarray analysis of pmoA gene showed that a specific group of type I methanotrophs (a subgroup of the *Methylobacter* clade) became dramatically prominent when protozoa were not inoculated (Figure 2).

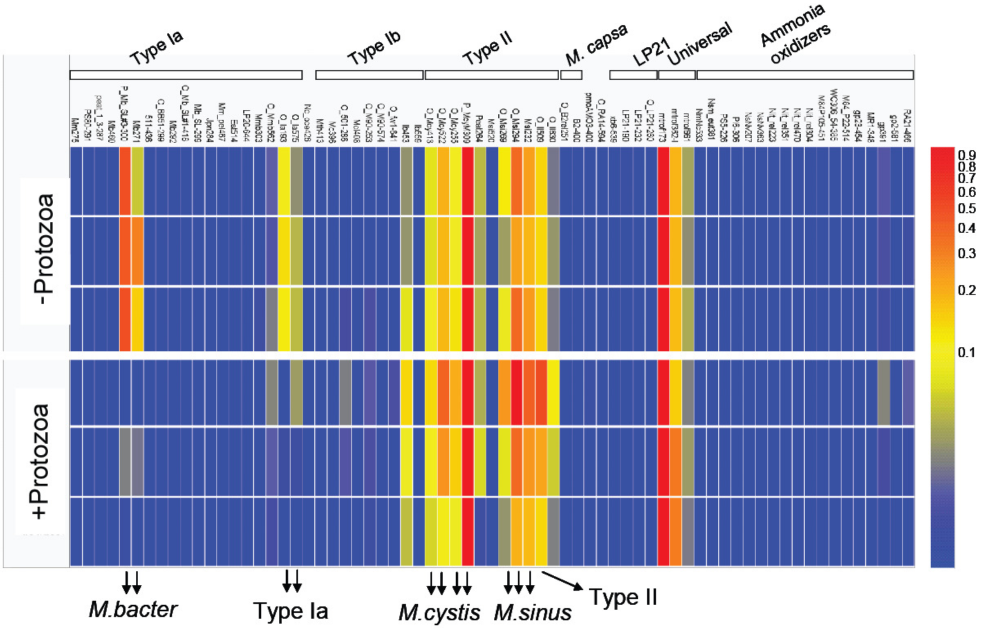

Figure 2. Microarray results showing the efficiency of hybridization of *pmoA* PCR products from soils with and without protozoa (n=3).

Selectivity of protozoan grazing on methanotrophs

Protozoa, specifically naked amoebae and flagellates, grew densely, accompanied by a decrease in the number of food bacteria in the medium. Such growth was not observed in the wells lacking food bacteria, which indicated that the protozoa fed on the food bacteria. The MPN counts (summed numbers of flagellates and amoebae) enumerated on day 7 were lower in media containing methanotrophs than in the medium containing *E. coli* (Figure 3). On day 21, seven of ten methanotrophic strains yielded protozoan MPN counts comparable with *E. coli* (10^4 MPN/[g soil dry wt.]), while three strains of *Methylocystis* spp. (strains RP1, Pi54, and LR1) yielded significantly lower numbers of protozoa (10^2–10^3 MPN/[g soil dry wt.]) than *E. coli*. The amoebae isolated from positive wells with different food bacteria generally showed a similar pattern of grazing preference on methanotrophs (Table 2); they fed on all methanotrophs except *Methylocystis* sp. strains RP1, Pi54, and LR1. The flagellate fed on *Methylocystis* sp. strain Pi54 more actively than on *Methylocystis* sp. strain H9a, and the *Hartmannella* amoeba grew as well on strain RP1 as on strain H9a.

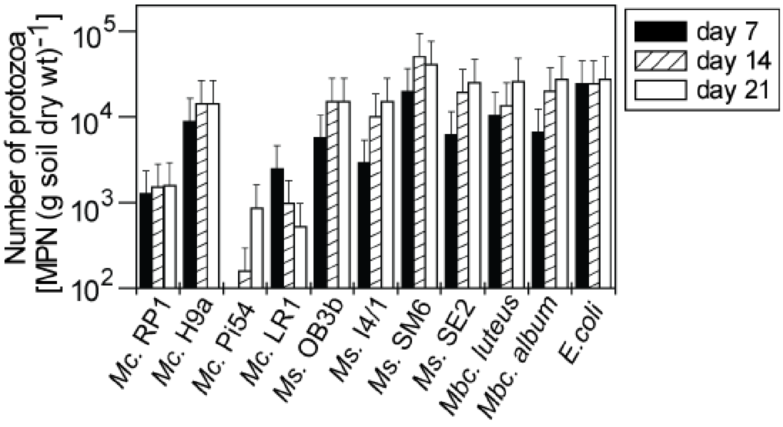

Figure 3. MPN counts of protozoa in rice field soil feeding on methanotrophs. Mc., *Methylocystis* sp.; Ms., *Methylosinus* sp.; Mbc., *Methylobacter* sp. Redrawn from Murase and Frenzel (2008).

Conclusion

Methanotrophic biomass that assimilated methane carbon was incorporated into microbial predators such as protozoa and myxobacteria. Protozoan grazing dramatically changed the composition of the methanotrophic community with decreased dominance of Type I methanotrophs. The culture dependent study showed that

Type I methanotrophs supported the growth of soil protozoa, while some of Type II methanotrophs did not. A series of our studies is the first demonstrating the impact of protozoa on a defined group of soil bacterial population performing the same ecological functions. Protozoa are an important biotic factor shaping the methanotrophic community in situ by selective grazing. Further study is needed to understand the effect of protozoa on methane oxidation and methane cycle in a rice field soil.

Table 1. Growth of protozoa isolated from the MPN plates on different methanotrophs1) (Murase and Frenzel 2008).

Strain name	Food bacteria in MPN plates	Taxonomy	Food bacteria tested										
			Methanotrophs										
			Mc. RP1	*Mc.* H9a	*Mc.* Pi54	*Mc.* LR1	*Ms.* OB3b	*Ms.* I4/1	*Ms.* SM6	*Ms.* SE2	*Mb. luteus*	*Mbc. album*	*E. coli*
H9a_3E	*Mc.* H9a	Unidentified Lobosea	-	++	-	-	+++	++	+++	++	+	++	++
H9a_6E	*Mc.* H9a	*Filamoeba*	-	+++	+	-	+++	++	+++	++	++	++	++
OB3b_3A	*Ms.* OB3b	*Acanthamoeba*	+	+++	+	-	+++	+++	+++	+++	+++	+++	++
I4_6E	*Ms.* I4/1	Unidentified Lobosea	-	+++	-	-	+	++	++	++	++	++	+++
I4_5E	*Ms.* I4/1	*Filamoeba*	+	++	-	+	++	++	+++	+++	++	+++	+++
SM6_6A	*Ms.* SM6	*Acanthamoeba*	+	+++	+	-	+++	+++	+++	+++	+++	+++	+++
SE2_6F	*Ms.* SE2	*Acanthamoeba*	-	+++	+	-	+++	+++	+++	+++	+++	+++	++
Mb_5C	*Mb.* luteus	Unidentified Lobosea	+	++	+	-	+++	++	+++	++	++	++	+++
Mbc_7D	*Mbc.* album	Unidentified Lobosea	-	++	-	-	++	++	+++	+++	+++	+++	++
Mbc_3C	*Mbc.* album	*Spumella*	+	+	+++	-	++	++	+++	+	+	++	+++
Mbc_3E	*Mbc.* album	*Acanthamoeba*	+	+++	+	-	+++	++	+++	++	+++	++	++
Mbc_3H	*Mbc.* album	*Hartmannella*	++	++	-	-	+++	+++	+++	+++	+++	+++	+++
E_5F	*E. coli*	*Comandonia*	-	++	+	-	+++	++	+++	++	++	++	++
E_5C	*E. coli*	*Acanthamoeba*	-	+++	+	-	+++	+++	+++	+++	+++	+++	+++
E_5E	*E. coli*	*Comandonia*	-	+++	++	-	+++	+++	+++	+++	+++	+++	+++

1) -, no growth; +, silightly grown; ++, moderately grown; +++, actively grown. See text for the classification

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Abiotic and biotic changes of sulphur, iron, and carbon speciation after aeration of wetland soils

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Abstract

For organic surface and mineral soil horizons of terrestrial and intertidal wetland soils from Germany and Thailand, the kinetics of speciation changes of sulphur, iron, and organic carbon (OC) after aeration was assessed by synchrotron-based K-edge X-ray absorption near-edge spectroscopy (XANES), solid state ^{13}C CPMAS NMR spectroscopy, and wet chemical/GC analyses. The kinetics of speciation change was investigated in a laboratory incubation experiment, in which subsamples were held in contact with ambient air for different time periods, ranging from 1 minute to 21 days under controlled boundary conditions. In different experimental variants, abiotic changes were distinguished from biotic changes. The results show that oxygenation of wetland soils results in rapid oxidation of reduced inorganic sulphur and iron species (e.g. Fe(II) sulphide) to oxidized species (sulphate, Fe(III)oxides). Under anoxic conditions, labile OC species (O-alkyl-C, e.g. plant-derived sugars such as glucose, arabinose, and xylose) are prevented from microbial degradation. Aeration of these samples resulted in considerable OC losses, microbial degradation of glucose, arabinose, and xylose, and formation of microbial OC compounds (alkyl-C), including the sugars galactose and mannose. Our results suggest rapid, marked losses of labile OC species (terrestrial wetland soil only) and rapid oxidation of reduced S and Fe after aeration of wetland soils due to changes of their hydrological regime.

Key Words

XANES, ^{13}C CPMAS NMR spectroscopy, kinetics, Fe oxidation, S oxidation, microbial C degradation.

Introduction

In many regions of the world, the hydrologic regime of wetland soils is altered or threatened to get altered by artificial drainage or climate change. This alteration is often associated with a change of the soil redox status from anoxic or suboxic to oxic conditions. The elements S and Fe are well-known as redox-sensitive, under anoxic and suboxic conditions reduced forms of S and Fe (e.g. Fe(II) sulphide) prevail, whereas under oxic conditions oxidized forms, such as Fe(III)oxyhydroxides and sulfate dominate. According to Prietzel *et al.* (2009), oxic sample transport, storage, and pre-treatment of wetland soil samples results in considerable changes of S and Fe speciation. At the moment, no information exists about changes of the speciation of organic carbon (OC) in wetland soils after contact with atmospheric oxygen, Particularly the kinetics and the relative importance of abiotic and biotic processes for speciation changes of C, S, and Fe in wetland soils after aeration is unknown.

Methods

Study sites and soils

Samples were taken from the organic surface (H) and a mineral topsoil (HCr) horizon of (i) the permanently anoxic Histosol Schlöppnerbrunnen 1 (acidic fen) in the Fichtelgebirge, Germany; Prietzel *et al.* (2007, 2009) and (ii) a calcareous Histosol near the town of Eichstätt, Germany. Additionally, samples from intertidal soils were taken (iii) at the Wadden Sea close to the town of Büsum, Germany at three different locations, where different sedimentation patterns had resulted in deposition of sandy, loamy, and clayey soils, respectively, and (iv) at the SE shore of the island Ko Samui, Thailand. The sampled soils differed in OC content, texture, pH, and climate conditions.

Anoxic soil sampling and sample pre-treatment

To avoid artificial changes due to undesired contact with oxygen before start and after commencement of the incubation experiment, the samples were stored, dried, and prepared for XANES, NMR and wet-chemical analysis under solid CO_2 or N_2/Ar atmosphere as described in detail in Prietzel *et al.* (2007, 2009).

Laboratory incubation experiments

Field-moist subsamples of samples taken from organic surface and mineral topsoil horizons of the Histosols were allowed to react at room temperature (20°C) with atmospheric oxygen for different times (0, 1, 2.5, 5, 10, 30, 60, 90 minutes, 3, 6, 12, 24, 48, and 96 hours), before they were freeze-dried under Ar and analysed. In one experimental variant, biotic changes of the sample were prevented by repeated addition of 1% NaN_3 solution; in the other variant, both biotic and abiotic changes were allowed by repeated addition of deionized water instead of NaN_3 solution.

Field-moist subsamples of the uppermost 20 cm of the intertidal soils were allowed to react at room temperature (20°C) with atmospheric oxygen for different times (0, 1, 2.5, 5, 10, 30, 60, 90 minutes, 3, 6, 12 hours, 1, 2, 4, 7, 14 and 21 days), before they were freeze-dried under Ar and analysed. As with the Histosols, in one experimental variant, biotic changes of the sample were prevented by repeated addition of 1% NaN_3 solution; in the other variant, both biotic and abiotic changes were allowed by repeated addition of deionized water instead of NaN_3 solution.

Synchrotron-based sulphur and iron K-edge XANES

For selected samples, the speciation of S and Fe was assessed after grinding and freeze-drying by synchrotron-based S and Fe K-edge XANES (Prietzel *et al.* 2003, 2008, 2009). All XANES analyses were conducted at Beamline 8 of the 1.2 GeV electron storage ring at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand. S and Fe K-edge XANES spectra were acquired in the energy ranges 2465 – 2495 eV (S) and 7085 – 7240 eV (Fe) with a InSb(111) and a Si(111) monochromator (energy resolution: 0.25 eV and 0.5 eV for S and Fe, respectively) and a dwell time of 10 sec. Fluorescence signals were recorded with a 13-channel Ge detector. For energy calibration, $FeSO_4$ and Fe° were used. After base-line correction and normalization, the spectra were deconvoluted by Linear Combination Fitting (LCF), using the software Athena and SixPack (Ravel and Newville 2005; Webb 2005).

^{13}C CPMAS NMR spectroscopy

Different OC species in the freeze-dried, fine-ground samples were quantified by solid state ^{13}C cross polarization magic angle spinning (CPMAS) NMR spectroscopy (BRUKER DSX 200 NMR spectrometer; resonance frequency: 50.323 MHz), applying the cross polarization magic angle spinning technique (Schaefer and Stejskal, 1976). The spectra were obtained with a pulse delay of 500 ms and using a ramped 1H-pulse during the contact time of 1 ms in order to circumvent Hartmann-Hahn mismatches (Peersen *et al.* 1993). The chemical shift is given relative to tetramethylsilan (= 0 ppm) and was calibrated with glycine (176.03 ppm). For quantification of different C species, the ^{13}C NMR spectra were divided into four chemical shift regions which are assigned to specific C groups (Wilson 1987; Knicker and Lüdemann 1995): 0-45 ppm alkyl C (lipids, cutin, amino acids), 45-110 ppm O/N-alkyl C (carbohydrates, cellulose, methoxyl C, C-N of amino acids, hemicellulose), 110-160 ppm aryl C (lignin, tannin, aromatic compounds, olefines), 160-220 ppm carboxyl/amide and carbonyl C (carboxylic acids, amide, aldehyde and ketone groups). The respective areas were quantified by integration.

Determination of plant- and microbial derived sugars

Non-cellulosic polysaccharides, including the plant-derived sugars arabinose and xylose as well as the microbial sugars galactose and mannose, were determined according to Spielvogel *et al.* (2006) by gas chromatography (Agilent GC equipped with a flame ionisation detector) after hydrolysis with trifluoroacetic acid, derivatisation of their neutral sugar monomers by reduction to alditols, and subsequent acetylation.

Results

Incubation of samples from the Histosols at room temperature and presence of O_2 resulted in rapid, considerable OC losses (Figure 1). After 3 hours, 10% of the initial SOC were mineralized. After 6 hours 20% of the initial OC was lost; longer incubation did not result in additional C losses. The SOC losses were almost exclusively caused by losses of O/N-alkyl C (Figure 1). Alkyl-C and aryl-C amounts increased, but could not compensate the O/N-alkyl C losses. The sugar content decreased by 30% within 90 minutes and by 60% within 6 hours of incubation (Figure 2). The decreases were mainly caused by losses of the plant-derived, easily decomposable sugars glucose, arabinose, and xylose. Concomitantly, the pools of the microbial sugars galactose and mannose increased. When biotic activity was inhibited by addition of NaN_3 during incubation of the Eichstätt Histosol, in contrast to the variant without NaN_3 addition no breakdown and conversion of sugars was observed, emphasizing biotic turnover as key process for C speciation changes.

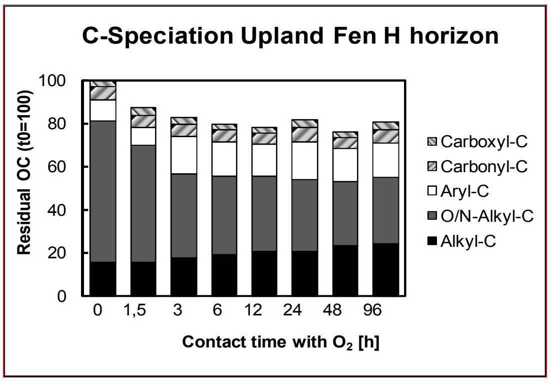

Figure 1: Pool changes of different OC species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±5%).

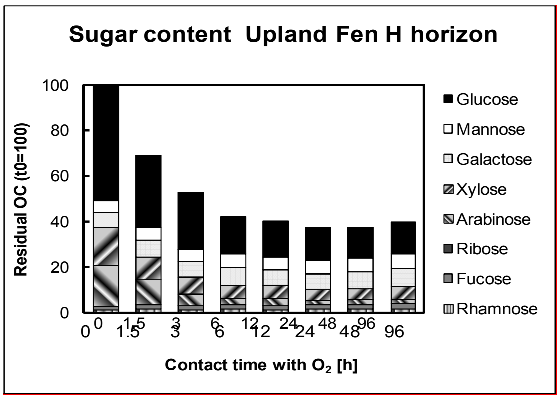

Figure 2: Pool changes of different neutral sugar species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±2%).

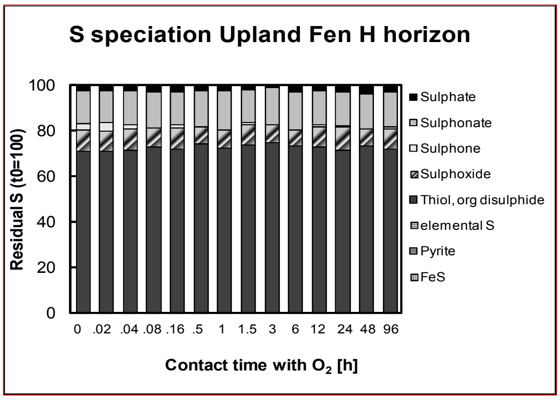

Figure 3: Pool changes of different sulfur species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±10%).

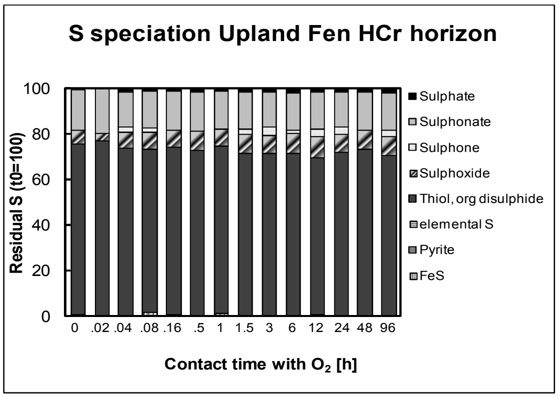

Figure 4: Pool changes of different sulfur species during incubation of an HCr horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±10%).

In the organic surface (H) and mineral topsoil horizon (HCr) of the upland fen, no inorganic reduced sulphur species (e.g. FeS, pyrite) were present, and reduced organic S (thiol/organic disulphide S) contributed about 75% of total S (Figure 3,4). In contrast to OC, the incubation did not result in any sulphur losses, and sulphur speciation during aeration of the upland fen did not change for the H horizon (Figure 3). For the anoxic mineral topsoil horizon (HCr), a decrease in thiol/organic disulphide S and a concomitant increase in sulphoxide and sulphate were noticed (Figure 4). Aeration of the intertidal sediments resulted in considerable changes of the speciation of S and Fe; reduced S and Fe species (e.g. FeS) decreased markedly, oxidized S and Fe species (FeIII oxyhydroxides, sulphate) increased.

Conclusion

Aeration of wetland soils results in rapid oxidation of reduced inorganic iron and sulphur species (e.g. Fe(II) sulphide) to oxidized species (Fe(III) oxyhydroxides, sulphate). For the terrestrial wetlands, most of the sulphur and iron was oxidized within minutes rather than hours or days, whereas the oxidation process was much slower for the intertidal soils. Under anoxic conditions, labile OC species (O-alkyl-C, e.g. plant-derived neutral sugars such as glucose, arabinose, and xylose) are prevented from microbial degradation. Aeration of these samples results in rapid (<6 h) and considerable (20%) C losses, degradation of plant-derived sugars, and formation of microbial OC compounds (alkyl-C), including the neutral sugars (galactose and mannose). Our results suggest that increased aeration of wetland soils due to changes of their hydrological regime results in rapid and considerable losses of labile, redox-stabilized OC species (terrestrial wetlands) and in rapid, significant changes of S and Fe speciation (terrestrial and intertidal soils).

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Acidity fluxes following rewetting of sulfuric material

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Abstract

We selected two sites with soil materials of clay and sand and used mesocosms to study the effect of rewetting sulfuric material with sea water and fresh water. The materials behaved differently due to different water seepage rates and acid stores. The water seepage rate was low for the clay soil (0.8×10^{-3} m/d) compared to the sandy soil ($8–15\times10^{-3}$ m/d). Initial acid flux rates were higher (0.1–0.2 mol/m^2/d) compared to long term rates (0.007–0.014 mol/m^2/d). For the clay soil, the low seepage rate and higher stored acidity resulted in a net flux of solutes from the soil to the water column. In contrast, the higher seepage flux of the sandy material resulted in a flux of water and solutes from the water column into the soil profile, displacing acid pore water deeper into the soil profile. However there is a residual acid flux into the water column probably due to the ongoing and slow dissolution of residual acid oxidation products. In both materials, sea water mobilised more acidity. Comparing the measured flux and calculated advective and diffusive fluxes highlighted the importance of solid phase reactions such as dissolution and surface exchange reactions.

Key Words

Acid sulfate soil, Lower Lakes.

Introduction

The Murray-Darling Basin is currently experiencing the worst drought conditions in recent record. The Lower Lakes (LL) are under extreme stress from a combination of low water levels, salinity increases and the exposure of acid sulfate soils (ASS; Fitzpatrick *et al*. 2008a). The most significant risks are likely to occur during reflooding of sulfuric materials, largely due to potential mobilisation of acidity and trace elements made available during previous oxidation of sulfidic soils. The transport and fate of acidity and bioavailable metals is poorly understood in these systems. The complexities in the local geology, soil type and landscape position means that metal mobilisation characteristics are likely to be site specific, and also be governed by re-wetting scenarios. The aim of our study was to determine acid fluxes upon rewetting sulfuric material.

Methods

We selected two sites in L. Alexandrina: (a) Boggy Ck. where sulfuric materials have formed in the sandy clays of drier areas; and (b) on the south side of Pt. Sturt peninsula where sulfuric materials formed in sands. The materials at these sites provided a contrast in soil physical and chemical properties and are considered representative end members of materials likely to be encountered in the lake. The location of the experiment sites is shown in Figure 1. Soils were described and classified using the Australian Soil Classification (ASC; Isbell 1996) and assigned to a class using the key developed for the Atlas of Australian Soils (Atlas; Fitzpatrick *et al.* 2008b). The soil at the Boggy Ck. site is a sulfuric cracking clay soil (Atlas) and according to the ASC a Redoxic Sulfuric Bleached-Vertic Hydrosol. The soil texture varies from a sandy clay loam in the top 0.03 m through fine sandy clay to light clay from 0.2 to 0.38 m, then a fine clayey sand to the limit of sampling at 1.8 m. The soil at the Pt Sturt site is a sulfuric soil (Atlas) and according to the ASC a Redoxic Sulfuric Acidic Hydrosol. The texture is sand to 0.6 m then sandy clay to the limit of sampling at 1.6 m. We also measured soil physical parameters including porosity, bulk density and seepage rate. The clay soil bulk density from 0–0.05 m was 0.88 t/m^3 and from 0.05–0.5 m it was 1.28 t/m^3. Porosities were 0.67 and 0.52 respectively. Seepage rates were very low and rates were similar for both treatments at 0.8×10^{-3} m/d. In the case of the sandy soil, the bulk density was uniform from 0.03–0.65 m at 1.53 t/m^3 with a porosity of 0.42. Seepage rates ranged from $8–15\times10^{-3}$ m/d for the fresh water and sea water treatments respectively.

At these sites we trialled rewetting of the sulfuric material using fresh water (River Murray water) and sea water treatments. Treatments were replicated and carried out in mesocosms set one metre into the soil. For each treatment, one mesocosm was installed with redox electrodes in the water column and at various depths below the surface and soil solution samplers. Dialysis chamber samplers (Batley *et al.*1993) were used to capture a snapshot of soil solution at 0.01 m resolution to ~0.30m bgl 28 days after rewetting.

Seepage rate was calculated from the amount of water supplied to maintain a constant mesocosm water depth, rainfall and class A pan evaporation. No local measurements of evaporation have been available since 2003 and interpolated data from Silo Data Drill (Jeffrey *et al.* 2001) was used. Evaporation values ranged from 0.8–6.8 mm/d. A comparison of measured and interpolated evaporation values from 1987–2003 showed that for the time of year covering the period of investigation, the difference between measured and interpolated values is ±0.2 mm/d. The net acidity flux to the mesocosms was estimated from the alkalinity change (after accounting for inputs and outputs). The diffusive and advective flux of 'acidic' cations (H^+, Al^{3+}, Fe^{2+}, and Mn^{2+}) was calculated using the flux equation $F_{z=0} = F_d + F_a + F_s$ where d, a and s are the diffusive, advective and solid phase fluxes (Stumm and Morgan 1996) and parameterised using soil physical data and data from the dialysis chambers. Fluxes of individual cations were calculated and summed to determine the total flux. These values were compared with the measured fluxes.

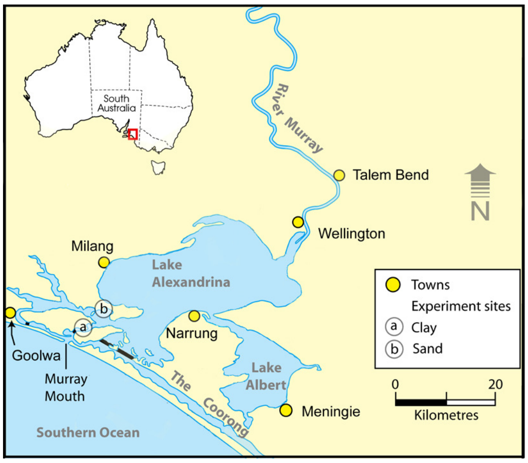

Figure 1. Location map of the study sites.

Results

Flux measurements

The initial acidity flux rate was higher for all sites, soils and treatments. The flux rate for the seawater treatments was also higher (Figure 2). This agrees with laboratory studies (Simpson *et al.* 2009) which found higher concentrations of toxic metals and metalloids in the overlying water for soil corer-reactors and sea water. A possible explanation for the difference between the fresh and sea water treatments is that an initial filling and saturation of the soil profile with the high ionic strength sea water resulted in the acidic cations in efflorescences on the surface, in precipitates, on exchange sites and weakly bound to metal oxides in the near surface being dissolved or displaced directly into the water column. These mobilised acidic cations consume alkalinity and cause an initial sharp drop in alkalinity. This is consistent with the smaller initial change in alkalinity for the fresh water treatment where the initial acid input is likely to be limited to the dissolution of surface efflorescences and sparingly soluble acidic oxidation products in the near surface.

At Pt. Sturt, the higher seepage rate means the water column alkalinity was relatively stable with a small initial decrease likely due to the dissolution of surface efflorescences followed by a later increase due to evapoconcentration. However when alkalinity inputs and seepage losses are taken into account there is a small acidity flux into the water column of 0.007(±0.001) mol $H^+/m^2/d$. For the sandy soil there is a net flux of solutes into the soil profile. This can be observed in the $Cl:SO_4$ ratio (Figure 3). At 0.2 m bgl, the ratio has increased and is approaching the supply water value. For pore water at 0.2 m bgl at 0.5 and 1.0 m bgl, the ratios are decreasing and are approaching the starting value for the water from 0.2 m bgl. This indicates a net flux of solutes from the water column into the soil profile and that the shallow pore water is being displaced by piston flow deeper into the soil profile. Despite the evidence of piston flow, changes in the moisture characteristics of the soil prior to flooding may alter subsoil rewetting characteristics. Additionally the experiment design means that lateral flow was prevented by the tank walls until 1 m bgl. Despite the advective flux of surface water into the soil profile, the pH of the pore water at 0.2 m bgl remains acid with a pH of ~ 3 and an acidity of ~1 mmol H^+/L for the fresh water treatment and 3 mmol H^+/L for the sea water treatment. In both cases the major component of the acidity at 0.2 m bgl is H^+ (Figure 4) although there is some contribution from Al and Fe in the case of the sea water treatment. The source of these ions is unclear but it is likely that they result from the dissolution of sparingly soluble acid oxidation products.

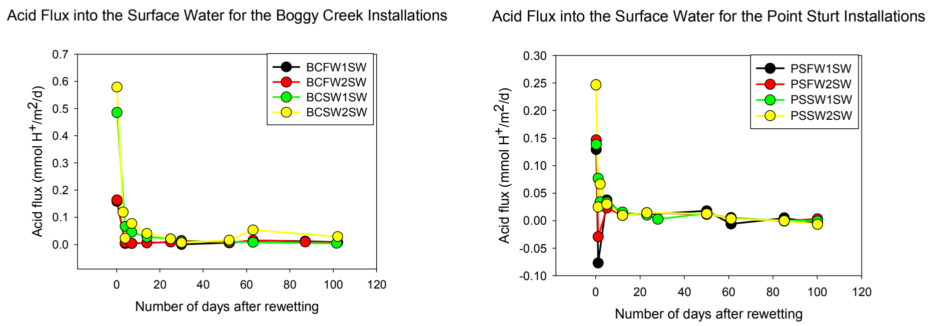

Figure 2 Acid flux rate

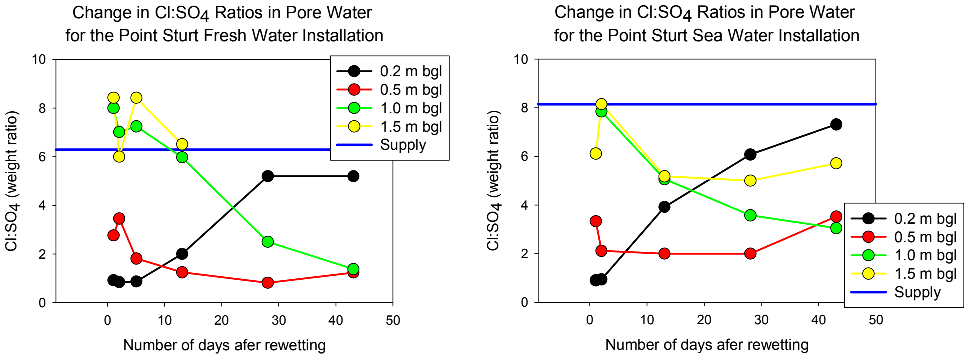

Figure 3 Time series for Cl:SO$_4$ ratios

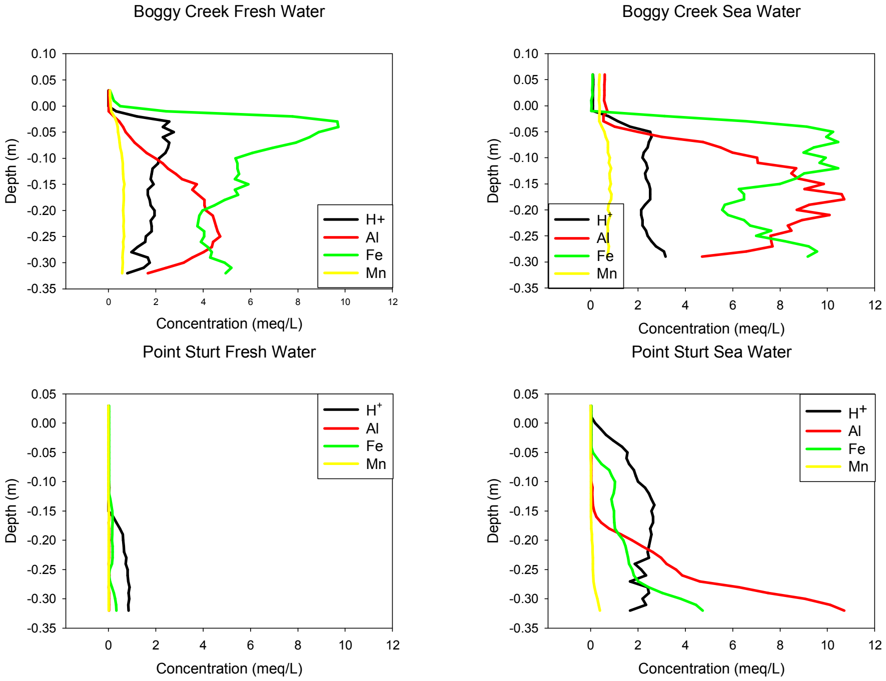

Figure 4 Dialysis chamber profiles for 'acidic' cations

Flux calculations

Examination of the dialysis chamber profiles shows that the major contributors to the acid flux differ between sites. For the clay soil, Fe is the major contributor to the acid flux, whereas for the sandy soil the H^+ is the major contributor (Figure 4). For the clay soil, values for the measured flux rates are two orders of magnitude greater in the case of the initial flux rate and up to an order of magnitude greater for the longer term flux rate. In the case of the sandy soil the net advective + diffusive flux is from the water to the soil, whereas the measured flux is a small flux from the soil to the water column (Table 1). These differences are probably due to the last term in the flux equation, the flux due to solid phases. The solid phase acidity stored in the exposed ASS of the LL is present in a number of forms in both the dry soil and in the unsaturated and saturated zones. In the solid phase, these include sparingly soluble 'acidic' oxyhydroxide and oxyhydroxy sulfate minerals that can accumulate as concentrated surface precipitates as well as more diffusely in the bulk soil. Acidic cations also exist adsorbed to oxides and on cation exchange sites. The precipitates have different solubilities and dissolution rates (e.g. see Bigham and Nordstrom 2000) so that the acid flux on rewetting will have a number of sources that vary in their difficulty to identify and measure. While surface reactions and exchange with iron oxyhydroxides have been incorporated into models (see Appelo and Postma 2005) in general the ability to reliably predict such solid phase flux terms is limited.

Table 1 Calculated and measured flux rates (mol $H^+/m^2/d$). Negative values indicate flux from the soil to the water column and positive values flux from the water column to soil.

Location	Calculated			Measured	
	Acid	Alkalinity	Net		
Boggy Ck.				Day 1	Day 7+
Fresh water	-1.5×10^{-2}	2.2×10^{-3}	-1.3×10^{-3}	$-1.61\pm0.02\times10^{-1}$	$-10\pm1\times10^{-3}$
Sea water	-1.1×10^{-2}	2.1×10^{-3}	-8.5×10^{-3}	$-5.3\pm0.5\times10^{-1}$	$-14\pm1\times10^{-3}$
Pt. Sturt				Day 1	Day 5+
Fresh water	-5.4×10^{-4}	3.6×10^{-2}	3.5×10^{-2}	$-1.38\pm0.09\times10^{-1}$	$-7\pm1\times10^{-3}$
Sea water	-6.1×10^{-4}	2.1×10^{-2}	2.0×10^{-2}	$-2.8\pm0.3\times10^{-1}$	$-7\pm1\times10^{-3}$

Conclusion

The acidity stored in the exposed ASS is present in a number of forms in both the dry soil and in the unsaturated and saturated zones. In the solid phase, these include sparingly soluble oxyhydroxide and oxyhydroxy sulfate minerals that can accumulate as concentrated surface precipitates as well as diffusely in the bulk soil. Acidic cations also exist adsorbed to oxides and on cation exchange sites. Following rewetting this acidity can be transported into the water column or the soil profile. The precipitates have different solubilities and dissolution rates so that the acid flux on rewetting will have a number of sources that vary in their difficulty to identify and measure. While the decrease in water column alkalinity provides a simple direct measure of the net acid flux to the water column, predictive models will require information on solid phase and surface reactions for which the exchange isotherms, cation exchange parameters and solubility terms needed are poorly characterised. Additionally redox changes will ‘dissolve’ iron oxyhydroxides and alter these reactions. van Breemen (1975) produced a conceptual model of these processes in ASS however further research is still required for incorporation of these processes into predictive numerical models.

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Development of bulk density, total C distribution and OC saturation during paddy soil evolution

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Abstract

Considerable amounts of organic matter (OM) are stabilized in paddy soils, and thus a large proportion of the terrestrial carbon is conserved in wetland rice soils. Nonetheless the mechanism for stabilization of total organic carbon (TOC) in paddy soils as driven by redox cycling is largely unknown. The aim of the project is to identify the role of organo-mineral complexes for the stabilization of organic carbon in a chronosequence of paddy soil use and thus duration of management-induced paddy soil formation. Soil profiles were sampled, including paddy sites and non-irrigated control sites. First analyses include bulk density, the TOC and total inorganic carbon (TIC) concentrations of bulk soil and the concentration of organic carbon as well as the organic carbon stocks of physical soil fractions. First results indicate distinctly different depth distributions between paddy and non-paddy (control) sites. The paddy soils are characterized by relatively low bulk densities in the puddled layer (between 0.9 and 1.3 g/cm^3) and high values in the plough pan (1.4 to 1.6 g/cm^3) and the non-paddy soils by relatively homogeneous values throughout the profiles (1.3 to 1.4 g/cm^3). In contrast to the carbonate-rich non-paddy sites, we found a significant loss of carbonates during paddy soil formation, resulting in decalcification of the upper 20 cm in 100 y old paddy soils, and decalcification of the total soil profile in 700, 1000 and 2000 y old paddy soils. The calculation of the organic carbon stocks of each horizon indicate that paddy sites have always higher values in top-soils compared to non-paddy sites, and show increasing values with increasing soil age. The capacity of fine soil fractions to preserve OC was calculated by using the formula of Hassink (1997). With increasing duration of paddy soil use, the fine fractions indicate an increasing saturation level of the potential capacity to preserve OC.

Key Words

Soil organic matter (SOM), particle size fractionation, top-soil, OC-saturation.

Introduction

Paddy soils are described as important accumulator for OM (Zhang and He 2004). In southeast China, paddy soils have the second highest OM stocks (Zhao *et al.* 1997). The paddy soil management is believed to be favourable for accumulation of organic matter, as its content in paddy soils is statistically higher than that of non-paddy soils (Cai 1996). However, the mechanism of OM storage and the development of OM distribution during paddy soil evolution are largely unknown. Soil chronosequences are valuable tools for investigating soil development processes. In the Zhejiang province (Yangtze River Delta, China), during the past 2000 years new farmland was created through consecutive land reclamation by protective dikes. The construction of the dikes is historically well-dated and provides the unique chronosequence of soil formation under agricultural use. Parts of the land were used for paddy rice, other parts for a variety of non-irrigated crops (non-paddy sites).This provides the unique opportunity to document the effect of soil redox conditions over long time periods on the evolution and distribution of soil organic matter (SOM) properties during pedogenesis.

Methods

Study area

The study sites are located around Cixi (30° 10′ N, 121° 14′ O), Zhejiang province in the eastern part of PR China. During a joint sampling campaign in June 2008, soil profiles of the following chronosequence were sampled, including paddy sites (a) and non-paddy sites (b): 50 y (a+b), 100 y (a+b), 300 y (a+b), 500 y (a+b), 700 y (a+b), 1000 y (a) and 2000 y (a). The soils are described in more detail by Cheng *et al.* (2009).

Basic soil parameters

Total carbon concentrations (C_{total}) of each soil sample were determined in duplicate by dry combustion at 950°C on a Vario EL elementar analyser (Elementar Analysensysteme, Hanau, Germany). Using the same elemental analyser, total inorganic carbon (TIC) of bulk soil material was analysed after 4 h in a muffle furnace at 550 °C to remove TOC. The TOC concentration was calculated by subtracting the concentration of TIC from the C_{total} (equation 1):

$$C_{total} - TIC = TOC \text{ (mg/g soil)} \qquad (1)$$

The bulk density (bd) was calculated by dividing the mass of oven dry soil by the core volume. The organic carbon stock for each horizon of each paddy and non-paddy profile was calculated according to equation 2. For each soil profile, the carbon stocks were added up with soil depth in order to present the stocks as cumulative curves.

$$\text{OC stocks (kg/m}^2\text{)} = \text{OC (g/kg)} * \text{bd (kg/dm}^3\text{)} * \text{depth (cm)} * 10^{-2} \qquad (2)$$

Particle size fractionation and OC storage capacity of fine mineral fractions

Particle size fractionation was done according to Schöning *et al.* (2005); using a first ultrasonic treatment with an energy input of 60 J/ml to destroy macroaggregates (> 200 µm) and entire dispersion of microaggregates (< 200 µm) was achieved with an additional ultrasonic treatment (440 J/ml). The fraction less then 20 µm was further separated by using sedimentation in an Atterberg cylinder. Weight proportion and OC concentration for each soil fraction was determined. The OC saturation level of the particles < 20µm was calculated and compared with the potential storage capacity to preserve OC by using the formula of Hassink (1997) (equation 3):

$$\text{OC in fraction} < 20\ \mu\text{m} = 4.09 + 0.37 * \%\ \text{particles} < 20\ \mu\text{m} \qquad (3)$$

Results

Depth distribution of TIC, TOC and bulk density as well as organic carbon stocks

The 50 y old paddy site contains carbonates throughout the soil profile. However, top-soils of 100 and 300 y old paddy sites are free of carbonates but there are abrupt higher values below the plough layer. Decalcification of the total soil profiles was observed in 700, 1000 and 2000 y old paddy sites. In contrast, there is nearly no decalcification in non-paddy sites of the total soil profiles. Only the top-soil of the 700 y old non-paddy site is almost free of carbonates. Younger non-paddy sites contain carbonates throughout the soil profiles and show decreasing TIC concentrations with increasing soil age. Conclusively, decalcification requires approximately 700 years in paddy and more than 700 years in non-paddy soils. This result is can be explained by the wetland management. Carbonates were washed out by periodical flooding and drainage of the paddy soils.

Generally, there are higher concentrations of TOC in top-soils of paddy sites compared to non-paddy sites. Within the paddy soil chronosequence, increasing values in top-soils with increasing soil age (except 1000 y old paddy site) were observed. Within the non-paddy sites, there are very low TOC concentrations and slightly increasing values in top-soils with increasing soil age. Differences on TOC accumulation are caused by the paddy soil management and especially by flooding of the fields during rice growth. Under waterlogged conditions, soil OM decomposition and humification (formation of stable humic substances) proceeds at a slower rate than in well-drained, aerated soils.

Bulk densities show low values (between 0.9 and 1.3 g/m^3) in puddled top-soil layers of paddy sites, reflecting the effective soil loosening during puddling. The highest values are measured in the plough pan (1.4 to 1.6 g/m^3). Below the plough pan, slightly decreasing values with soil depth are observed. But there is no differentiation between the age groups. These results confirm a short-term formation of a compacted, permanent plough pan in order to reduce infiltration rates and to increase water use efficiency. The non-paddy sites indicate a more homogeneous distribution of bulk densities (1.3 – 1.5 g/cm^3) and additionally slightly increasing values with soil depth.

Organic carbon stocks of paddy soils

Compared to non-paddy sites, the paddy sites are always characterised by higher OC-stocks in top-soils (Figure 1). While 50 and 100 y old sites indicate relatively similar values, the 300 and 700 y old sites indicate clearly higher OC stocks in paddy compared to non-paddy sites. The 700 y old paddy soil is the site with highest values of OC stocks in sub-soil (except the 300 y old paddy site). The OC stocks of paddy soils increases with increasing soil depth. Apparently OC accumulation with soil depth is more pronounced in paddy compared to non-paddy soils.

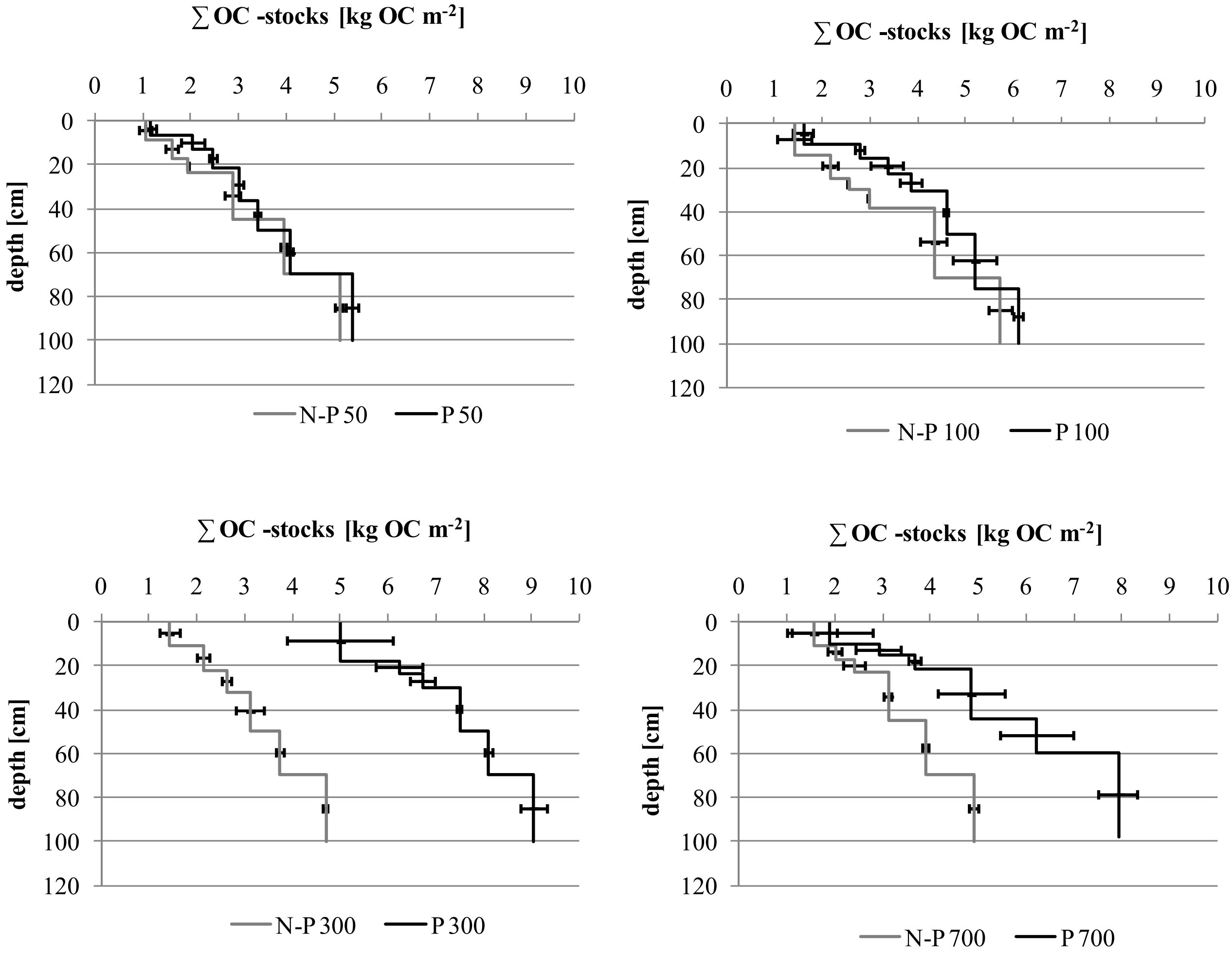

Figure 1. Cumulative OC-stocks of 50, 100, 300 and 700 y old paddy (black) and non-paddy soil profiles (grey). (Error bars show standard deviation of added up OC-stocks of 3 replicates).

Particle size distribution and storage capacity of OC in fine mineral fractions of paddy soils
The distribution of OC in different particle size classes was analysed for A horizons of paddy soils (Table1). The mass proportion of fine fractions (20 µm to < 0.2 µm) is between 70 and 80% of the total bulk soil. The OC concentration of paddy soil ranged from 2.0 in medium silt-sized classes to 55.5 mg/g in clay fractions. The fractions 2 – 0.2 µm and the < 0.2 µm fractions exhibited the highest OC concentrations in almost all age groups.

According to Hassink (1997), the potential capacity of paddy soil fraction to preserve OC is independently from soil age between 30 and 35.5 g OC/(kg soil) (Table 2). However, the calculated saturation level increases with increasing soil age from 10 to 20 g OC/(kg soil). This underlines the importance of fine fractions for increasing OC storage during paddy soil evolution.

Table 1. Particle size distribution after physical fractionation (g/kg) and OC concentrations (mg/g) of fine fractions of 50, 100, 300, 700, 1000 and 2000 y old paddy sites.

Site	Depth	6.3µm – 20µm		2µm – 6.3µm		2µm – 0.2µm		< 0.2µm	
		mass	OC	mass	OC	mass	OC	mass	OC
	(cm)	(g/kg)	(mg/g)	(g/kg)	(mg/g)	(g/kg)	(mg/g)	(g/kg)	(mg/g)
P 50	0-7	422	2.0	113	22.4	185	25.6	82	26.0
P 100	0-9	479	3.6	112	25.3	138	35.6	51	40.1
P 300	0-18	402	4.9	113	37.5	134	47.5	53.6	46.0
P 700	0-10	474	4.7	114	40.4	170	48.2	57	44.5
P 1000	0-9	521	2.2	116	16.0	148	27.6	62	29.1
P 2000	0-15	459	9.8	128	36.3	148	55.5	46.3	55.0

Table 2. Storage capacity of paddy soil fractions to preserve OC.

Site	Depth (cm)	Actual OC saturation (g OC/kg soil)	Potent. capacity to preserve OC Hassink (1997)
P 50	0-7	10.2	33.7
P 100	0-9	11.5	32.9
P 300	0-18	15.1	30.1
P 700	0-10	17.6	34.2
P 1000	0-9	8.9	35.4
P 2000	0-15	19.9	33.0

Conclusions

The faster decalcification of paddy soils compared to non-paddy soils indicates an accelerated soil development under flooding rice cultivation. This comes along with high accumulations of OC concentrations and OC stocks compared to non-paddy soils, as paddy sites indicate higher organic carbon concentrations in top-soils and show also increasing values in top-soils with increasing soil age compared to non-paddy sites. Paddy soils indicate also higher values of organic carbon stocks in top-soil compared to non-paddy sites. In the present study, A horizons are characterised by high proportions of fine mineral fractions (70 to 80% of particles < 20 µm). The calculated OC saturation levels of the fine fractions strongly increase with increasing soil age. This underlines the importance of fine fractions for increasing OC storage during paddy soil evolution. Further investigations will help to clarify how far potential OC storage capacities of fine fractions can be saturated during paddy soil development. Conclusively, paddy soil management leads to an accelerated soil development compared to non-irrigated cropland sites. In addition, increasing OC stocks, especially in the fine mineral associated OM fractions underline the relevance of paddy soil management for OC sequestration.

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Distribution and stabilization of organic carbon in Danubian floodplain soils

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Abstract

Floodplain soils are assumed to act as sinks for organic carbon (OC). To date, our knowledge on OC distribution and stabilization in these soils is only weak. We investigated OC stocks at 76 sampling sites in the Danubian floodplains and conducted density fractionation of selected soil samples. The soils were found to contain huge stocks of OC. The distribution (horizontal and vertical) of OC stocks and other soil properties is highly heterogeneous and determined by sedimentation dynamics. First results of density fractionation of organic matter (OM) and aggregate stability tests indicate that soils developed under different sedimentation conditions differ in the relevance of the different OM stabilizing mechanisms. Occlusion of OM within aggregates is more important in soils developed under dynamic sedimentation conditions, whereas formation of organo-mineral complexes is determining OM stabilization in soils developed under static sedimentation conditions. Testing aggregate stability is crucial to assess OM stabilization.

Key Words

Riverine floodplains, carbon sequestration, density fractionation, aggregate stability, ultrasound.

Introduction

Mineral soils of riverine floodplains often hold high stocks of organic carbon (OC) in both topsoil and subsoil horizons and are assumed to act as sink for OC (Batjes 1996). Two different mechanisms of OC enrichment are important in these soils: the sedimentation of allochthonous OC rich material during flood events (Pinay *et al.* 1992) and the above-average production of biomass within the floodplains (Giese *et al.* 2003, Naiman and Décamps 1997). To date, little data on the spatial distribution (horizontal and vertical) of OC and the mechanisms of organic matter (OM) stabilization in these soils is published. Aims of the study presented are to determine the distribution of OC stocks in the floodplains of the Danube river and to identify the influence of sedimentation dynamics on OM stabilization. In this context, we focus on the stabilization of OM within aggregates.

Methods

Investigation area and soils

Our study site is located in the "Donau-Auen National Park" near Vienna (Austria), one of the few remaining near-natural floodplain landscapes in Europe. Soils and vegetation were surveyed at 76 sites within an area of roughly 1.300 ha representing the typical riparian forest ecosystem of the national park (Figure 1). Vegetation structure and sedimentation dynamics were found to be closely related to each other. Using vegetational and geomorphological variables we identified a gradient in sedimentation dynamics (Cierjacks *et al.* in press). In addition, the horizons of seven soil profiles along this gradient were sampled.

OC stocks

Soil carbon content was determined in milled soil samples using a catalytic dry combustion CN-Analyser (Elementar®). Organic carbon content was calculated as the difference of total carbon content and carbon content of combusted (550°C) soil samples following Bisutti *et al.* (2006). OC stocks were calculated for each soil horizon based on OC concentration and bulk density.

Determination of OM stabilizing mechanisms

We run a density fractionation basically described by Golchin *et al.* (1994) and Grünwald *et al.* (2006) with the soil samples to fractionate organic matter (OM) based on its binding mechanism to soil components. Hereby, we are able to identify the amount of free, particulate organic matter (fPOM), intra-aggregate particulate organic matter (iPOM) and organic matter associated to mineral surfaces (MOM). These operationally defined fractions differ in their grade of stability against mineralization and OM turnover times, consequently (von Lützow *et al.* 2006). The air-dried and sieved (< 2mm) bulk soil was put into sodium polytungstate (SPT) solution with a density (ρ) of 1.6 g/cm^3. The fPOM fraction was separated in the first step (ρ <1.6 g/cm^3), afterwards soil aggregates were destroyed by applying an adjusted amount of ultrasonic induced energy. The released iPOM fraction (ρ <1.6 g/cm^3) was removed and MOM (ρ >1.6 g/cm^3) remains within the SPT solution.

Determination of aggregate stability
In a further experiment we will determine soil aggregate stability. We will use a standard ultrasonic device (Branson W-250®) and a high-precision ultrasonic device described by Mayer *et al.* (2002) which allows to determine the emitted energy by measuring the vibration amplitude. We will analyze dispersed particles after exposure to different amounts of energy. This will help to identify and to classify different energies of aggregate bonding. The data will be linked to the investigation on OM stabilization mechanisms.

Results

OC stocks in Danubian floodplains
Organic carbon stocks in the investigation area ranged between 42 and 354 t/ha (1 m in depth) with an average of 177 t/ha (distribution is shown in Figure 1). Large OC stocks are mainly found at sites with static sedimentation conditions. These stocks are huge compared to other terrestrial ecosystems (tropical rain forest 122-123 t/ha, temperate deciduous forest 96-147 t/ha, data taken from Prentice *et al.* 2001) and reveal that the area acts as a sink for OC. The large amount of OC sequestrated in the investigated floodplains is in line with findings of other studies on the OC sequestration potential of riverine floodplain soils (e.g. Giese *et al.* 2003).

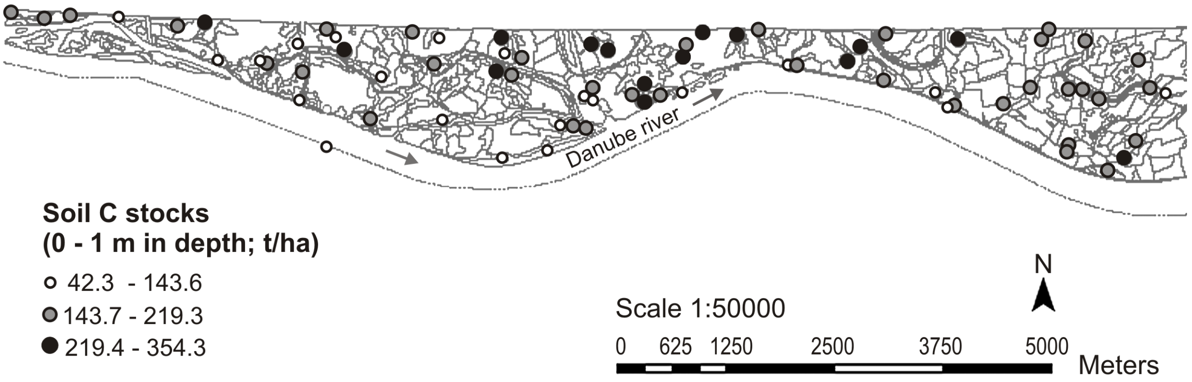

Figure 1. Distribution of OC stocks in the study area at the Danubian floodplains.

Aggregate stability in floodplain soils
First results show that aggregate stability varies among the investigated soils (Figures 2 and 3). Soil 1 contains the most stable aggregates: An application of 400 J/mL still causes disruption of aggregates (OM mass yield, see Figure 3) without releasing OM from mineral surfaces (OC content 30 to 37 %, Figure 2). Soil 2 contains aggregates of lower stability. After applying energy of 100 J/mL iPOM is released (OM mass yield found, OC content 35%), whereas higher energies obviously lead to a dispersion of soil minerals and lower OC contents and no significant mass yields, consequently. Soil 3 reveals the least stable aggregates. The application of 50 J/mL releases POM occluded within aggregates (OM mass yield found, OC content 41%), higher energy levels cause the release of OM from mineral surfaces as indicated by decreasing OC contents and the absence of additionally extracted material.

OM stabilizing mechanism in floodplain soils
Results of density fractionation carried out with samples of topsoil and subsoil horizons developed under static and dynamic sedimentation conditions are shown in Figure 4. In all soils the distribution of recovered OC decreased in the following order: MOM >> iPOM > fPOM. All subsoil samples contain a lower relative amount of POM (fPOM and iPOM) than found in topsoil samples. Soils developed under dynamic sedimentation conditions are characterised by higher portions of recovered OC found occluded in aggregates compared to soil deriving from more static sedimentation conditions. Higher portions of occluded OC suggest a higher importance of aggregate formation for OM stabilization under dynamic than under static sedimentation conditions. As opposed to that association of OM to mineral surfaces is more dominant in soils developed under static sedimentation conditions.

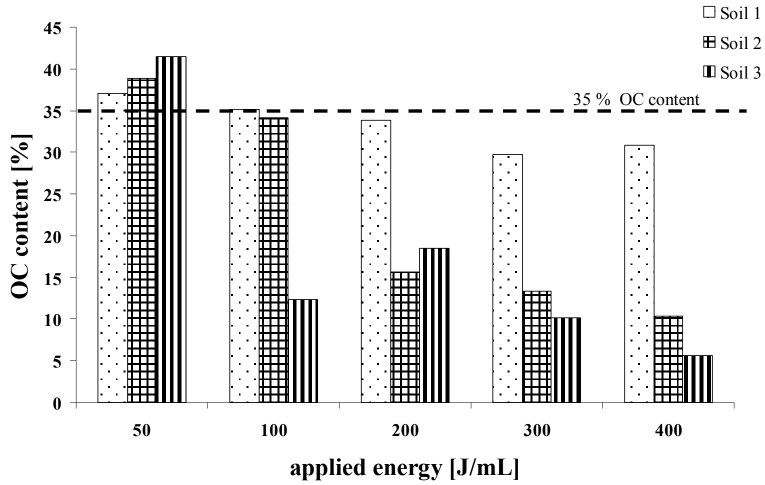

Figure 2. OC content [%] of material gained after application of different amounts of ultrasonic energies. Soils representing different aggregate stability are shown.

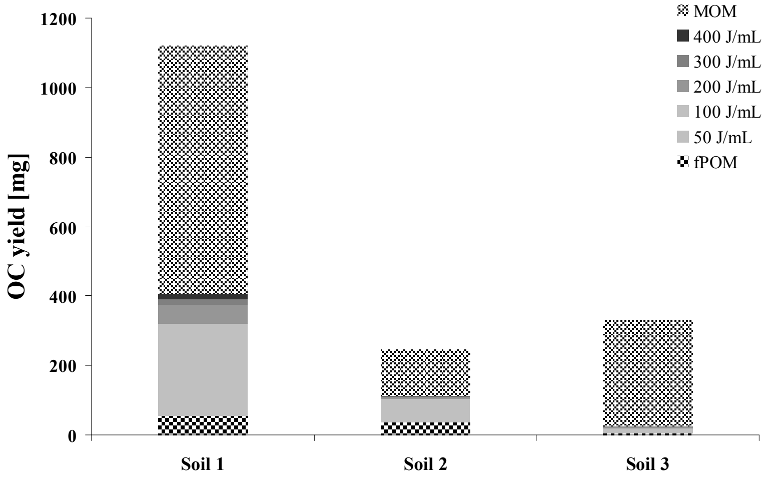

Figure 3. OC mass yield after density fraction and different energy levels to obtain aggregate occluded POM. Soils representing different aggregate stability are shown.

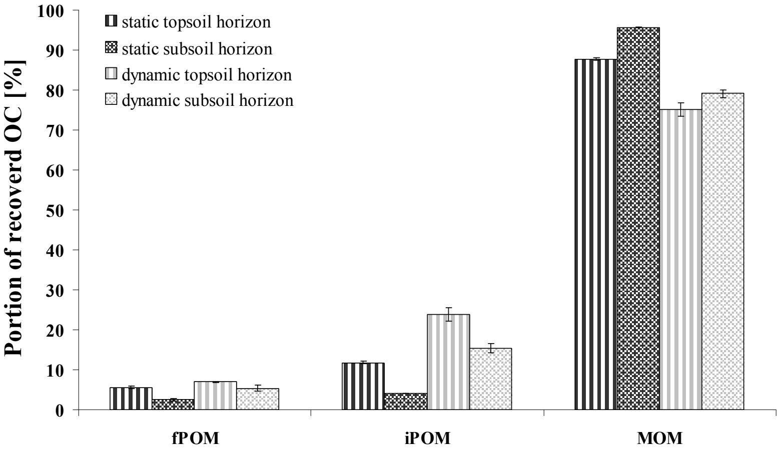

Figure 4. Distribution of recovered OC between fPOM, iPOM and MOM of topsoil and subsoil horizons developed under static and dynamic sedimentation conditions, respectively.

Conclusion

Sedimentation conditions control OM distribution (horizontal and vertical) and stabilization, as well as aggregate stability. For the assessment of the OC sequestration potential sedimentation conditions have to be considered. With focus on the importance of aggregates for overall OM stabilization ultrasonic experiments will help to understand the differences between 'static' and 'dynamic' sites.

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Impacts of sea level rise on the biogeochemistry of a coastal floodplain in eastern Australia

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Abstract

The effect of seawater inundation on the biogeochemistry of coastal floodplain soils was examined by subjecting intact soil cores to 0%, 50% or 100% dilutions of synthetic seawater. Soil cores sampled from a natural levee were slightly acidic, non-saline and showed a slight decrease in pH following inundation (eg. 7.41 to 6.73 in the 100% seawater treatment) and limited mobilisation of Fe^{2+} in the overlying waters in all treatments. Soil cores sampled from a scald were acidic, saline with high concentrations of soluble and exchangeable Al. Following inundation, there was a slight decrease in pH and limited mobilisation of Fe^{2+} in the overlying waters. Soil cores sampled from throughout the backswamp on the floodplain were saline, acidic with high concentrations of exchangeable Al. In most of the backswamp soil cores, pH decreased following inundation with seawater, with the greatest decreases occurring with the 50% seawater treatment. Fe^{2+} concentrations generally increased with time in the backswamp soils. These results have implications for surface water quality when these coastal floodplain wetlands are subjected to seawater or brackish water inundation as a result of sea level rise, storm surge or king tides.

Key Words

Climate change, seawater inundation, coastal lowland acid sulfate soil.

Introduction

Sea level has risen approximately 1.2 mm/year over the last 100 years (Hennessy *et al.* 2004) and is predicted to rise up to 80 cm by 2100 relative to 1990 sea levels (IPCC 2007). The number of extreme events related to sea level such as higher sea levels and increased inter-annual variability have also increased in frequency in the same time period (Hennessy *et al.* 2004). Coastal lowland acid sulfate soils (CLASS) are estimated to cover approximately 12-13 million ha globally (Andriesse and van Mensvoort 2006). These areas commonly occur at or below sea level (≈ 0 m Australian Height Datum; AHD) and are highly susceptible to pulses of saline water caused by saltwater intrusion, storm surge, king tides and rising sea levels.

Many Holocene coastal floodplains in eastern Australia contain large, low elevation (0-1 m AHD) backswamp basins which were originally semi-permanent wetlands and natural floodwater storage basins (Tulau 1999). These backswamp basins are frequently underlain by CLASS and sulfidic sediments. Following European settlement of the floodplains in the late 19th century (Tulau 1999), there has been extensive modification of the floodplain through the construction of drainage systems and expansion of agriculture (Johnston *et al.* 2003). This process has enhanced drainage of the floodplains and resulted in oxidation of CLASS and abundant surface accumulation of reactive Fe minerals (Dent 1986). The construction of extensive drainage systems has increased the susceptibility of the floodplain to seawater inundation by increasing connectivity to the estuarine channel.

Previous studies have shown inundation of CLASS can mobilise trace metals, which has implications for water quality in these floodplain wetland environments (Burton *et al.* 2008). However, controlled tidal exchange in degraded tropical floodplains can neutralise acidity and re-establish reductive environments to aid in reclamation of these areas (Johnston *et al.* 2009). The biogeochemical processes which occur at the surface water-soil interface following seawater inundation of CL ASS are complex and will only increase in importance in the future with predicted increases in sea levels. This study aims to determine the surface water-soil interactions over the short term following seawater inundation in coastal floodplain backswamps containing CLASS.

Methods

Field sampling and site description

Intact soil cores were sampled from the floodplain in the Rocky Mouth Creek (RMC) sub-catchment of the Richmond River in the sub-tropical region of eastern Australia. Rocky Mouth Creek is subject to regular tidal movement and joins the Richmond River at Woodburn, approximately 42 km upstream of the river mouth. The floodplain in the RMC sub-catchment is characterised by extensive, well-developed natural levees grading into a large backswamp basin with elevations mostly < 1 m AHD. Cores were sampled from six sites on the floodplain; natural levee (Le), scald (Sc) and four backswamp sites (Bs1, Bs2, Bs3, Bs4). Vegetation was cut to ground level and intact soil cores were sampled with PVC pipe of diameter 0.1 m. The pipes were driven in to the ground to a depth of approximately 0.2 m, capped, sealed and stored at 4°C until analysis.

Sample preparation and laboratory analysis

Soil cores from each site were inundated for 14 days according to one of three treatments; 0, 50 or 100% synthetic seawater diluted in deionised water. Each treatment was undertaken in triplicate with the mean presented. The synthetic seawater consisted of the major cations and anions found in natural seawater (Cavanaugh 1975) with pH ≈ 8 and EC ≈ 46 dS/m. The 50% treatment was prepared by dilution of the 100% seawater solution and 0% treatment was milli –q water. Each core was inundated to a depth of approximately 0.2 m.

Surface water samples were taken via a port located approximately 0.05 m above the soil surface at 0 hrs, 2 hrs, 24 hrs, 48 hrs, 7 d and 14 d. Dissolved oxygen and pH were measured in situ prior to sampling. Samples were analysed for major cations, metals, and aqueous Fe and speciation. Major cations and trace metals were determined on the extracts by ICP-MS. Aqueous Fe speciation was determined using 1, 10-phenanthroline (APHA 2005). Fe^{3+} was determined from the difference between total Fe and Fe^{2+} following reduction with hydroxylammonium chloride.

Bulk soil from each site was also characterised. Soils were oven-dried at 40°C for 48 hours and lightly crushed to pass through a 2 mm sieve. Soil pH, EC and soluble cations were determined on 1:5 soil:water extracts (Rayment and Higginson 1992). Soil organic C and N were determined by high combustion LECO analysis. Exchangeable cations were extracted with 1:5 soil:2M $BaCl_2/NH_4Cl$. Where the $EC_{1:5} \geq 0.3$ dS/m, soluble salts were removed by washing three times with an ethanol/glycerol solution (Rayment and Higginson 1992). Soluble and exchangeable cations were determined by ICP-MS.

Results and discussion

Selected soil characteristics of the sampled cores are shown in Table 1. The Le soils were non-saline, slightly acidic and had the lowest concentrations of SOC, total N and exchangeable Al. The Sc soils were acidic, saline with high concentrations of soluble and exchangeable Al. Soil cores sampled from the backswamp on the floodplain (ie. Bs1-Bs4) were saline, acidic with high concentrations of exchangeable Al.

Table 1. Soil characteristics from each site.

Site	$EC_{1:5}$ (dS/m)	$pH_{1:5}$	SOC (%)	Total N (%)	Soluble Fe (mg/kg)	Soluble Al (mg/kg)	Exchangeable Fe (mg/kg)	Exchangeable Al (mg/kg)
Le	0.12	5.45	4.12	0.39	81.77	69.81	nd	63.21
Sc	0.56	3.83	5.36	0.42	115.95	3959.27	nd	8567.95
Bs1	1.35	3.66	6.34	0.46	10.65	1016.03	nd	8572.84
Bs2	1.16	4.14	7.87	0.61	16.21	152.83	nd	2730.09
Bs3	0.62	4.56	5.72	0.39	2.10	11.72	nd	2607.88
Bs4	0.67	4.40	9.62	0.76	13.46	78.56	nd	3911.86

Note: nd indicates not detected

Following inundation, the surface waters of the Le soils were circumneutral and showed a slight decrease in pH in all treatments (Figure 1). In the Sc soils, pH rapidly became acidic and showed a slight decrease following inundation. The lower pH at the beginning of the inundation period compared to the other soils is due to the dissolution of acidic salts on the surface, as salt efflorescence was present at the time of sampling. pH in Bs1, Bs2 and Bs4 decreased in all treatments following inundation. The initial decrease in pH in the 50% and 100% seawater treatments is likely to be the result of ion exchange of protons and acidic metal cations of the surface sediments following addition of a higher ionic strength solution. However, Bs3 did not show the same pattern after inundation. pH decreased slightly to Day 2, and then increased in all treatments at this site.

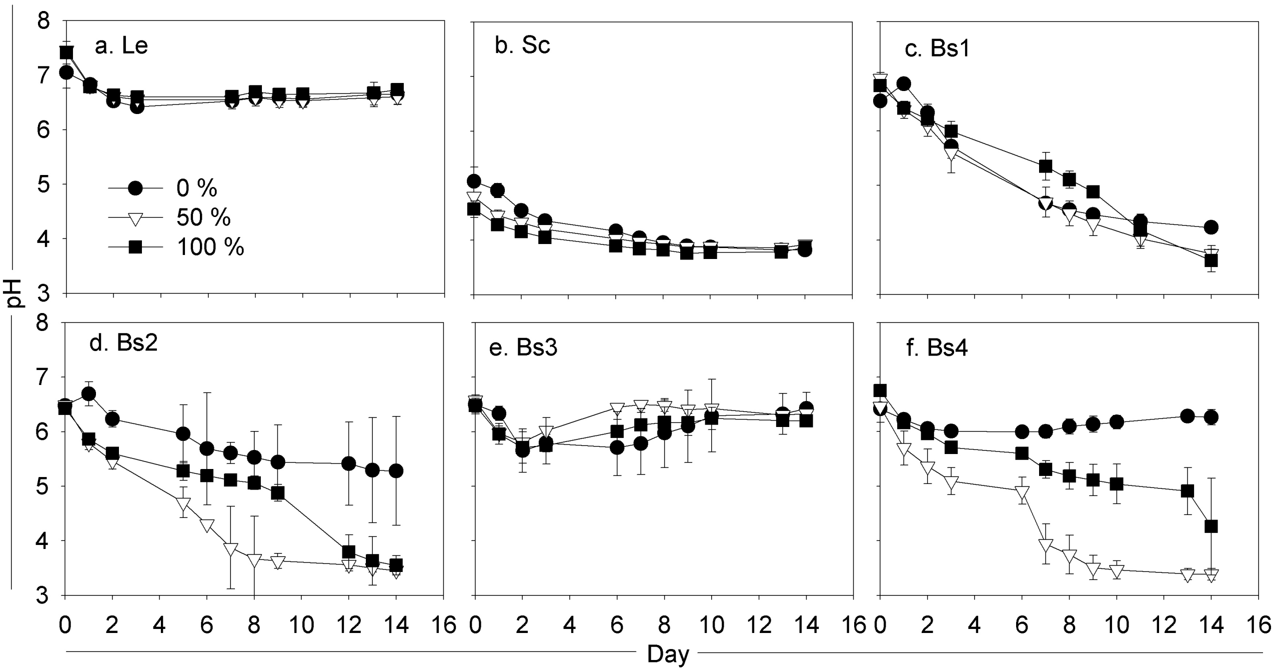

Figure 1. Change in pH over time following inundation with 0%, 50% and 100% seawater in a) Le; b) Sc; c) Bs1; d) Bs2; e) Bs3; and f) Bs4 soils. Vertical bars indicate standard deviation.

When detected, aqueous Fe concentrations were dominated by Fe^{2+} in all treatments at all sites. There was limited mobilisation of Fe^{2+} in the overlying waters of the Le and Sc soils across all treatments following inundation (Figure 2). In the backswamp soils, the highest concentrations of Fe^{2+} were found in 100% seawater treatment. Across all treatments, Fe^{2+} concentrations were highest in the Bs3 soils.

Anoxic conditions were establishing during the inundation period in the Bs3 soils in the 50% and 100% treatments, while the overlying waters from all other sites remained oxic (data not shown). Increasing Fe^{2+} concentrations with time and with increasing salinity in the backswamp soils is most likely the result of reductive mobilisation of metastable Fe-oxide minerals such as schwertmannite (Burton *et al.* 2007). These minerals commonly occur in floodplain backswamp environments in eastern Australia.

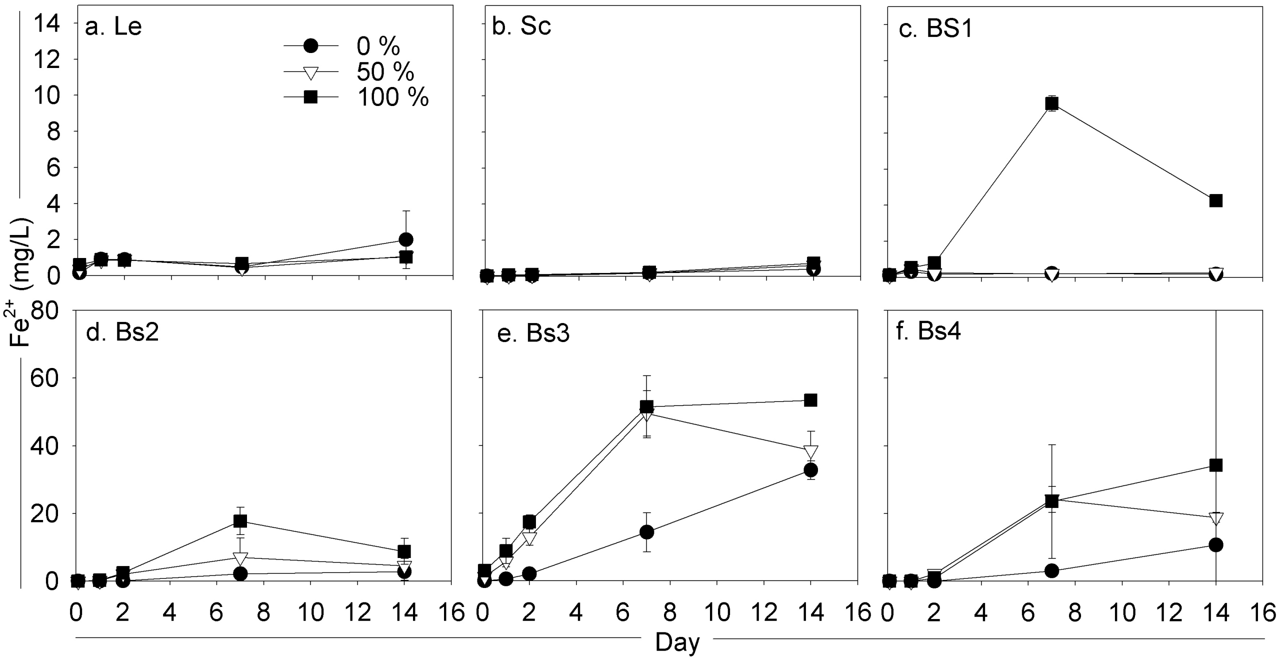

Figure 2 Fe^{2+} concentration in the overlying waters following inundation with 0%, 50% and 100% seawater in a) Le; b) Sc; c) Bs1; d) Bs2; e) Bs3; and f) Bs4 soils. Vertical bars indicate standard deviation.

The decrease in pH in the 50% and 100% seawater treatments has implications for water quality as a consequence of sea level rise. These experimental results suggest that over the short term, inundation with seawater or brackish water can result in a lowering of pH and an increase in concentration and mobility of Fe^{2+} and other trace metals in solution. These experiments were complimented with additional batch experiments, which were used to illuminate key processes occurring in the intact soil cores (Wong *et al.* 2010). In the batch experiments, trace metal concentrations increased and pH decreased with increasing seawater concentration. This is consistent with metal desorption via competitive exchange with marine-derived base cations and hydrolysis of acidic metal cations.

This study shows that seawater inundation of these backswamp basins initiates two distinct, sequential geochemical processes with different kinetics. Both of these processes influence acidity and trace metal behaviour in contrasting ways. It has been assumed that inundation with seawater and the alkalinity contained within will promote proton consuming processes, resulting in an increase in pH. Over longer time periods, prolonged seawater inundation will result in a shift to reducing conditions (eg. Johnston *et al.* 2009). However, experimental results show that a pulse-release of acidity and mobilisation of trace metals will occur in the shorter term during the transition to reducing conditions.

Acknowledgements

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Indicator of reduction in soils (IRIS) for wetland identification in Queensland

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Abstract

A large proportion of Queensland's wetlands are seasonal and ephemeral in nature. Identifying these wetlands is complex as field indicators (such as soil features and hydrophytic vegetation) may only be present at times of saturation. The Indicator of Reduction in Soils or IRIS method was developed in the USA (Castenson and Rabenhorst 2006, Jenkinson and Franzmeier 2006, Rabenhorst and Burch 2006). The method uses synthetic iron oxides painted on PVC pipes to determine whether a soil is in a reduced state. Trials were conducted at 8 wetlands in Southeast Queensland to assess the applicability of the IRIS method in reflecting reduced conditions in soils, to assist in wetland identification. The zone of saturation in a soil profile was the most influencing factor in indicating reduced conditions through the removal of iron oxide paint. An area over the entire surface of PVC pipe which has 15% removal of iron oxide paint within 0.3 m of the soil surface is recommended as confirmation of reducing conditions, sufficient to support evidence of a wetland soil in Queensland. It is proposed that the IRIS method be utilised as an additional line of evidence to identify wetland soils at sites where soil features are lacking, or where evidence of a current hydrologic regime is required.

Key Words

IRIS, wetland soils, identification.

Introduction

Wetland legislative regimes in Queensland rely on the clear identification and delineation of wetlands to support management policies. Indicators that reflect hydrology, and are relatively unchanging once formed, are more useful for wetland identification. Direct observation of inundation or water table heights is the most accurate way to identify a wetland. This process however is not practical as it requires long periods of time to monitor accurate trends in water levels. Hydrophytic vegetation and soil features can reflect current hydrologic regimes and are used for wetland identification in Queensland currently.

Extensive ephemeral wetlands are present in the arid and semi-arid interior regions of Queensland and many wetlands in the tropical and sub-tropical climatic regions are only seasonally saturated. The definition of a wetland in Queensland (EPA 2005), was specifically tailored to capture the episodic nature of these wetlands, using terminology such as 'periodic' and 'intermittent' (EPA 1999). The periodic nature and variable extent of these wetlands affects their accurate mapping, as the boundaries can change from season to season or over several years. The problem with identifying these wetlands is that field indicators (such as soil features and hydrophytic vegetation) may only be present at times of saturation and change during drier times.

A wetland soil in Queensland is defined as having '*a substratum which is predominantly undrained soils that are saturated, flooded or ponded long enough to develop anaerobic conditions in the upper layers'* (EPA 2005). The *'upper layer'* depth is recommended to be 0.3 m (Bryant *et al*. 2008). In order to define whether a soil is a wetland soil there needs to be anaerobic conditions or indicators of anaerobic conditions present. An anaerobic environment can alter the chemistry of soil and this is reflected in soil morphological characteristics. Some characteristics conclusively identify a wetland soil (organic materials, acid sulphate soil material and gleyed soil matrix colours). Other features, like redox features (presence of mottles, segregations (iron and manganese), ferruginous root channel and pore linings, and decreasing matrix chroma), can be indicative of a wetland soil but not irrefutable (Bryant *et al.* 2008). Some soil features can form and persist in the environment which can be problematic as they may be relict features that do not reflect current hydrology. The identification of wetland soils is complex where soil indicators are not readily identifiable or where the interpretation of soil indicators requires evidence of a current hydrologic regime. This situation is commonly found within seasonal and ephemeral wetlands in Queensland.

The Indicator of Reduction in Soils or IRIS method was developed in the USA (Castenson and Rabenhorst 2006, Jenkinson and Franzmeier 2006, Rabenhorst and Burch 2006). The method is used to determine whether a soil is in a reduced state without relying on less conclusive visual soil indicators or using equipment which is time consuming and expensive. This method involves the use of synthetic iron oxides (predominantly ferrihydrite) to indicate the presence of reducing conditions in soils. PVC pipes are coated with a paint prepared from a synthetic iron oxide, and placed in the soil. Upon removal, the pipes are visually assessed for the loss of the iron oxide paint from the surface which indicates that reduced conditions are present. The objective of the study was to test the IRIS method and its interpretation procedures under Queensland conditions, to assess it's applicability in assisting with wetland identification. The IRIS method was trialled at 8 palustrine, seasonally inundated wetlands in Southeast Queensland in order to examine:

the time necessary for this test to be conducted in periodically inundated wetlands to provide an accurate representation of reducing conditions
the effect of different soils and soil conditions on the amount and pattern of reduction that occurs
the level of reducing conditions required to determine the presence of a wetland soil in Queensland
the applicability of the method across differing climatic regions and landscapes (as Queensland's wetlands and landscapes are much drier, variations on the method may be required for its use)

Methods

Site sampling

Transect sampling was used to assess the changes in paint removal from sites within the saturated zone of the wetland to sites considered external to the wetland. This method is the same employed by Bryant *et al.* (2008) when developing the methodology for wetland soil indicator use in Queensland. The three zones within the transect were categorised:

1) Saturated zone: The wettest lowest-lying area. For wetlands that were dry when sampled, this was the lowest part of the wetland that could be accessed. For wetlands that were inundated when sampled, this is the area at the water's edge.
2) Transition zone: This area appeared to be inundated intermittently or seasonally, with evidence of saturation through vegetation or landform features.
3) Outer zone: Above the high-water mark, no evidence of inundation at any time.

Soils were described at each site (or zone) to a depth of 1.0 m where possible and laboratory analysis was conducted for each soil profile with samples taken at 0.0-0.1 m and 0.2-0.3 m. Descriptions of microrelief, surface characteristics and water table heights were recorded. Each soil sample was analysed for pH, electrical conductivity (EC), nitrate (NO^{3-}), chloride (Cl^-), total carbon (TC) and total nitrogen (TN).

Pipe preparation

PVC pipes were cleaned first with acetone to remove any ink and then sanded with fine sandpaper (100 grit). Pipes were then cut to 600 mm lengths with the lower 500 mm painted with ferrihydrite paint. Pipes were painted with 2 coats with the first coat left to dry overnight. The paint was then tested for durability by trying to wipe the paint off with a finger (Jenkinson and Franzmeir 2006).
A method was devised to minimise paint loss from the surface of the pipes upon installation and removal. An unpainted pipe of the same length and width was first placed in the soil, removed and replaced by a painted pipe, in one movement attempting not to rotate the pipe (Bryant *et al.* 2008).

Up to 7 pipes were installed at each site to 0.5 m deep (where possible) in a random layout across an area approximately 1 m^2. To assess the length of time necessary for the IRIS method to provide an accurate representation of the redox status of a wetland, trials were run over 2 different periods (14 days and 28 days). Upon removal each pipe was washed down with water to remove any loose soil and then allowed to dry. Pipes were photographed by rotating them 120^0 to obtain 3 images which covered the entire surface. Photographs of the pipes were put together in Adobe Photoshop CS2 to form a single image (Jenkinson and Franzmeir 2006). A visual estimate of the percentage of paint removed was undertaken using standard charts (Castenson and Rabenhorst 2006). Two people independently assessed the percentage of paint removed and these figures were averaged for each pipe and site.

Results

A larger percentage of paint was removed from sites in the saturated zone compared with sites in the transition or outer zone across all 8 wetlands (figure 1). Sites which had a considerable amount of paint removed (>60% within the surface 0.3 m) were in areas which were inundated at some stage during the trials. The water table, at all wetlands, dropped during the trials. For several wetlands this had an effect on the zone of saturation within 0.3 m of the soil profile. Wetlands that were inundated or had water tables remain at or within 0.3 m of the surface had the largest amount of paint removed.

At sites where there was less than 2% of paint removed the water table had dropped below 0.3 m after 28 days. There was no distinct trend in the percentage removal of paint between the 14 or 28 day trial durations. The largest difference was at sites that were inundated throughout the trial. These pipes had a larger percentage of paint removed after 28 days.

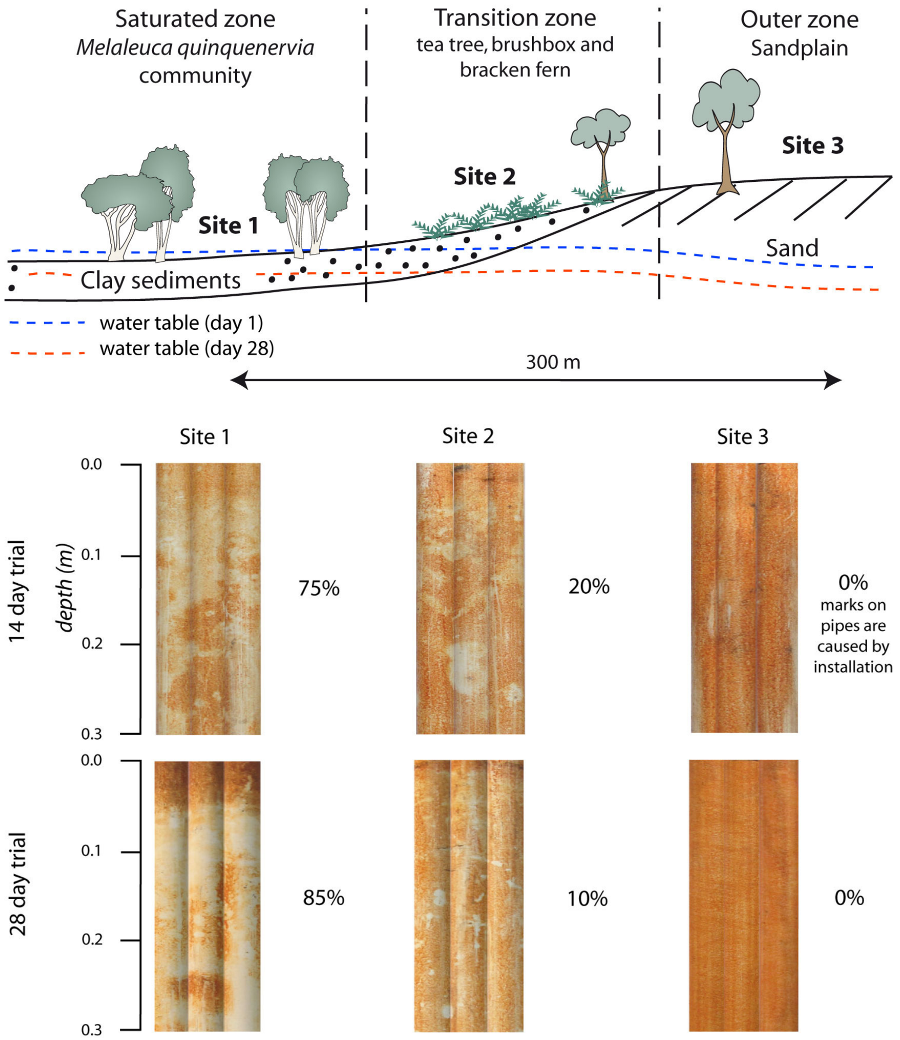

Figure 5. Example of one trial site, Bribie Island (Southeast Queensland): Average percentages of iron oxide paint removed from sites along transect.

The different soils types (sands, clays and organic dominated soils) do not appear to directly influence the removal of paint from the IRIS pipes. There were similar percentages of paint removed across differing soil types.

Organic carbon levels in the current trials ranged between 20.6% to 0.83% (in the surface 0.1 m) and 8.4% to 0.5% (in the subsurface 0.2-0.3 m). Where paint was removed from pipes organic carbon levels remained above 3.5%. This was however only at sites where there were also sufficient saturation levels for reducing conditions to occur. Soil temperatures were monitored at two trial sites and not fall below 13 C (at a depth of approximately 0.7 m) throughout the course of the trials, which is sufficient for microbial activity (Tiner 1999). It is therefore expected that microbial activity was not limited by temperature at any of the sites as they were located in a similar climatic region (sub-tropical).

Conclusion

The study has demonstrated that the IRIS method can indicate that soils are reducing and that this may assist with wetland identification in Queensland. Presently the method is not recommended to be utilised on it's own as a tool for wetland identification, but as an additional line of evidence to identify a wetland soil in the following situations.

1) Sites where wetland soil features are lacking. This may occur in transitional areas where soil indicators start to drop of the soil profile or in areas where soils are naturally lacking in minerals (particularly iron rich minerals) which form wetland soil features.
2) Sites where soil indicators described still require evidence of a current hydrologic regime, particularly to support the use of redox features in identifying wetland soils.

The most influencing factor in the percentage of paint removed was the zone of saturation within the soil profile. Soils that were completely saturated or were saturated in parts of the profile had the largest removal of paint. Soils which were moist but not saturated had no or very little removal of paint. Conducting this test at a time in which the wetland is not likely to be saturated will not accurately reflect the extent of reduced conditions.

Soil types appear to have minimal direct effect on the IRIS method. They do however influence the rate of transmission of water through a soil. In clay dominated soils water is transmitted slower and may allow water to pool and stagnate. In organic and sand dominated wetlands water movement is faster which may influence the level of aerated water that flows through a wetland and hence the time is takes for iron to become reduced.

A soil may be waterlogged but not become reduced for a long period of time if there is too little organic material (Vepraskas 1998). There are implications to applying the IRIS method in wetlands in the semi-arid and arid regions of Queensland. These wetlands have a lower soil carbon levels than others in Queensland, which would require longer periods of time to become reduced.

An area over the entire surface of PVC pipe which has 15% removal of ferrihydrite paint within 0.3 m of the soil surface (the average of at least 4 pipes installed at any one site) is recommended as confirmation of reducing conditions, sufficient to support evidence of a wetland soil in Queensland.

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Intensity and duration of waterlogging under rice crop estimated by micromorphology and mineralogy

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Abstract

Three Hydragric Anthrosols were examined in the south-central part of China. Soils are under the rice crop at the present time, which means the periods of waterlogging. The use of carbonate waters and the lime input into the soils resulted in the carbonatization i.e. in higher pH and formation of the specific iron-carbonate concretions in the upper part of the soils. Different macro and microfeatures were described in the soils according to their geomorphology, water regime and history of the land use. Modern and relict features were identified.

Key Words

Stagnic Anthrosols, gleyic features, Fe Mn and calcite pedofeatures, evolution.

Introduction

Rice is one of the most demanding plants in the world for food production, especially in Asian countries. Rice growth requires a certain period of submerged conditions which may be of various lengths up to the whole vegetation period. Sometimes soils under rice are referred as cultural hydromorphic soils. Artificial flooding necessary for rice culture creates certain changes especially in the surface and subsurface horizons, such as formation of a plough pan consequent to puddling; formation of surface gley; translocation of iron and manganese from the surface layer. Additional modifications may be caused by terracing and binding of rice fields. One may expect similar morphology and characteristics of soils under rice due to similar land use and extended waterlogging. Meanwhile soils with various initial properties and formed on different parent material may be used as the basis for rice cultivation. This means the difference in their texture, clay mineralogy, horizonation, chemical properties etc. Also the variation of submerging, the specificities of crop rotation, even the slight difference in geomorphology and microclimate may result in variable soil attributes and in particular variable expression of the redoximorphic features, different rate of carbon cycling and ability to storage. The aim of this research was to estimate the role of physiography in functioning of artificially waterlogged soils under rice crops.

Methods

Soils were studied, described and sampled in the soil pits up to the depth 80-110 cm, depending on the level to the perched ground waters. Samples from each horizon were taken for the regular chemical analyses. Undisturbed oriented soil samples were collected in the special boxes for the preparation of thin sections according to the standard procedure of impregnation by resin and polishing up to the 30 μn thickness (Bullock *et al.* 1985). Thin sections were described in planar and cross polarized light (XPL) using the optical microscope NIKON ECLIPSE E200 under the manifestations x40 to 80. Nodules collected from the soil pits were powder crushed in the mortar and studied by XRD method using Karl Zeiss Jenna X-Ray diffractometer XZG-4A. Diagnostics of the minerals was performed on a standard base (Soil mineralogy 1989).

Results

Three soils under rice crop were described and sampled in Guilin prefecture, Guangxi autonomous region in south-central part of China (GR-02: 25^{o} 03’20.3 N, 110^{o}14’23.9 E; GR-03: 25^{o} 58’762 N, 110^{o}20’623 E; and GR-04: 25^{o} 22’59.8 N, 110^{o}18’36.4 E). All three soils have iron-carbonate segregations above the plow pan, increase of $CaCO_3$ up to 25% in the topsoil and pH ranging from 7.6 to 8.3, which permitted to classify the soils as Recalcaric Hapli-Stagnic Anthrosols according to Chinese Soil Taxonomy (2001) or as Hydragric Anthrosols according to WRB (2006).

Recalcaric Hapli-Stagnic Anthrosols cover a total area of about 700 000 ha in the southern China where they are formed on alluvial deposits of various age under humid subtropical climate with MAT > +20°C and MAP above 1500 mm. Secondary carbonatization of these soils is due to the anthropogenic input of lime powder. The other sources of calcium carbonates are the ground waters coming from the Karst region nearby.

Field morphology and especially micromorphology in thin sections revealed common and specific features of all three soils under study in general chemical properties, and in particular in gleyization features and carbonate pedofeatures. Upper parts of the soils (up to 50 to 80 cm depth) reflect the high degree of the anthropogenic impact which strongly changed the initial soil properties due to waterlogging, input of the organic matter and lime powder. This resulted in particular in the increase of organic carbon, pH and silt fraction, formation of dense plow pan horizon. Specific hard segregations were described in the upper part of all three soils below the plow pan, which were expected to be secondary carbonate segregations formed as a result of lime input. The segregations have various sizes from 2-3 cm to 3-5 mm in diameter. They are more or less associated with iron according to variation of color from white or pale to ochre, rusty and red. Degree of gleyic features varies from weak olive-grayish color of the matrix to strongly expressed gray-bluish horizon. Bottom part of all three soils has grayish and orange-reddish fragmentary coatings around the aggregates.

Micromophology revealed a set of common features in all three soils including low content of the organic matter; increased silt content, carbonate impregnation and crystallitic b-fabric in the top horizons due to the lime input; common iron and iron-manganese nodules and segregations of various form, size and density together with the iron-free bleached zones and illuviated clay in the bottom part; humus-silty infillings; variety of calcite and complex iron-calcite nodules and pedofeatures (Figure 1 a-h). Some of them are of modern pedogenic origin, while the others may be also interpreted as relic features from previous stages of pedogenesis in drier and better drained environment, which are under degradation in present conditions. Both morphology and micromorphology suggest that various expressions of the described common features are explained by specificity of pedogenesis in each soil due to the difference in their parent material, geomorphology, history of the land use, length of waterlogging resulted in the various degree of clay, iron and carbonates mobility.

X-ray diffraction of powdery-crashed segregations identified their quartz-calcite or calcite-quartz composition with various ratios of gibbsite, goethite, hematite, lepidocrocite, chlorite and kaolinite as secondary components. Gibbsite as a mineral known to be common in Oxisols and Ultisols is believed to be the relic mineral indicating high degree of weathering under the excessive drainage environment of the past. Accumulation of various iron oxides and oxyhydroxides in form of nodules is mostly expressed in the upper horizons, which is explained by higher pH due to lime input there, while in the bottom part of the profiles iron is presented in form of soft impregnations and iron-clay coatings indicating higher iron mobility there (Figure 1 g, h).

Conclusions

Redoximorphic features associated with the excess of water under rice crop have various manifestations in the three soils under study. We interpret these differences by the different history of pedogenesis before the beginning of rice cultivation accompanied by excess of water, and by different intensity of current waterlogging in those three soils. As a result, we found two soils to be relatively similar, and the third soil quite different in its redoximorphic features, small size of Fe-carbonate segregations and strong degree of gleyization.

Macro- and micromorphic attributes reflect the combination of modern features associated with wetland conditions and relic features, which could be formed before rice cultivation. Specific iron-carbonate segregations were identified as modern wetland feature. They have the maximal size in soils with the most contrast water regime i.e. not only wet state, but pronounced dry period. The permanently wettest soil with highest perched water has the smallest iron-carbonate segregations, but at the same time contains abundant undifferentiated iron segregations of various morphologies (flakes, rings, impregnated plant residues, soft and hard typical nodules, iron associated with illuviated clay) in bleached iron-free zones, and evidence of the destruction of the lithogenic reddish iron-rich fragments. Differences in soil functioning resulted in the increased storage of inorganic carbon associated with iron-carbonate nodules in two of the investigated Irragric Anthrosols, while the third soil has limited potential to the carbon storage.

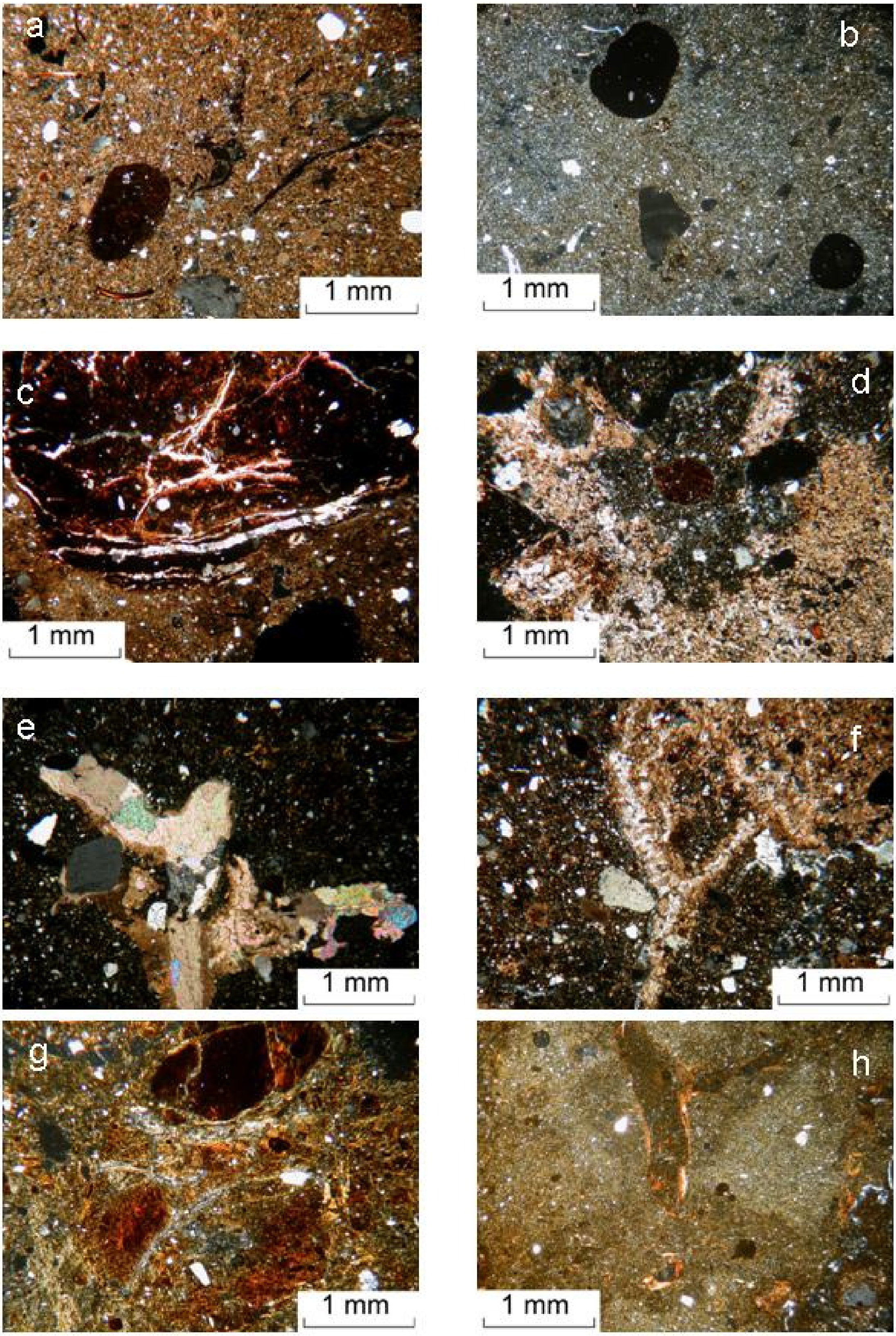

Figure 1. (a) GR-02 0-17 cm: Modern typic Fe-nodule and common ferruginisation of plant debris in humus-clay iron-carbonate groundmass; (b) GR-04 36-38 cm: Bleached iron-free silty-clay groundmass with modern rounded typic Fe-nodules; (c) GR-02 20-30 cm: Relict Fe-nodule with calcite filling the internal fissures; (d) GR-03 18-26 cm: Interpedal Fe nodule inside carbonate-free silty-iron-clay groundmass surrounded by sparite infillings; (e) GR-03 26-32 cm: Extra coarse sparite infillings in carbonate-free groundmass; (f) GR-03 18-26 cm: Sparite infilling along the intra-aggregate pores and microsparite impregnation of the groundmass; (g) GR-03 90-100 cm: Destruction of relict Fe-nodule, strong orientation of bleached plasma due to gleyization; (h) GR-04 70-80 cm iron redistribution with the formation of common compound Fe-clay coatings and Fe-humus clayey infillings in the voids associated with bleached zones. (all in XPL).

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Major and trace elements biogeochemistry and C sequestration in bog soils

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Abstract

Peat soils play a crucial role in the carbon cycle as they are generally net sinks for atmospheric carbon dioxide and net sources of greenhouse gases on a long term basis. Among peatlands, ombrotrophic bogs are also considered unique archives of past environmental conditions because their genesis is directly linked to the atmospheric conditions occurring during peat formation. Although several studies have been carried out in the last decades using ombrotrophic bogs in order to reconstruct the historical trends of heavy metal pollution due to anthropogenic activities, scientific literature is still rather controversial about the role of ombrotrophic bogs as reliable record peat of past climatic and environmental changes. To answer such a nodal point, it is extremely important to better understand the process of decomposition/humification in these ecosystems. According to the most renowned theories, decomposition is a catabolic process transforming highly complex biopolymers (e.g., cellulose, lipids, tannins, polyphenols) into smaller and simpler molecules, while humification is a reconstructive process which involves all the derived molecules occurring in the medium at various stages of decomposition; those molecules are then resembled to various extents, recombined and re-polymerized to form humic substances. Consequently, understanding whether all this "information" is effectively preserved in peat deposits during humification becomes an essential aspect to be tested before using bogs as natural archives. The main goal of this research is to test if ombrotrophic bogs are reliable archives of ancient and modern metal pollution and environmental changes by studying the role of HA in preserving or affecting these records.

Key Words

Peat, humic acids, isotopic signature, natural archives.

Introduction

For at least two centuries, peat has been recognized as an excellent archive of environmental change. William Rennie (1807), for example, interpreted stratigraphic changes in Scottish bogs not only in terms of natural changes in paleoclimate, but was also able to identify environmental changes induced by humans, namely deforestation and the hydrological impacts which result from such activities. The use of bogs as archives of climate change in the early 20th century was accelerated by studies of fossil plant remains such as those by Lewis in Scotland, and by systematic investigations of pollen grains pioneered by von Post in Sweden. In Denmark, Glob outlined the remarkably well-preserved remains of bog bodies and associated artefacts (of cloth, wood, ceramic and metal) in Danish bogs. In Britain, Godwin provided an introduction to the use of bogs as archives of human history, vegetation change, and Holocene climate, with a more recent survey provided by Charman.

Recent decades have provided many mineralogical studies of peat and there is growing evidence that many silicate minerals, whether derived from the surrounding watershed or the atmosphere (soil-derived dusts and particles emitted from volcanoes), also are well preserved in anoxic peatland waters. Similarly, geochemical studies have shown that a long list of trace metals, of both natural and anthropogenic origin, also are remarkably well preserved in peat bogs. Thus, there is growing evidence that ombrotrophic (i.e., "rain-fed", Clymo 1983) peat bogs are reliable archives of atmospheric deposition of a wide range of trace elements, including conservative, lithogenic metals (e.g., Al, Sc, Ti, Y, Zr, Hf and the REE), but also the potentially toxic Class B, or "heavy metals" (e.g., Cu, Ag, Hg, Pb, Sb and Tl). When high quality measurements of these elements is combined with accurate radiometric age dating, it becomes possible to create high resolution reconstructions of atmospheric soil dust fluxes, ancient and modern metal pollution, and Holocene climate change.

But peat bog soils play a crucial role in the carbon cycle as they are generally net sinks for atmospheric carbon dioxide and net sources of greenhouse gases on a long term basis. Although several studies have been carried out in the last decades using ombrotrophic bogs in order to reconstruct the historical trends of heavy metal pollution due to anthropogenic activities (e.g., Shotyk *et al.* 1988), scientific literature is still rather controversial about the role of ombrotrophic bogs as reliable record of past climatic and environmental changes.

To answer such a nodal point, it is extremely important to better understand the process of decomposition/ humification in these ecosystems. In fact, understanding whether all these "information" are effectively preserved in peat deposits during humification becomes an essential aspect to be tested before using bogs as natural archives. Consequently, in order to better understand if bogs are consistent archives, all the information about past human activities and environmental (climatic and vegetational) changes should be recorded into the fraction of peat more recalcitrant and refractory to the degradation, i.e., into humic substances (Stevenson 1994).

Methods

A 81 cm peat core was collected in 1991 from the Etang de la Gruère bog (Jura Mountains, Switzerland), cut into 3 cm slices, and age dated; after that, humic acids (HA) were isolated from each layer according to Swift (1996). The whole core, corresponding to ca. 2,100 years of peat formation, and the HA samples were characterized using several molecular spectroscopic methods (Ft-IR, UV-Vis, DSC, Fluorescence). Furthermore, both peat and HA samples were analyzed by XRF and ICP-OES (for major and trace elements), Low Background γ-spectrometry (for ^{137}Cs and ^{241}Am), and Isotopic Ratio Mass Spectrometer coupled with an Elemental Analyser (for isotope ratios, δ^{13}C and δ^{15}N).

Results

In general, Ft-IR, UV-Vis and fluorescence results, together with main atomic ratios, suggest significant variations of the molecular composition and chemical structures of the peat samples along the profile, underlining an increase of the humification degree with depth. In fact, the HA fraction accounts for 65.6 to 154.5 g kg^{-1} of bulk peat in the upper, poorly decomposed layer (from the living layer to ca. 24 cm), and for 200.5-327.3 g kg^{-1} of bulk peat in the bottom section, thus suggesting an increase of humification with depth. Among the studied major and trace elements, Br, Cu, and Hg showed a conservative behaviour as their distribution in HA mirrored that in peat. Actually, some authors suggested that the concentration of these elements in peat increases as result of mass losses during humification. Mercury data (Figure 1a), on the contrary, clearly underlined that: *i)* the magnitude of changes in Hg concentrations in peat samples along the profile is not directly correlated to their corresponding humification degree; *ii)* expressing both Hg concentrations per mass unit of peat, it is possible to identify a similar trend ($R^2 = 0.84$, $p<0.001$); and *iii)* most of the total Hg present in peat (66%, average value) is retained by HA molecules (Zaccone *et al.* 2009). This complexing behaviour may greatly limit the Hg mobility along the profile, thus suggesting a prevailing Hg immobilization that may reflect the different Hg deposition rates (Zaccone *et al.* 2007a).
On the contrary, other elements (e.g., Ca, Fe, Mg, Mn, Rb, Sr, Zn) showed a certain mobility along the profile (Figure 1b). Finally, Pb, although is considered a "soft" cation able to form inner-sphere complexes with the organic matter (OM), seems to behave similarly to Ti and Zr. Since the latter ones are known to be associated almost exclusively with dense accessory minerals (such as rutile and zircon) which are resistant to chemical reaction, even at the low pH (4) which is typical of ombrotrophic bogs, the absence of these elements in HA suggests that, during humification, the mineral phases bearing these elements are unaffected, and therefore that these metals are not available for chemical reaction (Zaccone *et al.* 2007a).
The occurrence of ^{137}Cs (Figure 1c) can be reasonably related to the 1986 Chernobyl disaster, even though its trend in the upper profile could be affected by plant uptake. The ^{137}Cs activity along the peat profile shows also additional peaks, one of which corresponding to the ^{241}Am peak, ascribed to nuclear explosions. The occurrence of ^{137}Cs in HA, although suggested a significant downward movement of ^{137}Cs along the profile, clearly remarks that the Chernobyl disaster is recorded also into the recalcitrant HA fraction (Zaccone *et al.* 2007a, b).

Finally, although big differences in the OM quality were observed along the peat profile, also isotopic ratios seem to have a certain conservative behaviour. In detail, the δ^{13}C (Figure 1d) ranges between -26.53±0.01 ‰ (in the living layer) and -24.77±0.05 ‰ (at 55-58 cm) in peat samples, and between -28.03±0.05 ‰ and -25.42±0.05 ‰ in corresponding HA, underling a greater "depletion" of ^{13}C in the latter fraction. Anyway, the δ^{13}C recorded both in peat and in HA samples shows a significantly similar trend with depth ($R^2 = 0.60$,

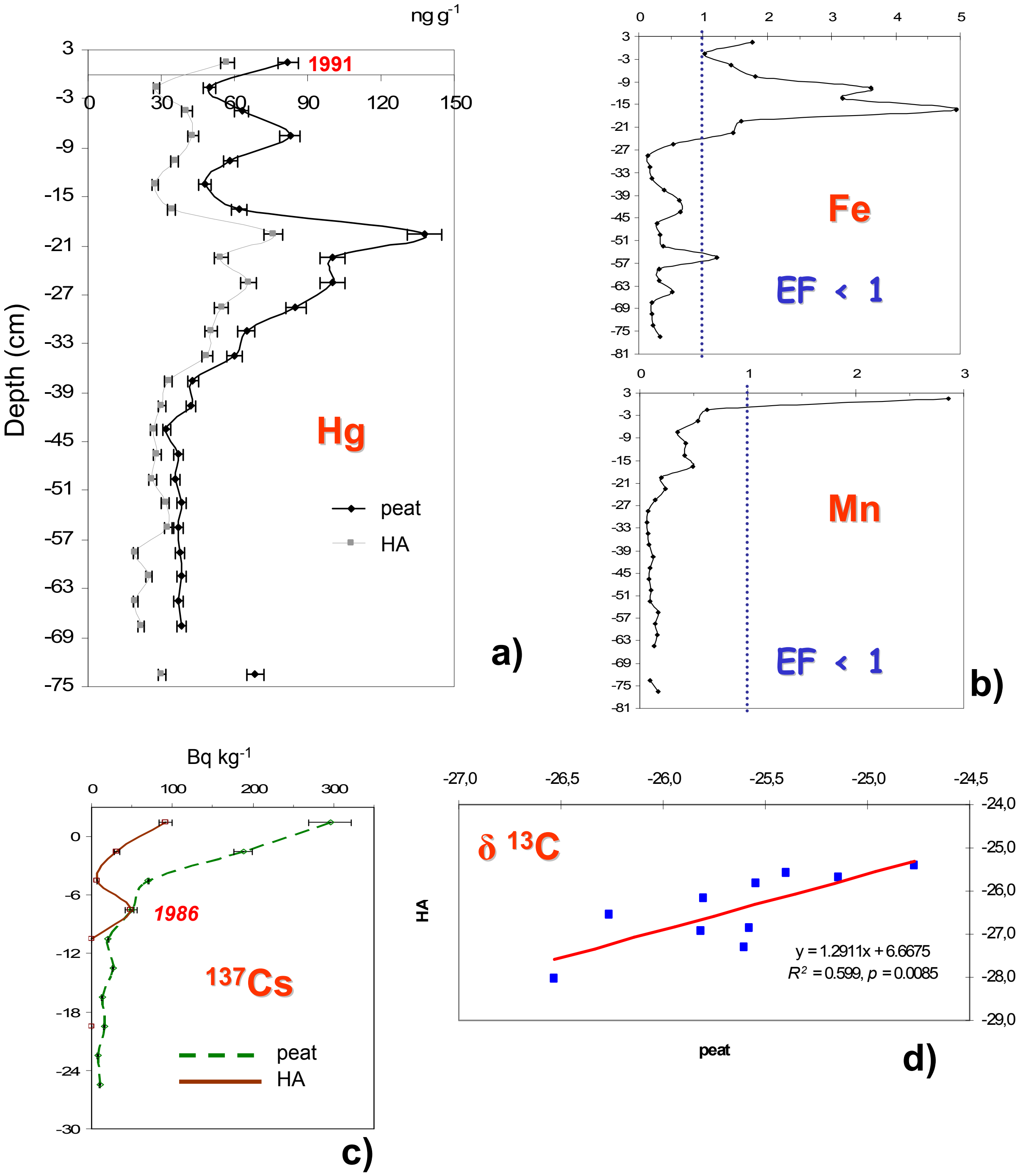

Figure 1. ***(a)*** **Mercury concentration in peat and corresponding HA;** ***(b)*** **Fe and Mn enrichment factor (EF) underlining a depletion of these elements;** ***(c)*** **^{137}Cs activity and** ***(d)*** **δ^{13}C in peat and corresponding HA samples.**

$p < 0.01$). Also the δ^{15}N features similarly in peat and HA throughout the profile ($R^2 = 0.68$, $p < 0.01$), showing values between -4.99±0.21 ‰ (in the living layer) and -2.36±0.06 ‰ (at 18-21 cm of depth) in peat samples, and between -4.15±0.05 ‰ and -1.06±0.24 ‰ in corresponding HA.

Conclusion

Can ombrotrophic bog constitute the "memory" of past human activity and environmental changes? Obviously, peat bogs cannot serve as archive of all these information. About major and trace elements, it will depend mainly on their nature and affinity for the OM in general, and for HA in particular. For example, data clearly showed that humification processes did not affect the Hg distribution along the profile. In fact, because the zone of elevated Hg concentrations seen in the surface layers of the Swiss peat core corresponds to the decades of greatest industrialization, the accumulation of this element is probably the result of both natural processes as well as anthropogenic inputs, with the latter clearly dominant during the past few centuries. The same behaviour was observed for Br. Moreover, HA are also witnesses of the Chernobyl disaster, as well as of nuclear explosions. About isotopic ratios, data apparently suggest that they are quite conservative in HA from peat, thus supporting on one hand the role of HA as recalcitrant, stable molecules with a long-term residence time, on the other hand the potential of ombrotrophic bogs to be used as "reliable archives" of climatic and vegetational changes occurring in the last 2,000 years.

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Mechanisms of phosphate dissolution from soil organic matter

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Abstract

Wetlands serve a critical role in removing nutrients and other contaminants from water moving from terrestrial to aquatic ecosystems. While reduced soils remove nitrogen from porewater by denitrification, these conditions are less conducive for retaining phosphate. The objective of this research was to determine the relative effects of pH and dissolved organic matter (DOM) on the retention of inorganic phosphate by soil organic matter. Sorption of phosphate was measured as a function of pH on Pahokee peat. Ferric iron was pre-sorbed to the peat at 1200 mmol/kg, and phosphate was added at 300 or 600 mmol/kg and equilibrated at pH ranging from 3 to 8.5. With increasing pH, sorbed PO_4 decreased from 300 (low P input) or 500 mmol/kg at pH 3 to approximately 50 mmol/kg at pH 8.5. Between pH 5 and 8.5, dissolved organic carbon (DOC) increased from 10 to 200 mg/L. Given that DOM tends to increase along with pH as aerobic soils become reduced, quantifying the relative effects of DOM and pH on dissolution of phosphate in reduced soils is important for managing phosphorus retention in wetlands.

Key Words

Wetlands, phosphorus, organics, redox, iron, DOC.

Introduction

Dissolved phosphate often increases as soils become anaerobic, but the trend is not consistent across all soils. Mechanisms that potentially contribute to reductive dissolution of soil phosphate in acid soils include (i) reductive dissolution of Fe(III) from oxide mineral surfaces or Fe(III)-phosphate minerals and concomitant dissolution of associated PO_4; (ii) decreased sorption of phosphate with a redox-coupled increase in pH; and (iii) competitive sorption of DOM displacing phosphate from soil components (Patrick and Khalid 1974; Roden and Edwards 1997; Hutchison and Hesterberg 2004). To help ensure that wetlands are created on soils that have suitable properties for retaining phosphate under reducing conditions, the relative importance of these and other dissolution mechanisms should be quantified.

Here we discuss the effects of pH and DOM on retention of inorganic phosphate in organic matter. Organic matter tends to accumulate in wet soils and DOM serves as an energy source for microbial reduction of nitrate, Mn-oxides, Fe-oxides, and sulfate. In addition to harbouring organic phosphorus, organic matter sorbs inorganic phosphate. Experimental evidence suggests that inorganic phosphate involves Fe(III) and Al(III) in organic matter as bridging cations (ternary complexes) (Bloom 1981; Gerke and Hermann 1992). The objective of this research was to determine the relative effects of pH and DOM on phosphate dissolution from soil organic matter.

Methods

Samples of organic-matter bound phosphate were prepared by first equilibrating Fe(III) then PO_4 with acid-washed Pahokee peat from the International Humic Substances Society. All reactions were done at 25°C. Binding of Fe(III) was accomplished by reacting $FeCl_3$ with peat (1200 mmol Fe/kg peat) at pH 2.5 in a 0.05 M KCl background and equilibrating for 2 hours. The sample was divided into separate subsamples, and 0.05 M KOH was added for pH adjustment to various levels between 3 and 8.5. The Fe-peat samples were equilibrated for 48 hours with periodic re-adjustment of pH before phosphate was added as 0.05 M KH_2PO_4 at concentrations of 300 or 600 mmol P/kg peat. The PO_4/Fe/peat samples were equilibrated for 48 hour while maintaining target pH through periodic adjustment. Equilibrated samples were centrifuged, and the supernatant solutions were filtered to <0.2 µm and analysed for dissolved reactive phosphate (DRP) colorimetrically, and dissolved organic carbon (DOC) by combustion. Auxiliary analyses not reported here included total dissolved Fe and Al. Sorbed inorganic PO_4 as a function of pH was determined as loss of added PO_4 from solution.

Results

Figure 1 shows sorption envelopes for PO_4 on Fe(III)-peat for additions of 300 or 600 mmol P/kg. The trend of decreasing PO_4 sorption with increasing pH is characteristic of sorption envelopes found for PO_4 on Fe(III)- and Al(III)-oxide minerals. However, our sorption envelopes were complicated by potential competitive effects of DOM. As shown in Figure 2, DOM increased with increasing pH, from a nearly-constant concentration of 10 mg/L between pH 3 and 5 up to 200 mg/L at pH 8.5. An increase in DOM with increasing pH is typical, but we also found that DOM increased during abiotic or biotic reduction of peat at constant pH (data not shown).

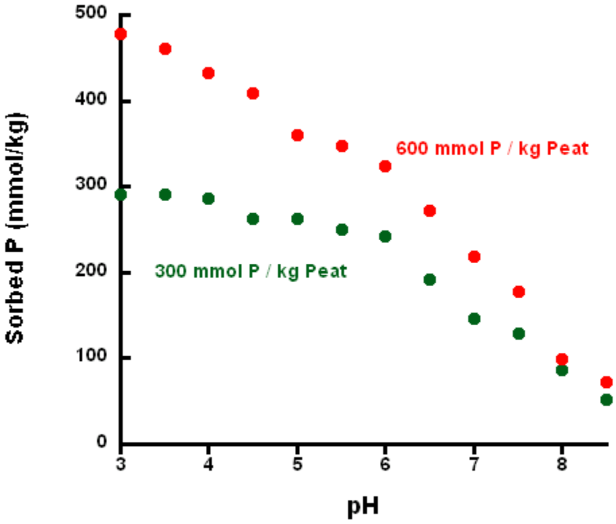

Figure 1. Sorption envelopes for phosphate on Pahokee peat containing 1200 mmol Fe/kg peat.

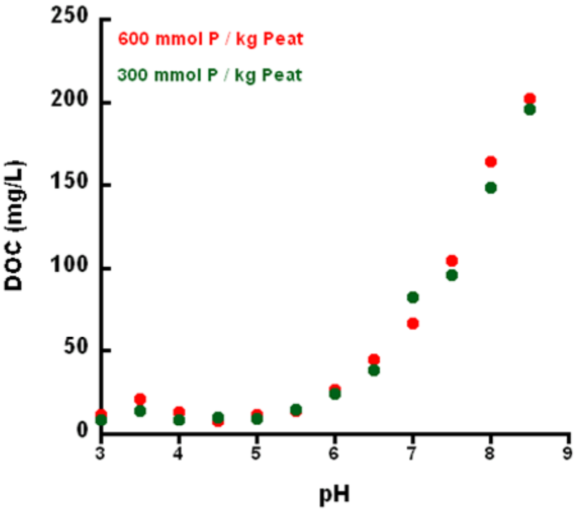

Figure 2. Dissolved organic C (DOC) in supernatant solutions (filtered to <0.2 µm) from the measurements of P sorption envelopes shown in Figure 1.

Between pH 3 and 5, where DOC is essentially constant (Figure 2), sorbed PO_4 decreased by 25% (from 482 to 364 mmol/kg peat) for the 600 mmol P/kg input, and by 10% (from 293 to 265 mmol/kg peat) for the 300 mmol P/kg input (Figure 1). These results highlight the pH dependence of PO_4 sorption at constant DOC, albeit over a narrow pH range. At pH > 5, we cannot separate the effect of pH from that of DOM from these results. For example, Figure 3 illustrates that the pH-dependent increase in DOM could potentially be contributing to an increase in dissolved PO_4, which is tied to a decrease in sorbed PO_4. This effect, if independent of any pH effect, is consistent with a mechanism of competitive sorption of PO_4 and DOM for binding sites on the peat.

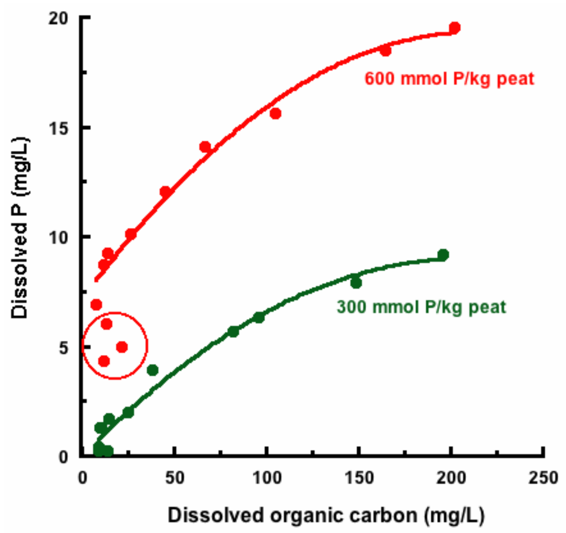

Figure 3. Dissolved phosphate increased with increasing dissolved organic carbon (DOC) concentration for Pahokee peat. Quadratic models are fit to the data to show trends (circled points were omitted from the model for the 600 mmol P/kg treatment).

Conclusions

Under the conditions of our experiments, pH-dependent sorption of inorganic phosphate on Fe(III)-peat showed sorption envelopes analogous to those for phosphate sorption on oxide minerals. However, for pH > 5, dissolution of organic matter from the solid-phase peat appeared to increase dissolved phosphate, probably by competitive binding to Fe(III). Accordingly, increases in both pH and DOM during reduction of soils likely contribute to phosphate dissolution and diminished phosphate retention capacity in reduced soils. The effects of pH and DOM on organic-matter bound inorganic phosphate are important, regardless of any direct effects of Fe(III) reduction on phosphate dissolution.

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Mediterranean wetland soil classes and its relationship with vegetation and land-uses types

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Abstract

This study performs a wetland soils mapping approach of the 'El Hondo' Natural Park in southeastern Spain by using aerial photographs and geographical information systems (GIS). Vegetation types and land-uses were also mapped to assess their relationship with the soil types. Calcisols, Gleysols and Histosols were identified. Agricultural uses and associated vegetation were closely related to the Calcisols. The saltmarshes on abandoned farmland were also closely related to the Calcisols. Gleysols and Histosols were associated to the presence of vegetation in marshes and saltmarshes in the reservoirs, ponds and floodplains of the Natural Park.

Key Words

Soil mapping, vegetation, land-use, GIS.

Introduction

Wetlands provide enormous beneficial services to people in the form of water supply, the maintenance of fisheries, the support of agriculture (through the maintenance of water tables and nutrient retention in floodplains), timber production, energy resources, wildlife resources, transportation routes, and recreation and tourism opportunities (RAMSAR 2007). The basic characteristic that defines a wetland is the permanent or seasonal presence of water. Wetland soils function as sinks and as transformers of nutrients, toxic metals and organics (Reddy *et al*. 2000). The task of mapping wetlands is difficult because these habitats are relatively poorly known (due to limited access) and vary seasonally (due to water fluctuations) (Novo and Shimabukuro 1997). Studies of marsh loss and degradation are usually based on field site investigations or aerial photographic analysis (Rogers and Kearney 2004). The combined employment of remote sensing (aerial or satellite) and geographical informations systems (GIS) provides a powerful tool to model and monitor environmental and socio-economic processes and phenomena. Remote sensing offers the capability of rapid and synoptical monitoring of large areas (Andrew and Ustin 2008). The objective of this study was the mapping of soil classes for a Mediterranean wetland according with the World Reference Base for Soil Resources (IUSS Working Group WRB 2006). Soil classes were identified by visual inspection of aerial photographies combined with field observations. The relationship among soil classes and, vegetation and land-uses was assessed.

Material and methods

The 'El Hondo' Natural Park is located in a coastal zone of south-east Spain, near the town of Elche (province of Alicante, Spain). The topography is very flat and altitudes range from sea level to several meters above sea level. The Natural Park comprises a series of human-made dams and ponds built on top of a lagoon that was dried a few centuries ago. The climate in this Spanish coastal region is semiarid Mediterranean, with a mean annual rainfall of less than 300 mm and a mean annual temperature of 17ºC. The climate is considered arid or semiarid according to the aridity index of Martonne (De Martonne 1926) and the aridity index of UNEP (1997) respectively. The 'El Hondo' Natural Park is included in the RAMSAR list of wetlands of global importance and in the NATURE-2000 network of the European Union. The park accommodates a wide range of migratory and nesting bird species some of which are critically endangered, for instance, the marbled teal *(Marmaronetta angustirostris)*. Open water bodies, reed communities, saltmarshes and irrigated agricultural fields are the dominant land-cover types within and around the Natural Park. The water cycle in the park is controlled by the need for water extraction for agricultural irrigation and wildlife conservation. A mosaic of colour aerial photographies acquired in summer of 2007 (1m of spatial resolution) was used for soil classes delineation. Aerial photographies were georreferenced in a GIS and soil classes were digitised by visual inspection of the images and field observations. A vector cartography of soil classes was obtained. Vegetation and land-uses maps were also obtained with the same procedure. In order to assess the relationship among soil types and vegetation and land-uses classes, vector cartography was converted to raster format and a cross-tabulation analysis was performed with the resulting raster maps.

Results and discussion

Major soil classes of the study area were Calcisols, Gleysols and Histosols (Figure 1). Gleysols and Histosol were located around permanently inundated areas (in years with no extreme droughts). Soil sealing areas correspond with roads, buildings and recreational areas. Calcisols were preferentially located in the perimeter of the Natural Park area were soil saturation by is less frequent. The network of channels and paths that cross the wetland area defines some soil classes limits resulting in a map with some linear inter-soil boundaries suggesting the great influence of human activities on the soil. Histosols are located in the northern of the Natural Park and corresponds with an area of stable marsh since more than fifty years ago.

Figure 1. Major soil classes map for the 'El Hondo' Natural Park.

Marshes (dominated by *Phragmites sp*. stands) and saltmarshes (e.g. *Salicornia sp., Suaeda sp., Arthrocnemum sp.*) were the most abundant vegetation types (Figure 2) and are preferentially located in and around water bodies. Some bare soil areas with no vegetation result form the reduction of the water table in summer. Palm tree (*Phoenix sp*.), fodder crops and citrus tree agriculture areas were located in the perimeter of the Natural Park were soil are less saline. Artificial areas correspond with roads, buildings and recreational areas (soil sealing).

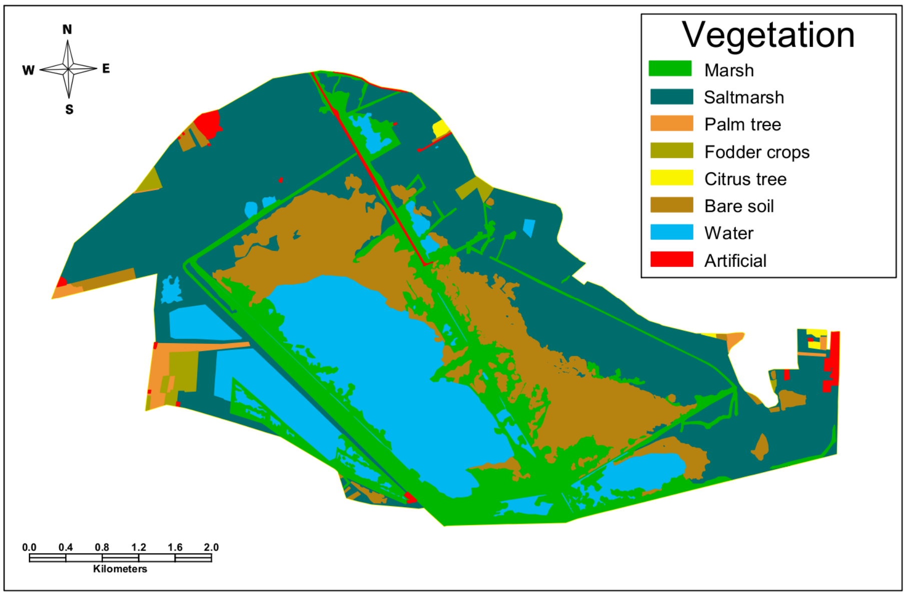

Figure 2. Vegetation types map for the 'El Hondo' Natural Park.

The current configuration of 'El Hondo' Natural Park is based on the existence of two large reservoirs of water for agricultural use in surrounding agriculture areas and a set of ponds employed for hunting (Figure 3). Marshes are located on the reservoirs, pond and flooded areas. Saltmarshes occupy abandoned farmland areas. Two classes of abandoned farmland areas were identified: 1) abandoned farmland class which corresponds with agriculture fields that were abandoned many years ago and nowadays salthmarshes are highly developed and the boundary between ancient fields has virtually disappeared under the vegetation canopy; and 2) recently abandoned farmland class were saltmarshes are in the process of colonisation of agriculture fields that were abandoned only a few decades ago. Artificial areas correspond with roads, buildings and recreational areas (soil sealing).

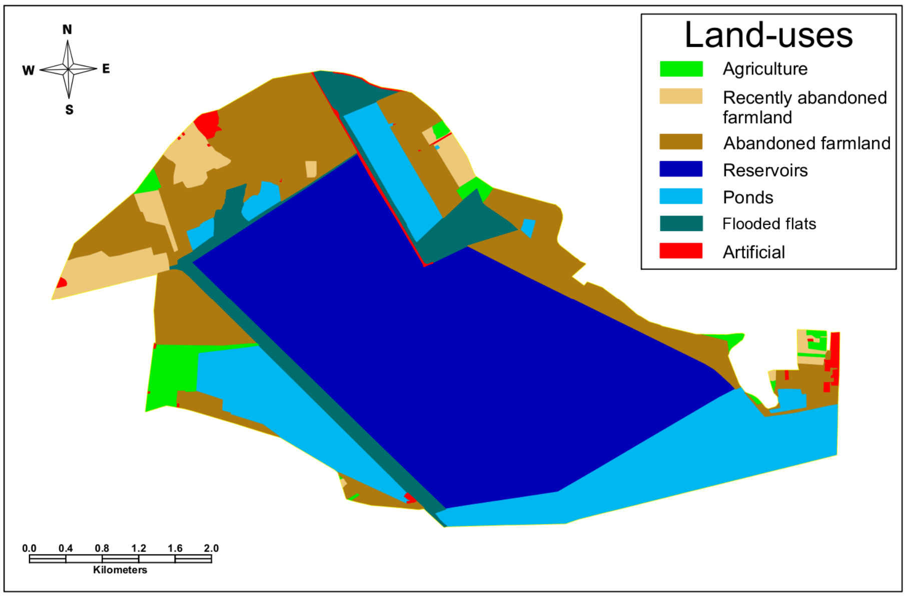

Figure 3. Land-use classes map for the El Hondo Natural Park.

The relationship between soils and vegetation was assessed with a cross tabulation matrix and their relative presence in each soil class was estimated (Figure 4).

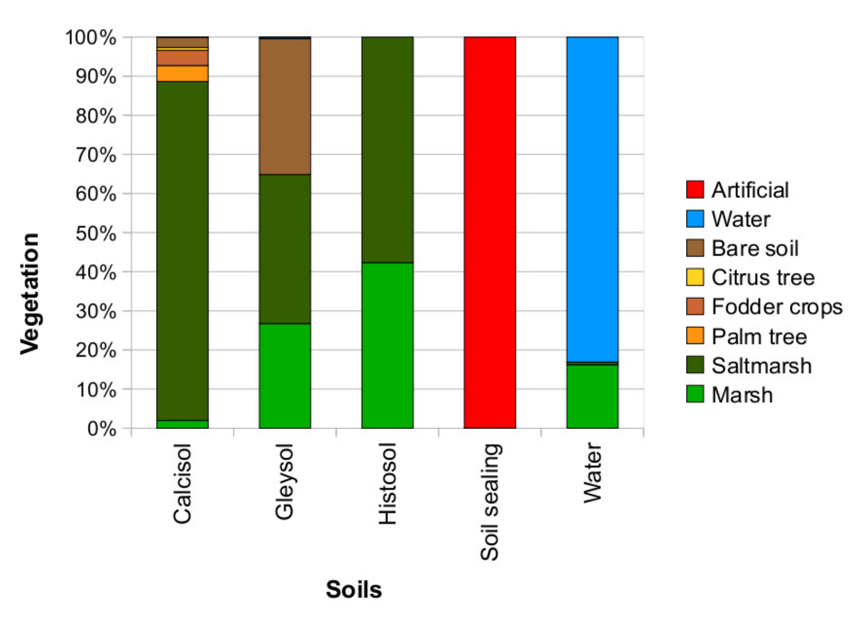

Figure 4. Relative presence of vegetation classes in each soil class.

Vegetation types related with agriculture (palm tree, citrus tree and fodder crops) were exclusively on Calcisols. Saltmarsh was the dominant vegetation on Calcisols. Gleysols were occupied by saltmarsh and marsh vegetation classes and some areas were bare soil. Such areas correspond with floodplains that were dry at the time of acquisition of the aerial photography. Undisturbed since more than fifty years ago marshes and saltmarshes were developed on the Histosols which are very scarce in the Natural Park. Soil sealing class corresponds with artificial areas while water class is occupied by open water tables and some inundated marshes. Finally, the relationship between soils and land-uses was assessed with a cross tabulation matrix and their relative presence in each soil class was estimated (Figure 5). Land-uses developed on Calcisols were agriculture, the two types of abandoned farmlands, some human made ponds and a small portion of the reservoirs. Gleysols were occupied by reservoir, pond, flooded flats and abandoned farmland land-uses. Gleysols were the most characteristic soil type of the wetland while the scarce Histosols were only developed on floodplains and agriculture fields abandoned many years ago. Soil sealing class corresponds with artificial areas. Reservoir, ponds, flooded flats and abandoned farmland were the land-uses classes of the permanent water class.

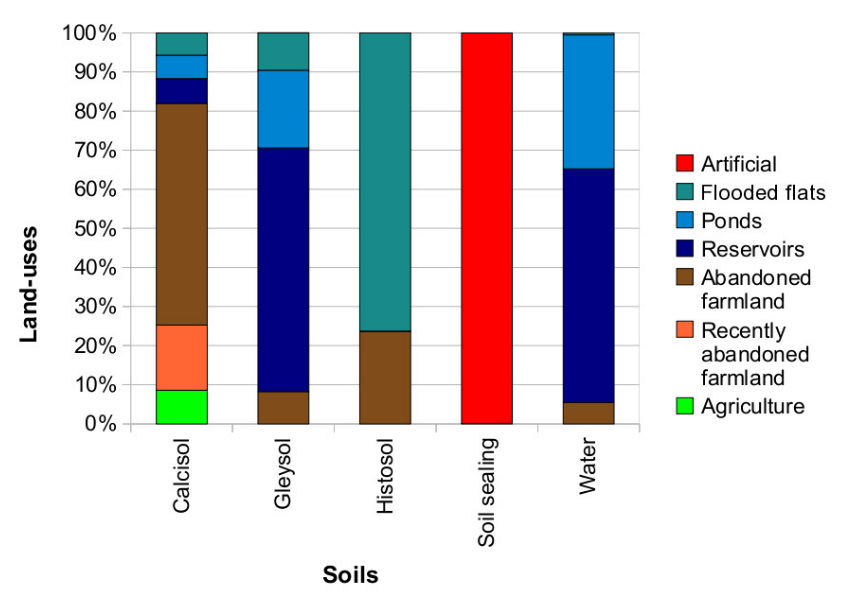

Figure 5. Relative presence of land-uses classes in each soil class.

Conclusion

Soils mapping plays an important role in soil science, providing valuable information for land management. This study served to make a first approach to mapping the soils of the 'El Hondo' Natural Park with an accuracy hitherto unrealised. The study showed the interdependence between vegetation types and land uses that are present in the Natural Park and the soils on which they are developed. Future studies should serve to improve the mapping and increase their use in wetland management

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Mercury transformations in wetland soils in relation to C, S and Fe biogeochemistry

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Abstract

Net production of the toxic and bioaccumulating methyl mercury (MeHg) molecule in wetlands is a major environmental health issue. In this paper factors and processes in control of MeHg net production in wetlands are covered. Of major importance are methylation, demethylation and photo-induced redox processes. All these reactions are linked to the biogeochemistry of C, S and Fe via an intricate interplay with iron(III) and sulphate reducing bacteria. A special focus is put on the link between the chemical speciation of Hg(II) and uptake of bioavailable forms of Hg(II) by methylating bacteria. A key role is played by organic substances. They control the transport of Hg(II) and MeHg, as well as the bioavailability of Hg(II) and the energy source for methylating bacteria. Research needs are identified. In particular, limited fundamental knowledge about demethylation processes may restrict society to make correct decisions regarding e.g. restoration efforts of wetlands.

Background

Mercury (Hg) is one of the most toxic elements and there is currently a worldwide concern about negative health effects, in particular in human populations highly dependent on fish consumption (Mergler *et al.* 2007). On a global scale, the major source of Hg is emission of elemental Hg^0(g) as a consequence of combustion of fossil fuels. The residence time of Hg^0 in the atmosphere is about one year, resulting in a long-range transportation from industrial areas to areas without significant local Hg sources. The pool of atmospheric Hg^0(g) is gradually oxidized and the product, Hg(II), is deposited in association with particles or dissolved in precipitation. In arctic areas, atmospheric mercury depletion events have been reported to result in locally relatively high concentrations of Hg(II) (Steffen *et al.* 2008). Once deposited, Hg(II) may undergo a number of biogeochemical reactions. From a human health perspective, processes directly and indirectly involved in the production and degradation of the most abundant toxic and bioaccumulating form of organic Hg; monomethyl mercury (MeHg) is of greatest concern. Together with marine environments, hypolimnetic waters and lake sediments, wetlands are known to be environments in which MeHg is net produced. Most research focus has been on wetlands in temperate areas, but also in sub-tropic and tropic wetlands the formation of MeHg is an issue. It is well-established, by laboratory experiments and by studies in the field, that MeHg formation can be linked to the activity of iron(III) and sulphate reducing bacteria (FeRB and SRB, respectively) (Benoit *et al.* 2003). This means that factors stimulating the activity of these groups of bacteria, such as the availability of electron donors and acceptors, may result in an increased net MeHg production. However, because these groups of bacteria obviously affect the chemistry of sulphur and iron geochemistry, there is an intricate interplay with both the chemical speciation and transformations of Hg(II) and MeHg that need to be fully understood.

The objective of this paper is to provide an overview of the current knowledge about the link between mercury and organic carbon, sulphur and iron biogeochemistry in wetland environments. Special focus is put on the link between chemical speciation, mobility of Hg(II) and MeHg and the transformation of Hg(II) to MeHg.

Chemical speciation of mercury in wetland soils

Complexation with organic thiols

In order to be able to discuss important transformation processes of Hg(II) and MeHg, the chemical speciation of these two forms under natural conditions in wetlands needs to be understood. Because of the “soft” properties of mercury, it forms exceptionally strong bonds with sulphur. Under oxic conditions, complexes with organic thiols (RSH) highly dominate the chemical speciation of both Hg(II) and MeHg in organic rich environments such as wetlands (Skyllberg 2008). The binding to organic thiols is strong enough to out-compete Cl^- and Br^- also in marine or estuarine wetlands. Organic thiol functional groups are associated to natural organic matter (NOM) both in the solid and aqueous phases (pore water) of soils. In the aqueous phase low molecular mass (LMM) thiols may occur. Concentrations up to 250 nM have been reported for LMM thiols like cysteine and thioglycolic acid in wetlands (Zhang *et al.* 2004). This concentration of RSH would be equal to the concentration of thiol groups associated with DOM in a water containing 2 mg DOC/L, if we assume that RSH in NOM corresponds to 0.15 % of OC, as reported from spectroscopic determinations (Skyllberg 2008). Assuming that the affinity of Hg(II) and MeHg for LMM thiols and thiol groups associated to NOM is the same, this suggests that Hg(II) and MeHg are mainly associated to NOM in wetland pore waters (having DOC > 2 mg/L). Adsorption of Hg(II) and MeHg to other solid phases (e.g. iron oxyhydroxides or clay minerals) than NOM is insignificant under oxic conditions.

Suboxic conditions

Under suboxic conditions, FeRB, SRB and sulphide oxidizing bacteria (SOB) are active, which results in the formation of Fe(II), inorganic sulphides (H_2S, HS^-) and elemental S. Elemental S, which may be formed by the activity of SOB and SRB (e.g. 6), reacts with HS^- under the formation of polysulphides (S_n^{2-}). Hg(II) and MeHg form complexes with HS^- having a quite similar chemical stability as complexes with organic thiols (Skyllberg 2008). In wetlands with significant minerogenic influence, amorphous FeS(s) can be expected to control the concentration of HS^-, via the reaction $FeS(s) + H^+ = Fe^{2+} + HS^-$ (Rickard and Luther 2007). This reaction therefore, indirectly, affects the chemical speciation of Hg(II) and MeHg in the aqueous phase. Chemical speciation modelling of Hg(II) in a wetland soil (pH 4-7) showed that concentrations of dissolved complexes with organic thiols [$Hg(SR)_2(aq)$] and with inorganic sulphides [$Hg(SH)_2^0(aq)$, HgS_2H^-, HgS_2^{2-}] were approximately equal at 0.5 μM of S(-II) and 50 mg DOC/L (Skyllberg 2008). At the same conditions, concentrations of MeHg complexes with organic thiol [MeHgSR(aq)] and inorganic sulphide [$MeHgSH^0(aq)$, $MeHgS^-$] were approximately equal. However, if polysulphides are formed, organic thiols and inorganic sulphides are out-competed. For MeHg stability constants with polysulphides are unknown.

Anoxic conditions

With increasing anoxic conditions, elemental S and polysulphides will be reduced to inorganic sulphides, making the speciation of Hg(II) in the aqueous phase somewhat less complicated. In the solid phase, however, amorphous metacinnabar [HgS(s)] may form. It is known that organic substances on one hand diminish the aggregation and crystallinization of metacinnabar (Ravichandran *et al.* 1999), but on the other hand organic molecules stabilize amorphous nanoparticles of HgS(s) (Deonarine and Hsu-Kim 2009). Thermodynamic modelling suggests that metacinnabar is stable at a concentration of HS^- exceeding ~10 μM at neutral pH in organic soils (Skyllberg 2008). Below this concentration, complexes with organic thiols associated to NOM are the dominant form of Hg(II) in the solid phase. Recent spectroscopic studies have shown that Hg(II) reacts with FeS(s) to form metacinnabar, and that organically complexed Hg coexist with HgS(s) in the solid phase of organic soils. At increasing anoxic conditions (i.e. increasing concentrations of HS^-), the solubility of Hg(II) increases and $Hg(SH)_2^0(aq)$, HgS_2H^-, HgS_2^{2-} and $MeHgSH^0(aq)$, $MeHgS^-$ completely dominates the chemical speciation of Hg(II) and MeHg in solution.

Biogeochemical transformations in wetland soils with focus on MeHg net production

With focus on the formation of MeHg, the two perhaps most important biogeochemical transformation reactions of mercury in wetlands are the methylation and demethylation processes. The current consensus is that the former process is biotic (intracellular) and linked to the activity of FeRB and SRB, whereas the latter is known to be both biotic and abiotic (Benoit *et al.* 2003). Also redox reactions involving Hg(II), Hg(0) and MeHg need to be considered, as these processes will indirectly affect the formation of MeHg.

Influence of C, S and Fe biogeochemistry on methylation processes

The following factors are generally considered to be in control of methylation rates: 1) the concentration of Hg(II) in bioavailable form, and the availability of 2) electron-donors (energy source) and 3) electron-acceptors [Fe(III) and sulphate] for methylating bacteria.

Organic C is in indirect control of 1) and in direct control of 2). One reason for northern wetland – forested regions to be high risk environments for MeHg net production and bioaccumulation is its production of recalcitrant, soluble humic substances. The transportation of Hg(II) with humic substances from upland, forested environments to methylation "hot-spots", such as certain types of wetlands, is a key process for MeHg net production. Similarly, dissolved humic substances transport MeHg from methylation "hot-spots" to streams and surface waters with biota that accumulate MeHg. In addition, LMM organic C molecules (e.g. acetate, propionate, lactate, fatty acids) serve as electron-donors to methylating bacteria. Several studies of different reducing environments highlight the importance of LMM organic molecules for MeHg production (e.g. Benoit *et al.* 2003; Drott *et al.* 2007).

Sulphur containing ligands (HS^-, S_n^{2-}, and RSH) highly affect methylation processes by controlling the solubility and concentrations of bioavailable forms of Hg(II). There is currently little consensus regarding the forms of Hg(II) taken up by methylating bacteria. A number of laboratory and field studies indicate that a passive uptake of neutral forms of Hg(II) by methylating bacteria may limit the net production of MeHg. Given the dominance of the $Hg(SH)_2^0$ molecule under anoxic conditions in wetlands, this species is the most reasonable candidate to be taken up by SRB (Benoit *et al.* 2003; Drott *et al.* 2007). The suggestion that the species $HOHgSH^0$ is the predominant form of neutral Hg-sulphides (Benoit *et al.* 2003) is controversial because it builds on an unreasonably large stability constant for the formation of this complex (Skyllberg 2008). Under suboxic conditions neutral forms of polysulphides (e.g. HgS_5) have been suggested (but not confirmed) to be bioavailable (Jay *et al.* 2002). A recent study shows that LMM Hg(II)-thiols are actively taken up by FeRB (Schaefer and Morel 2009). This is reasonable given that FeRB are active under redox condition under which neutral Hg(II) complexes (e.g. $Hg(SH)_2^0$) show very low concentrations. Even if there is not a consensus regarding which forms of Hg(II) that are bioavailable for methylating bacteria (and mechanism for their uptake), there is no doubt that all reasonable candidates involve inorganic or organic S as major ligands.

Sulphur (in form of the sulphate ion) acts as an electron acceptor for SRB. Several studies have shown that amendments of sulphate to wetlands result in increased concentrations of MeHg. This may be caused by an increased methylation, indicating that SRB were limited by sulphate. If, however, only the pore water concentration of MeHg is measured (which unfortunately has been the case in several studies), increased concentration of MeHg may simply be an effect of HS^- formation (reduction of sulphate) and a subsequent increased solubility of MeHg by formation of $MeHgSH^0(aq)$ and $MeHgS^-$. Because of this, there are only a few studies in support of sulphate limitation of the methylation process.

Iron has two major effects on the methylation processes. Under sub- and anoxic conditions, FeS(s) is in control of the concentration of HS^- (and indirectly of the concentration of $Hg(SH)_2^0$). Furthermore, Fe(III) is an electron acceptor for FeRB. In both of the two studies in which Fe(II) and Fe(III) compounds has been amended to wetlands, a decrease in MeHg net production has been observed (Mehrotra and Sedlak 2005). This has been interpreted as indirect inhibitory effect by formation of FeS(s) and decrease in the concentration of presumably bioavailable $Hg(SH)_2^0$.

Demethylation and photo-induced redox processes

Biotic demethylation may be either reductive or oxidative. Reductive demethylation is a detoxification process (it costs energy) involving the mercury resistance *mer* operon (Barkay *et al.* 2003), degrading MeHg to Hg^0 and CH_4. This process is believed to be induced by relatively high concentrations of Hg(II), and is used by a broad spectrum of bacteria. During oxidative demethylation MeHg is degraded to Hg^0 and CO_2. This process is assumed to be part of microbial metabolism (e.g. SRB) and is believed to be the dominant process at less contaminated sites (Marvin-DiPascale *et al.* 2000). There is currently very little knowledge about the variability in demethylation rates among different environments (e.g. different types of wetlands) and even less knowledge concerning the influence of external factors (e.g. C, S and Fe biogeochemistry). This is one of the most urgent research needs to be filled in the near future. Some new results will be presented at the symposium, suggesting that certain types of wetlands may act as sinks for MeHg because of high demethylation rates.

Photo-degradation of MeHg is an important demethylation process in water columns of lakes (Sellers *et al.* 1996), and the importance of this process needs to be investigated in open wetlands. Photo-reduction of Hg(II) to Hg(0) and photo-oxidation of Hg(0) to Hg(II) are important processes occurring in open wetlands. It has been shown that chromophoric groups associated to DOM plays an important role in the electron transfer in both these processes. Also the redox-couple Fe(II)-Fe(III) has been indicated to be involved (Zhang 2006).

Research needs for mercury biogeochemistry in wetlands

Not all types of wetlands are net sources for MeHg. One of the most urgent research need is to identify sites, processes and environmental factors in control of MeHg demethylation. Limited knowledge on how different types of wetlands respond to human activities (e.g. restoration efforts), as well as to climate change, restrict society from making correct decisions.

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Microbial biomass and activities in a Japanese paddy soil with differences in atmospheric CO_2 enrichment, soil/water warming and rice cultivars

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Abstract

Paddy surface and subsurface soil samples were collected from former Rice-FACE (free-air CO_2 enrichment) sites with elevated soil/water temperature treatment in successive rice crop season to investigate effect of CO_2 and temperature on microbial biomass, enzyme activities, and methanogenic and methanotrophic activities in a paddy soil. The FACE experiment was conducted in the field, with two CO_2 levels, ambient and ambient + 200 µL/L (FACE), located in Shizukuishi, Iwate, Japan until 2004. A warming treatment of soil/water temperature of 2 degree from transplanting until harvest (May-September 2006) was set up with water-proof heater in flooded water in the field. Soil microbial biomass C were significantly larger in surface layer than those in subsurface soil, but effect of previous CO_2 treatment and warming treatment on microbial biomass were both not significant. Dehydrogenase activity and dissolved organic carbon (DOC) had no significant difference between elevated and ambient temperature, though significantly higher in surface soil than sub-surface soil. Methane (CH_4) production (methanogenic) activity was increased by elevated temperature, but no effect on CH_4 oxidation (methanotrophic) activity. These results indicated that elevated temperature may affect soil microbial processes in different ways.

Key Words

Paddy soil, methane production and oxidation, dissolved organic carbon, temperature.

Introduction

Microbial biomass is important nutrient pool especially for nitrogen (N) in paddy soil (Inubushi *et al.* 1991; Shibahara and Inubushi 1995; Inubushi *et al.* 2002a). Microbial biomass can be also more sensitive early-warning indicator than total soil organic matter to see environmental impacts such as increasing concentrations of greenhouse gases on soil ecosystems, warming temperature, farmers' practices and so on such as in upland soil (Powlson *et al.* 1987) and in paddy soil (Hoque *et al.* 2001). Atmospheric concentrations of CO_2 and methane (CH_4) have been annually increasing at a rate of 0.5% and 0.8%, respectively. The increasing CO_2 is mainly attributed to fossil fuel combustion and land use changes, and its concentration is expected to double by the middle of this century compared with preindustrial values (Lal and Kimble 1995; IPPC 2001). Methane, another important greenhouse gas, accounts for about 20% of the current increase in global warming, which is caused by an imbalance between CH_4 sources and sinks (IPPC 2001). Paddy fields have been regarded as major anthropogenic sources of global CH_4 emission, with annual estimates ranging from 47 to 60 $TgCH_4$ (Houghton *et al.* 1995; IPPC 2001).

Effect of elevated CO_2 in the atmosphere on soil microbial biomass in paddy field has been examined in rice-FACE (Free-air CO_2 Enrichment) experimental site in Shizukuishi, northern part of Japan (Inubushi *et al.* 2001; Hoque *et al.* 2002). Under standard N application level, elevated CO_2 (ambient + 200µL/L) significantly increased biomass N in the upper soil layer at harvest by 25–42% compared to ambient CO_2, regardless of N application rate. In low N soil, these significant increases were also observed at the ripening stage (Hoque *et al.* 2002). However the effect of elevated CO_2 on microbial biomass was not examined for long-term, except Lou *et al.* (2006) who measured CH_4 production potential of soils, taken 2 months after rice harvest, by incubation method and found that CH_4 production potential was approximately 2–4-fold higher in FACE soil than ambient soil and approximately 500–1,000-fold greater in surface soil than sub-surface soil. In general, the FACE soil contained more DOC than ambient soil, particularly in the surface soil layer. In previous reports, we also showed effect of elevated CO_2 on CH_4 emission from paddy field in the FACE sites to find more CH_4 emitted under elevated CO_2 conditions, indicating positive feedback of greenhouse gas increase (Inubushi *et al.* 2003). Methane is end product of anaerobic decomposition of organic matter in paddy field as well as natural wetlands. Microbial biomass and its debris can be substrate for methane production. Dissolved organic carbon in soil under elevated CO_2 conditions was more than ambient soil in the FACE site (Lou *et al.* 2006). Part of CH_4 produced in soil is oxidized by methanotrophic bacteria (Inubushi *et al.* 2002b). However we do not know yet how microbial biomass related to CH_4 emission and oxidation, and dissolved organic carbon in paddy soils planted with various rice varieties under elevated CO_2 condition. Effect of soil/water warming in paddy field is not investigated especially in relation to soil microbial biomass and their activity, such as methane production potentials.

Objectives of this study are to investigate microbial biomass dynamics in paddy soil as affected by CO_2 and temperature elevation to find effect of CO_2 and temperature conditions in relation to microbial biomass CH_4 production and oxidation.

Methods

Experimental sites

The FACE experiment was conducted in the filed, with two CO_2 levels, ambient and ambient + 200 µL/L (FACE), with 4 replicate rings, located in Shizukuishi, Iwate, Japan until autumn 2004 (Inubushi *et al.* 2003; Lou *et al.* 2006). Warming treatment of soil/water temperature in 2 degree from transplanting until harvest (May-September 2006) was set up in each FACE and ambient rings with water-proof heater in flooded water in the field, monitored and recorded (Borjigidai *et al.* 2006).

Soil sampling

Paddy surface (0-1cm) and subsurface (1-10cm) soil samples (Andisol paddy soil type) were collected in August 2006 from ambient-temperature (Ambient 1) and warming subplots in FACE ring and from non warming subplot in the ambient CO_2 ring (Ambient 2) to investigate effect of former CO_2 treatment and successive warming effects on microbial biomass, enzyme activities, and methanogenic and methanotrophic activities in a paddy soil.

Analysis

Soil microbial biomass was determined by chloroform-fumigation extraction method (Inubushi *et al.* 1991). Dehydrogenase activity was measured by TTC reduction method (Trevors 1984). Methane production potential was measured by incubation method (Lou *et al.* 2006) and oxidation activity was measured by propylene oxidation method (Watanabe *et al.* 1995).

Results

Soil microbial biomass C was significantly larger in surface layer than those in subsurface soil (Figure 1). Effects of previous CO_2 treatment and warming treatment on microbial biomass were both not significant. Dehydrogenase activity and dissolved organic carbon (DOC) had no significant difference between elevated and ambient temperature, though significantly higher in surface soil than sub-surface soil (Figure 2). Methane (CH_4) production (methanogenic) activity was increased by elevated temperature, but no effect on CH_4 oxidation (methanotrophic) activity (Figure 3). These results indicated that elevated temperature may affect soil microbial processes in different ways.

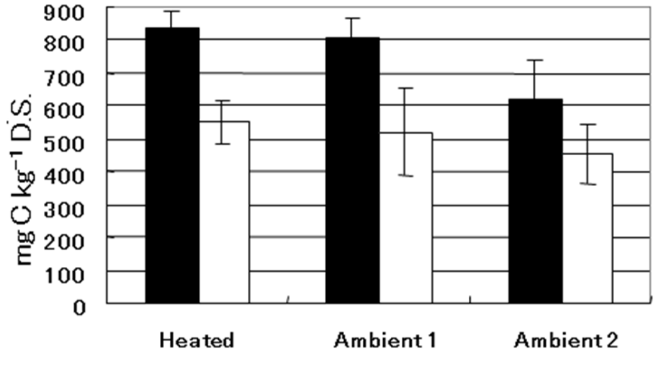

Figure 1. Microbial biomass in surface (■) and subsurface (□) soil as affected by CO_2 and temperature elevation.

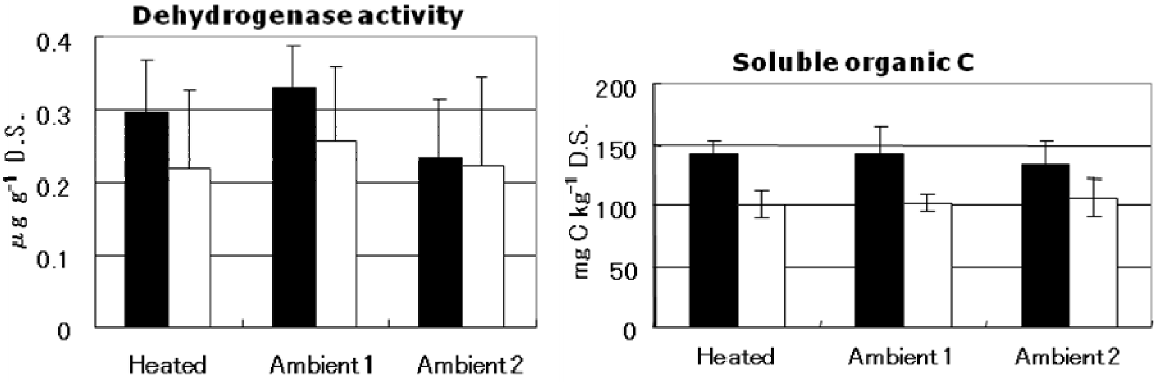

Figure 2. Dehydrogenase activity and dissolved organic carbon (DOC) in surface (■) and subsurface (□) soil as affected by CO_2 and temperature elevation.

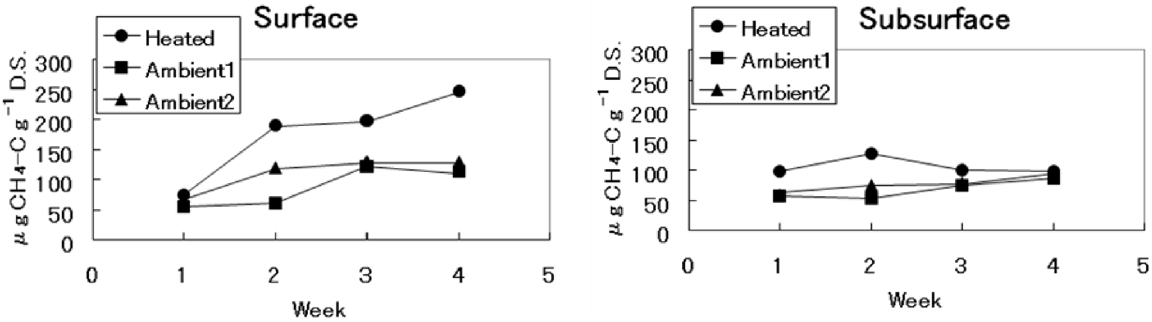

Figure 3. CH_4 production activities in surface and subsurface soil as affected by CO_2 and temperature elevation.

Conclusion

Soil microbial biomass C were significantly larger in surface layer than those in subsurface soil, but effect of previous CO_2 treatment and warming treatment on microbial biomass were both not significant. Dehydrogenase activity and dissolved organic carbon (DOC) had no significant difference between elevated and ambient temperature, though significantly higher in surface soil than sub-surface soil. Methane (CH_4) production (methanogenic) activity was increased by elevated temperature, but no effect on CH_4 oxidation (methanotrophic) activity. These results indicated that elevated temperature may affect soil microbial processes in different ways.

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Mineralogical assemblage and iron oxides of soils of the Pantanal biome, Brazil

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Abstract

The Pantanal biome is the largest wetland area of the world. Located in the centre of South American continent, it is being affected by the expansion of agricultural use. The effect of this occupation on environmental components of this complex biome such as flooding, sedimentations, vegetation and the characteristics of soils can not be evaluated due to scarce scientific information related to these factors. This study aimed to obtain information related to the forms of iron oxides features and mineralogical assemblage of the predominant soil classes found in this environment, once these characteristics reflect changes introduced by modifications in drainage conditions, flooding and sedimentation processes. The Gleysols present higher clay content than the Planosols and Plinthosols studied, probably related to deposition of clay in the lower position of the landscape, where they occur. The Plithosols, in spite of their lower clay content, showed the largest increase in Fe_d and $Fe_d – Fe_o$ content, which must be related to the better oxidation conditions of this soil found on low ridges and mounds. The uniform mineralogical assemblage of the studied soils indicates that the origin and composition of the sediments and/or the pedogenic processes were similar in these soils.

Key Words

Pantanal biome, agricultural expansion, sedimentation processes, pedogenetic processes.

Introduction

The Pantanal biome, located in the middle of the South American continent (16° - 20°S and 58° - 50°W), predominantly in Brazil, is considered the world's largest wetland, occupying an area of about 200,000 km^2 (Por 1995). The landscape is characterized by a mosaic of landforms, such as permanent and temporary rivers and lagoons, vast extensions of floodplains and non-flooded mounds and ridges usually covered with woody vegetation (Haase 1999). The distinct areas have received different types of sediments resulting in a different behavior of water dynamics in the soil profile, which determines the occurrence of different pedogenetic process (Couto and Oliveira 2009). Hydromorphism is the predominant acting pedogenetic process where the redistribution of iron and the development of grey soil colors and reddish mottling (gleying) is the most viewable consequence. In non-flooded landforms podzolization and laterization are the main acting pedogenetic processes. At the Barão de Melgaço region, located in Northern Mato Grosso State, Brazil, three main soil classes are identified: Gleysols (exchangeable aluminum-rich) in seasonally flooded areas, Planosols (sodium-saturated with eutric character) and Plintosols (low cation exchange capacity and base saturation) in slightly more elevated landforms (Couto and Oliveira 2009).

The environmental impact of the increasing land use in this biome is not assessed yet. This is related to the existence of poor scientific environmental information about the relationship between landforms, vegetation and distribution of soils. In order to improve the understanding of the environmental responses to the anthropogenic influence, this study aimed to collect information about mineralogical assemblage and iron oxides features of the main soil classes of Pantanal biome in Northern Mato Grosso State, Brazil.

Methods

The study was developed at RPPN-SESC Pantanal at Barão de Melgaço sub region located between Cuiabá and São Lourenço Rivers, 145 km away from Cuiabá, capital of Mato Grosso State. The landscape is plain to gently sloping with elevations ranging from 80 to 150 m. Local climate is classified as Aw, with mean annual temperature ranging from 22 to 32 °C, with a well defined dry season from May to September and a rainy season from October to April. The total annual precipitation is around 1000 to 1200 mm. Data of three modal soil profiles was obtained from SBCS (2002): Umbric Gleysol (GLum), Haplic Planosol (PLha) and Haplic Plinthosol (PTha).

The pipette method was used for granulometrical analysis after sample dispersion with 1.0 mol/L NaOH solution. Total iron oxides (oxides, hydroxides and oxi-hydroxides) (Fe_d) were estimated by the dithionite-citrate-bicarbonate method and iron from poorly crystalline oxides (Fe_o) were extracted with 0.2 mol/L NH_4 oxalate (pH 3.0). Air-dried, K-saturated (subjected to successive heat treatments), Mg-saturated and glycolated samples of clay fraction were analyzed by X-ray diffraction (XRD).

Results

Clay and iron oxides features

Among the studied soils, the greatest clay contents were found in the Glum soil. All samples showed an increase of clay content with soil depth (Figure 1a), and this behavior was also observed for Fe_d and Fe_d - Fe_o contents (Figure 1b and d). PTha soil showed the largest increase in Fe_d and Fe_d - Fe_o contents with depth in spite of its lower clay content (Figure 1b and d) and this result was related to the occurrence of Fe^{3+}-rich nodules and mottles formed in aerated soil pores during reductive conditions.

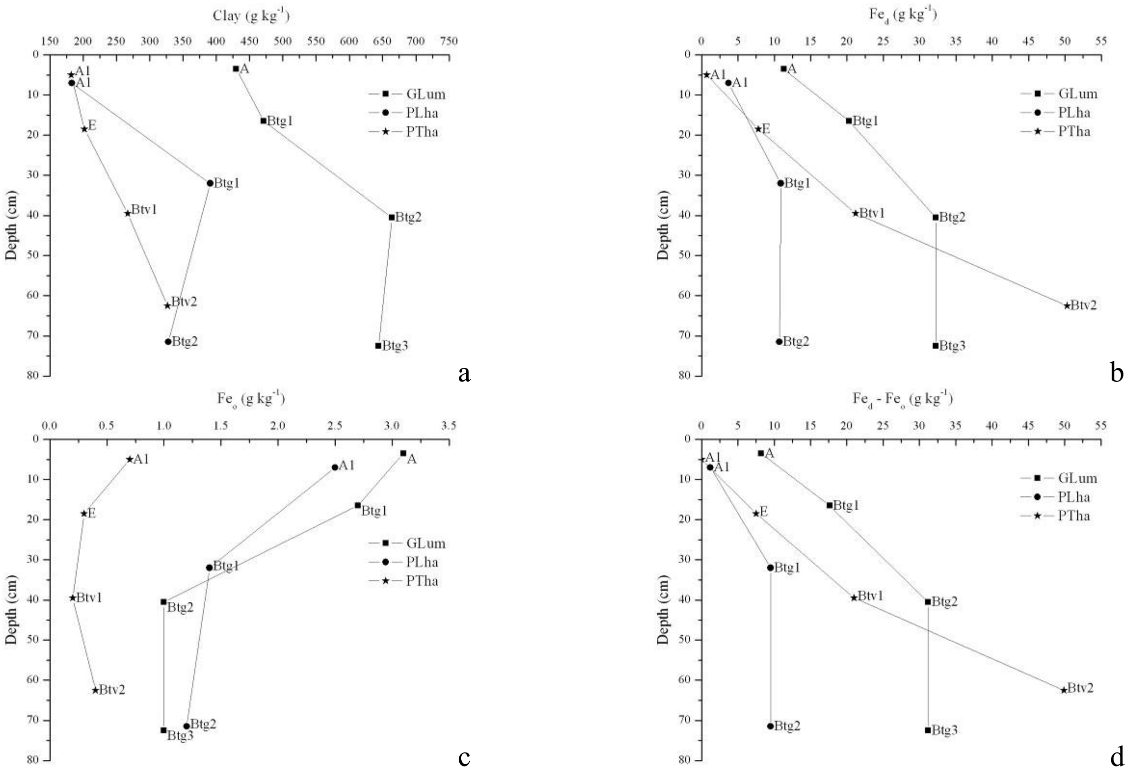

Figure 1. Clay and iron oxides contents in three modal soil profiles of Pantanal biome, Mato Grosso, Brazil.

Fe_o content in GLum and PLha soils were high in surface layers and decreased considerably with depth, while in PTha the contents were low and relatively uniform along the profile (Figure 1c). Greater contents of Fe_o on upper horizons can be assigned to the complex formation with soil organic matter, which hinders the crystallization of amorphous Fe oxides forms (ferrihidrite and lepidocrocite) into more stable ones (hematite and goethite) (Dalmolin *et al*. 2007). Consequently, the ratio Fe_o/Fe_d was higher in upper horizons and decreased with depth (Figure 2a). Values of Fe_o/Fe_d below 0.20, recorded for deeper horizons (< 0.30 m) suggest that translocation of Fe oxides in these soil profiles is not relevant. The extremely low value of Fe_o/Fe_d in PTha (< 0.05) is coherent for plintic horizons (Daugherty and Arnold 1982). This behavior demonstrates that crystallization degree of Fe oxides increases when a mottled horizon turns into a plintic one during pedogenetic evolution.

The increase of crystalline Fe forms with depth, indicated by a reduction of Fe_o/Fe_d, suggests that in deeper horizons crystalline rather than amorphous Fe forms may be dissolved preferentially by acting as terminal electron acceptors during bacterial anaerobic respiration (Munch and Ottow 1980). The high variability in Fe oxides features observed in the present study indicates a different dynamics regarding the total reducible Fe content (van Bodegom *et al*. 2003). The highest Fe_d/Clay values in deeper layers observed in the PTha soil (Figure 2b) (0.00 to 0.15) can be attributed to a segregation of Fe oxides from soil matrix during plinthite genesis. According to Blume and Schwertmann (1969) the occurrence of uniform Fe_d/Clay values along soil profile, as shown by GLum and PLha might indicate that Fe oxides and clay are being mobilized together.

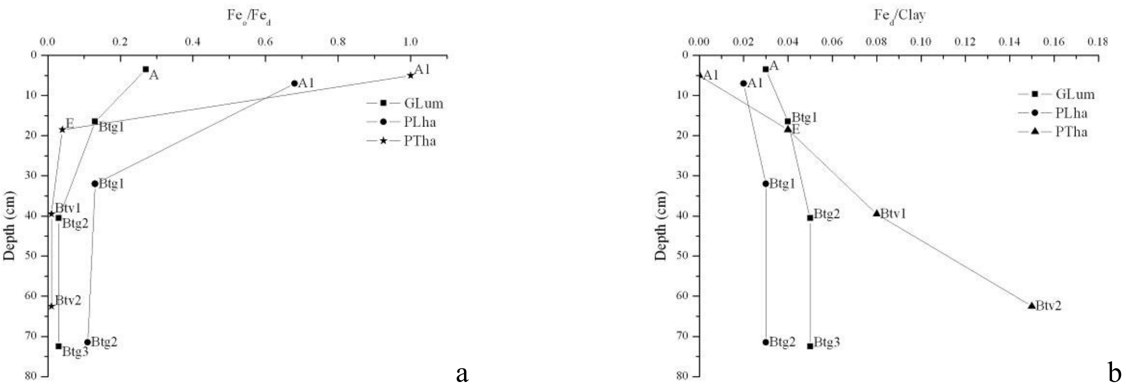

Figure 2. Fe$_o$ to Fe$_d$ (a) and Fe$_d$ to clay (b) ratios in three modal soil profiles of Pantanal biome, Mato Grosso, Brazil.

Mineralogical assemblage

The XRD difractograms of clay fraction showed a very similar pattern in the studied soil evidencing a low diversity in its mineralogical composition (Figure 3). Occurrence of micaceous minerals was indicated by peaks around 0.5, 0.445 and 0.255 nm. Furthermore, the peaks at 1.0 e 0.33 nm (illite) were not altered after saturation and heating treatments, confirming this assumption. According to Kämpf and Curi (2003) high contents of micaceous minerals may be found in soils originated from sandstone, which is one of the most important sources of sediments for Pantanal (Buchas *et al*. 2000).

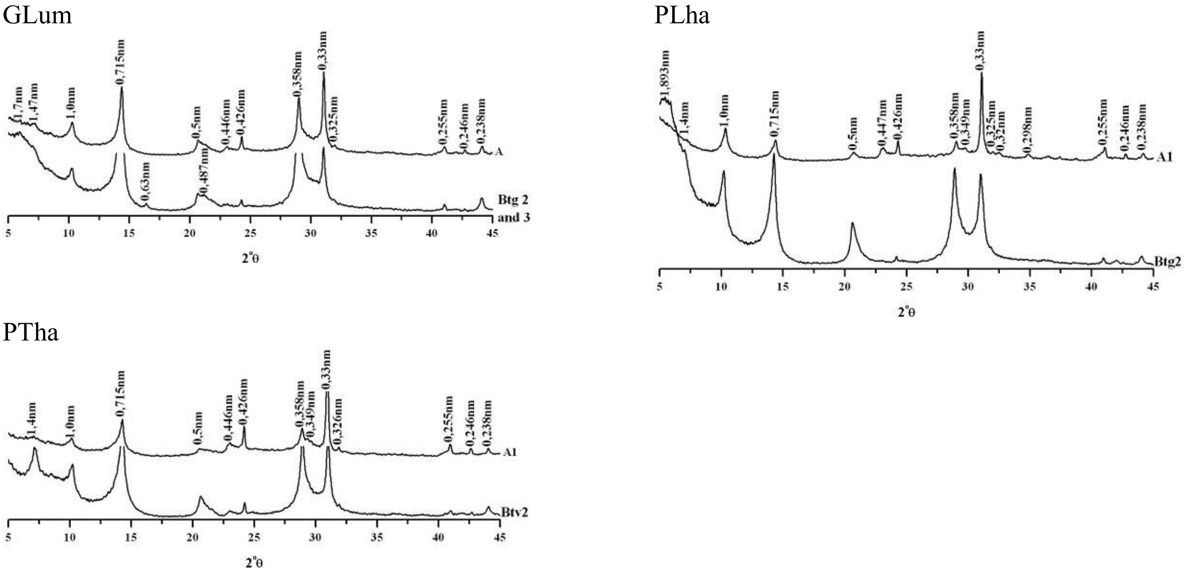

Figure 3. XRD patterns of the clay fraction in three modal soil profiles of Pantanal biome, Mato Grosso, Brazil.

Occurrence of kaolinite was identified in all soil horizons due to highest intensity of diffraction peaks at 0.715 e 0.357 nm which disappear after heating at 550 °C. Probably, due to adverse pedogenic conditions (alkalinity and high base saturation) kaolinite has an exogenous origin, coming mainly from well-drained sites outside Pantanal (Furquim *et al.* 2009). Under reductive (alkaline) medium dissolution of these minerals may occur with consequent liberation of Si, Al and Fe into solution (Huertas *et al.* 1999). Diffraction peaks at 0.426, 0.33 and 0.246 nm indicate the occurrence of quartz, while diffraction peaks around 0.299, 0.322, 0.324 and 0.348 nm indicate the occurrence of feldspar in all soil horizons.

GLha soil also showed diffraction peaks at 0.63 nm assigned to the presence of lepidocrocite in B horizons as a result of the precipitation of Fe oxides in mottles and nodules. Hydroxy-Al interlayered vermiculite (HIV) was identified after partial collapse of diffraction peak around 1.4 nm in K-saturated and heated samples. Occurrence of hydroxy-Al increases vermiculite stability and allows its coexistence with gibbsite assigned to the diffraction peak around 0.487 in GLha. HIV was also identified in PLha and PTha. Abundance of micaceous minerals in Pantanal soils indicates that the formation of HIV may follow the ordinary weathering sequence: feldspar – mica – illite – vermiculite – HIV (Barnhisel and Bertsch 1989).

Conclusion

GLum soil present the highest clay contents when compared to the other soil classes. PTha showed the largest increase in Fe_d and Fe_d - Fe_o contents with depth in spite of its lower clay content. Fe_o content in GLum and PTha decreased considerably with depth while small variation occurs in PTha. Higher contents of Fe_o on upper horizons indicate that transformation of amorphous Fe oxides forms into more stable ones is being retarded. The high variability in Fe oxides features results in differences among soils which is related mainly to C contents and drainage conditions. The mineralogical characteristics were not good parameters for distinguishing Pantanal soils. In spite of their sedimentary origin that resulted in remarkable lithological discontinuities and poor drainage environments, affecting sensitively soil granulometry and Fe oxides features, mineralogy has shown a great uniformity.

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Organic carbon transformation along a salinity gradient in Louisiana wetland soils

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Abstract

Wetlands constitutes one of the major sources of global terrestrial carbon (C) pool and play an important role in global carbon cycle. In this study, organic C transformation and its relation to C gas and N_2O emissions in wetland soils of a forest swamp (FS), freshwater marsh (FM) and saline marsh (SM) in coastal Louisiana were studied. Molecular C compositions of bulk soils and purified humic acids were determined using NMR and pyrolysis GC/MS. Carbon gas emissions and the impacts of electron acceptors were investigated through incubations. The three wetland soils exhibited distinctive molecular C characteristics with more polyphenols in FS as compared to more lignin in FM. Both NO_3^- and SO_4^{2-} inhibited CH_4 production but only NO_3^- decreased CO_2 production from FM soil under anaerobic condition. On the other hand, FM soil tended to yield greater incomplete denitrification, which could result in higher emission of N_2O. Higher contents of phenolics and aldhydes/ketonics in SOM, however, decreased denitrification in these wetland soils.

Key Words

Soil organic carbon, wetlands, greenhouse gas, humic acids.

Introduction

Louisiana coastal wetlands, located on the Mississippi delta plain, have been subsiding due to the compaction of recent alluvial sediments. As a result, these wetlands have been increasingly under the influence of seawater intrusion. Mississippi river water is currently being diverted into these wetlands with the aim to decrease salinity and provide sediments (LDNR 2005). While the seawater intrusion brings in SO_4^{2-} and other ionic species, the diverted Mississippi river water carries elevated levels of NO_3^- (Donner 2004). These nutrient environments could have different impact on soil organic carbon (SOC) transformation and C gas emissions in these wetlands, which has not been fully evaluated. Recently, organic matter accretion along with sediment addition has been considered as major controlling factors in stabilizing these wetlands (DeLaune and Pezeshki 2003). Yet, little is known about organic matter structure and its transformation especially under existing and anticipated conditions (Dodla *et al.* 2008). Therefore, this study was carried out to characterize SOC transformation in these wetland soils within a salinity gradient and evaluate the specific effects of NO_3^- and SO_4^{2-} on C gas productions (CH_4 and CO_2) from these wetlands.

Methods

Site and soil characteristics

Three sites of a bottomland forest swamp (FS), freshwater marsh (FM), and saline marsh (SM) located in the Louisiana Barataria Basin estuary were selected for this study. Mississippi River water has periodically diverted in to the northern region of the Basin as part of effort to restore these wetlands (LDNR 2005). The major vegetation types in FS, FM, and SM are *Taxodium distichum*, *Sagittaria lancifolia*, and *Spartina alterniflora* respectively. The soils at the FS, FM and SM sites were Barbary muck (Very-fine, smectitic, nonacid, hyperthermic Typic Hydraquents), Allemands muck (Clayey, smectitic, euic, hyperthermic, Terric Haplosaprists), and Timbalier muck (Euic, hyperthermic, Typic Haplosaprists), respectively. Fifteen composite soil samples from different horizons at each site were collected and thoroughly mixed. A portion of each sample was freeze-dried and the reminder was stored frozen or directly analyzed (Table 1).

Table 1. Selected physical and chemical properties.

Site	Soil	pH	EC dS/m	TOC	Total N
				(------g/kg-----)	
FS	Barbary muck	6.2	1.2	66	4.6
FM	Allemands muck	6.3	3.1	292	18.2
SM	Timbalier muck	7.3	38.9	159	8.7

NMR and Pyrolysis-GC/MS characterization

Molecular C composition of wetland SOM and humic acids purified based on the procedure of International Humic Substances Society (Swift 1996) was determined using solid-state ^{13}C nuclear magnetic resonance (NMR) and pyrolysis-gas chromatography/mass spectrometry (Py–GC/MS). ^{13}C NMR spectra were obtained using a Bruker Avance wide bore 400 MHz instrument with a double resonance 4mm CP-MAS probe. The cross polarization total sideband suppression magic angle spinning (CP-TOSS-MAS) technique was used to acquire the ^{13}C NMR spectra (Cook and Langford, 1998). Chemical shifts were expressed relative to tetramethylsilane (TMS). The peaks between 0 -230 ppm chemical shift range were assigned to various C moiety groups as aliphatic C (0-50 ppm), polysaccharides (50-108 ppm), aromatic C (108-165 ppm), carboxyl C (165-190 ppm), and aldehydes and ketonic C (190-230 ppm). Chemical shift range 108-165 ppm was further divided into aryl C (108 -140 ppm) and phenolic C (140 – 165 ppm). Py-GC/MS analysis was performed using a CDS 5000 pyrolyzer, directly connected to a Varian 3900 GC coupled to a Varian Saturn 2100T ion trap mass spectrometer. The identification of pyrolysis products was based on a comparison of their mass spectra with those of standard compounds and NIST 2005 mass spectral library, literature data and GC/MS characteristics.

Field carbon gas emission and laboratory microcosm experiments

Monthly characterizations of CO_2 and CH_4 emissions from these sites were conducted over a two year period to evaluate the difference in C gas emissions among these sites. Laboratory anaerobic incubation experiments were also carried out to determine the influence of NO_3^- and SO_4^{2-} on C gas production from the FM soil. Ten-gram field moist soil samples were weighed into glass jars followed by adding 130 mL of deionized water. Sample slurries in the jars were flushed with N_2 gas to remove any dissolved/ trapped O_2. Treatment solutions were added to bring final concentrations of NO_3^- to 3.2 and 5 mM NO_3^- and SO_4^{2-} to 2 and 5 mM, respectively. All incubations were carried out in triplicates and conducted in dark at room temperature (22±0.5 °C) for 214 days. The CO_2 and CH_4 in the headspace of each jar were periodically analyzed using a Varian 3800 GC. In addition, separate incubations were carried out to determine potential denitrification rates (PDR) of these wetland soils. In doing so, 10 g field-moist soils were mixed with 10 mL solutions of 0.14 or 0.71 mM NO_3^- -N in sample vials. The mixtures were treated with or without acetylene and incubated. The N_2O concentration in the headspace of each sample vial was determined using a Shimadzu GC. The amount of N_2O present in the headspace of sample vials with acetylene represents the potential for the amount of NO_3-that can be denitrified, whereas the amount of N_2O in the head space of sample vials without acetylene represents the potential for incomplete denitrification (Hunt *et al.* 2007). PDR was estimated from the steepest portion of the curve plotted between total amount of N_2O released (with acetylene treatment) and incubation time (Dodla *et al.* 2008).

Results

Soil organic carbon characteristics

Pyrolysis-GC/MS analysis of bulk samples of these wetland soils showed that out of all identified peaks, organic matter in FS soil was dominated by compounds derived from polyphenols whereas organic matter in FM soil was by those derived from lignin. SM soil organic matter contained the lowest percentage of N-bearing compounds (Table 2). ^{13}C NMR analysis showed that humic acids extracted from FM soil were significantly more aromatic than SM humic acids (Figure 1). The aromaticity of the humic acids, estimated by % peak area between 110 to 165 ppm to peak area between 0 to 165 ppm was 47.2 % for FM-HA as opposed to 35.4% and 39.7% respectively for humic acids from FS and SM soils. On the other hand, FS humic acids were found to be more aliphatic than those from SM and FM. Closer examination of aliphatic region indicated an increasing intensity in 31 ppm spectrum peak along with these wetlands of increasing salinity (Figure 1). This peak has been attributed to long crystalline or condensed polymethylenic $(CH_2)_n$ chains (Hu *et al.* 2000). The result could suggest that the increased salt concentration or associated saline environment enhance the crystallinity of alkyl C in humic acids in these soils.

Table 2. Relative distribution of C compounds determined by Py – GC/MS for three wetland soils.

Soil	Alkyl	Lignin	N-containing	Polyphenols	Polysaccharides	Total
	(--		%		--)	
FS	19.5	16.0	12.4	26.7	11.4	86
FM	20.0	31.3	16.1	5.4	10.1	82.9
SM	21.5	20.8	9.7	11.5	13.9	77.4

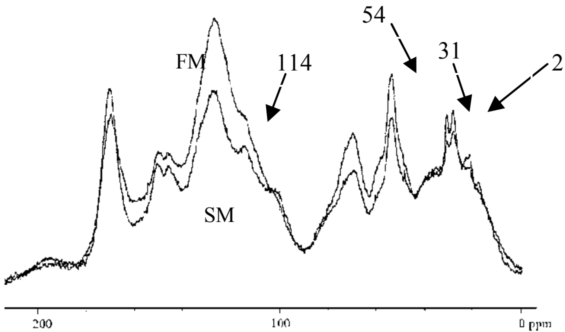

Figure 1. ^{13}C NMR spectra of FM and SM soils.

Carbon gas emissions

Field monitoring showed that FS soil had generally higher CH_4 emissions than FM and SM soils (Figure 2). FS soil also had higher CO_2 emissions than FM and SM soils. The emission difference between FM and SM soils was small.

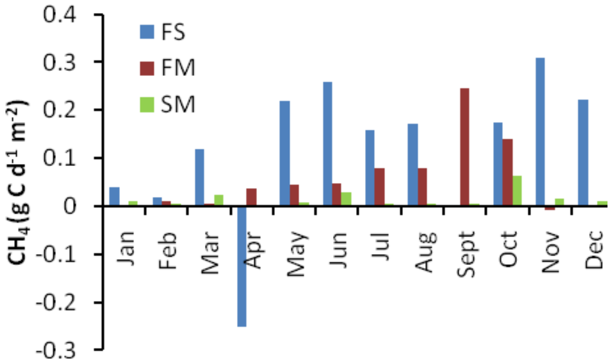

Figure 2. Two-year average seasonal emission of methane from three wetland soils.

Further laboratory incubation study of FM soil, where it is likely to be influenced by integrated effect of seawater intrusion and Mississippi river diversion, showed that the presence of NO_3^- and SO_4^{2-} affected C gas productions differently (Figure 3). Under anaerobic condition as these wetlands often are, both NO_3^- and SO_4^{2-} presence decreased CH_4 production. The NO_3^-, however, almost completely inhibited CH_4 production (> 99 %) as compared to 78-90% reduction by SO_4^{2-}. On the other hand, the presence of NO_3^- (at 3.2 mM) significantly decreased CO_2 productions from FM soil whereas SO_4^{2-} did not (Figure 3).

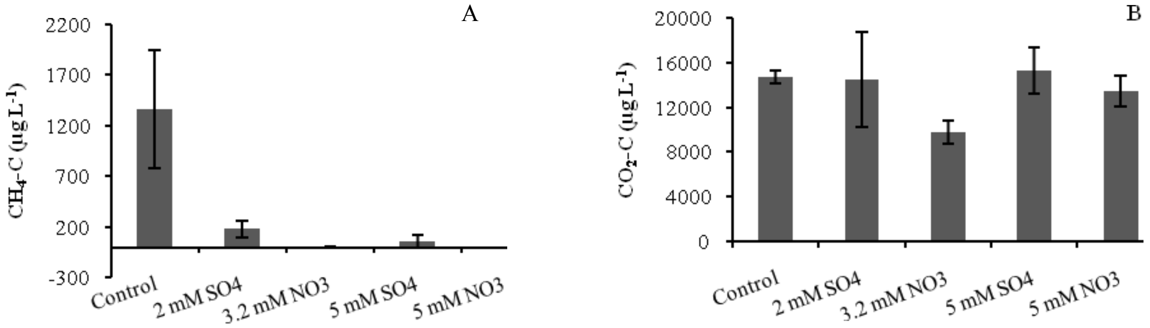

Figure 3. Total production of (A) CH_4-C and (B) CO_2-C from FM soil as influenced by different concentrations of NO_3^- and SO_4^{2-} under anaerobic incubation for 214 days.

Carbon quality and denitrification

Besides the release of C gases, transformation of SOC also affects the emission of other trace gas such as N_2O from denitrification process. Analysis of PDR and molecular C composition of SOM showed that PDR was positively related to polysaccharide-C (R^2=0.75) but negatively related to phenolic C (R^2=0.49) and aldhydes/ketonic C (R^2=0.65) in these wetland soils. On both unit weight and unit volume basis, FM soil profile exhibited the highest PDR as compared to FS and SM. In addition, FM soil tended to yield higher percentage of N_2O release as compared to the FS and SM soils (Table 3), suggesting a greater incomplete denitrification and potential for emission of N_2O into atmosphere.

Table 3. Percentage of added NO_3^- -N released as N_2O-N at two levels of treatments.

Soil	Depth (cm)	NO_3^- Treatment 0.14 mM	NO_3^- Treatment 0.71 mM
FS	0-25	15.4	2.7
	25-50	15.2	8.2
	50-75	3.3	0.9
	75-100	1.5	0.1
FM	0-25	38.3	18.8
	25-50	3.3	0.6
	50-100	23.1	0.9
	100-150	0.5	0.5
SM	0-50	-	0.03
	50-75	-	0.06
	75-100	0.9	1.02
	100-150	-	0.02

Conclusion

Wetland soils along a salinity gradient in Louisiana Gulf coast likely have different SOC transformations as evidenced by the differences in molecular C composition of humic acids as well as organic matter in bulk soils. These differences in SOC transformations could affect differently the emissions of C gases and N_2O from these soil systems.

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Peatlands, carbon, and climate: the role of drought, fire, and changing permafrost in northern feedbacks in climate change

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Abstract

Peatlands store ~30% of the world's soil carbon and are located primarily at northern latitudes, where they are experiencing rapid climate warming. As climate change alters peatland hydrology and soil temperatures, changes in ecology and biogeochemistry may alter rates of carbon storage as peat. Moreover, warmer and drier conditions may enhance the decomposition of old carbon in peatlands, accelerating greenhouse gas emissions with positive feedbacks to climate change. Here, I present findings from experiments, regional surveys, and modeling studies that examine the consequences of warming, drought, and disturbance on the ecology and carbon cycling of boreal peatlands. While fast ecosystem responses to drought include reduced ecosystem carbon storage, a long-term experiment showed that drainage increased woody inputs to soils and soil carbon storage. However, increased forest cover made these drained ecosystems more susceptible to burning during wildfires, leading to large carbon losses through fuel combustion and ecosystem succession. In addition to changes in ecosystem carbon storage and exchange, additional research on other aspects of radiative forcing, such as surface albedo change, is required for a more complete understanding of the role of peatlands in climate warming.

Key Words

Soil carbon mineralization, greenhouse gases, disturbance, vegetation productivity, plant-soil feedbacks.

Introduction

Over the past several decades, high latitude ecosystems have experienced rapid climate change that has resulted in soil warming, permafrost degradation, increased snow pack thickness, and longer growing seasons (Hinzman *et al.* 2005). Remote sensing studies show that lakes and wetlands in many boreal regions are drying, often accompanied by the encroachment of drier terrestrial vegetation (Riordan *et al.* 2006). However, in other boreal regions, permafrost thaw and increased upwelling of melt water is leading to wetland saturation and the formation of thermokarst lakes (Jorgenson and Osterkamp 2005). Peatlands represent only 1-3% of the world's land surface, but play a major role in the global carbon cycle. Peatlands have served as a long-term sink of carbon dioxide (CO_2), but also represent a natural source of atmospheric methane (CH_4). The position of the water table within a peatland serves as a dominant control on peatland-atmosphere carbon exchange, as it influences plant structure and productivity, rates of decomposition, and dissolved carbon export. With climate models predicting enhanced evapotranspiration under a 2 x CO_2 scenario, and therefore a lower water table position in peatlands, many studies have predicted that peatland CH_4 emissions will decrease while CO_2 emissions will increase in the coming decades.

Wildland fire is one of the most common and important disturbances affecting boreal forests, and its role in regulating forest ecosystem structure and function long has been recognized (Viereck 1973). Until recently, fire was not considered to be an important control on peatland carbon cycling because high water table positions in peatlands were thought to limit fire frequency (Kuhry 1994) and fuel combustion severity (Zoltai *et al.* 1998). However, recent work has shown that fire influences North American peatlands more regularly than previously thought. As a result of recent climate change, the annual area burned in boreal North America has more than doubled since 1950, raising the question of whether the deep organic soils currently stored in peatlands are becoming more vulnerable to burning. Understanding peatland feedbacks to climate change requires information on rates of peat accumulation, CO_2 and CH_4 fluxes as well as surface energy balance (*i.e.*, albedo). Here I present findings from experiments and modeling studies examining ecological and biogeochemical responses in peatlands to warming, drought, permafrost thaw, and wildfires.

Methods

The Alaska Peatland Experiment (APEX) is an ecosystem-scale experiment using soil temperature and hydrology manipulations to study the consequences of climate change on peatland carbon cycling. Since 2005, growing season CO_2 and CH_4 fluxes have been monitored across a factorial design of *in situ* water table (control, drought, and flooded plots) and soil warming (control vs. warming via open top chambers) treatments in a groundwater-fed fen that lacks surface permafrost. In 2007, the APEX study was expanded to include climate manipulations in a collapse scar that experienced recent permafrost thaw as well as in a forested bog with intact permafrost. While the APEX study examines fast ecosystem responses to altered soil climate, on a decadal scale changes in succession is likely to govern ecosystem responses to disturbances such as drought. In the mid-1980's, several peatlands in western Canada were drained in a government experiment intended to explore the potential for enhanced forest harvesting in peatlands. Today, this experiment provides a novel opportunity for exploring the effects of several decades of lowered water table position on peatland ecology and biogeochemistry. The Canadian Large Fire Database and peatland distribution maps have been used to explore patterns of burn area in peatlands across western Canada, representing about 40% of the Canadian land-base. Measurements of organic matter consumption have been made in a variety of natural and experimental fire events in both western Canada and Alaska to better understand vegetation and fire weather controls on carbon losses during burning. These data have been used in fire emissions models to estimate continental-scale emissions of carbon and mercury due to peat fires.

Results

Results from the APEX study show that the drought (lowered water table position) treatment increased net ecosystem exchange, making the drought plot more of an atmospheric C source relative to the control, by lowering gross primary production and light-saturated photosynthesis rather than by increasing ecosystem respiration (Chivers *et al.* in press). Soil flooding caused the site to become a greater C sink due largely to increased vegetation production. Soil warming increased both ecosystem respiration and gross primary production of CO_2, with no net effect on net ecosystem exchange. Both water table and soil temperature served as significant controls on CH_4 emissions, with the highest CH_4 emissions occurring in the flooded and warmed treatments (Turetsky *et al.* 2008).

While fast responses to drought (lowered water table position) in the APEX study included increased CO_2 fluxes to the atmosphere, 30+ years of experimental drainage in an Alberta peatland resulted in increased soil bulk density, faster rates of peat accumulation, and overall larger soil carbon pools compared to undrained sites. Increases in carbon pools post-drainage are due primarily to increased forestation, with greater tree density and growth rates that likely altered both the amount and quality of litter inputs to soils.

Analysis of annual peatland area burned in western Canada show that large areas of peatlands in continental Canada can burn, with interannual variability similar to annual area burned in forests. The total burn area of large fire events between 1980 and 1999 is positively correlated to the abundance of peatlands in western Canada, suggesting that these peatlands are particularly susceptibility to burning during large fire years and/or extreme fire weather conditions (Turetsky *et al.* 2004; Benscoter *et al.* in press). Published estimates of fuel consumption rates in Canadian peatlands range from 0.9-3.7 kg C/m^2 per fire event, which is similar to forest combustion rates (Benscoter and Wieder 2003; Turetsky and Wieder 2001). However, fuel combustion in permafrost forests with thick peat deposits in Alaska are much higher than previously anticipated. Patterns of fuel combustion in the long-term drainage sites in Alberta were 4-fold higher than in undrained peatlands, suggesting that deep soil carbon may be become more vulnerable to burning with increasing thaw depth and/or under sustained drought conditions.

Conclusion

Fast ecosystem responses to drought in our Alaskan experiment included increased CO_2 emissions to the atmosphere, primarily because of reduced CO_2 fixation by plants, and reduced CH_4 emissions. However, longer-term ecosystem responses to drought in Canada included changing plant community composition and substrate quality that favored peat accumulation, yielding larger soil carbon pools relative to pristine peatlands. In the forested peatlands of western Canada, about 30% of soil carbon is situated above the regional water table in aerobic peat layers and is vulnerable to burning under current climate conditions. However, deeper peat layers will become increasingly exposed to fire as these ecosystems are subjected to regional changes in both fire weather and drought. Both empirical and modeling results demonstrate that drought conditions that lower regional water tables and/or increase fire severity in peatlands greatly exacerbate regional emissions of carbon and mercury to the atmosphere (Turetsky *et al.* 2006). While peatlands in North America have served as a long-term carbon sink, drier climatic scenarios that lead to altered carbon mineralization rates or fire regimes could accelerate greenhouse gas emissions and cause much of the stored soil organic matter to be released back to the atmosphere.

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The effect of riparian buffers with controlled drainage on soil redox potential

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Abstract

Deteriorating surface water quality due, in part, to nitrogen from nonpoint sources has fueled much interest in solutions to these problems. To meet North Carolina mandates of reducing nitrogen loads in selected rivers by 30% over a five-year period, scientists proposed guidelines to meet this goal. Riparian buffers and controlled drainage are two Best Management Practices (BMPs) than have been shown to reduce the amount of nitrogen entering surface and subsurface waters as a result of denitrification, but they are not always effective or practical on all landscapes. A project to study the effect of using riparian buffers in conjunction with controlled drainage was initiated. Soil redox potential is an indicator that provides evidence as to whether or not conditions are favorable for denitrification. Four riparian buffers at widths of 7.6 or 15.2 m, with five vegetative treatments (fescue, switch grass, pine trees, field crop, and native vegetation), were established. Groundwater monitoring wells, at three depths, were installed at the edge of the ditch, the field edge, and in the field in each treatment. A water control structure was installed at the mouth of one of the ditches. A total of 176 redox electrodes were inserted to 76 cm or 152 cm at the ditch and field edges of the riparian buffers. By raising the water table with controlled drainage, conditions favoring denitrification were enhanced. Results from this one-year study show that buffers with controlled drainage at a depth of 152 cm had low redox values favorable for denitrification and subsequently lower nitrate concentrations in the groundwater as compared to areas with buffers, but no control.

Key Words

Redox, nitrate, riparian buffer, controlled drainage, water quality.

Introduction

Riparian buffers form an important transition zone between upland landscape positions and lower-lying bodies of water. This transition zone usually has soils that are somewhat poorly to very poorly drained. Riparian buffers are significant because of their recognized role in regulating the movement of pollutants, such as nitrogen, sediment, and phosphorus from upland surface and/or subsurface groundwater (Hill 1996).

Riparian Buffers

Research has consistently shown the effectiveness of riparian zones in nitrate removal. In the Middle Coastal Plain of North Carolina, Jacobs and Gilliam (1985) used chloride (Cl^-), a conservative ion, to trace the path of N leaving a cultivated field, which was located next to a riparian zone, via subsurface drainage. Chloride is not subject to gaseous losses or used in great quantities by plants. Decreases in nitrate/chloride ratios over space or time may indicate losses of nitrate possibly due to denitrification, while no change in this ratio may indicate dilution by water that contains less nitrate and chloride. This study showed decreases in nitrate/chloride ratios from the field edge and stream. The major loss of nitrate was attributed to denitrification, while a small portion of the nitrate was lost through uptake by riparian vegetation. The most important factor controlling the ability of riparian buffers to reduce nitrogen is hydrology (Gilliam *et al.* 1997). Nitrate is very mobile and is easily leached through the soil profile. Nitrate generally enters surface waters through subsurface flow. Much of the research on riparian buffers has been on similar geophysical regions in the Mid-Atlantic States and in the Southeast. Generally, soils in these areas have a restrictive layer within the profile that forces groundwater to flow laterally, rather than downward. Consequently, nitrate in groundwater enters surface water via this route. The interaction of this laterally flowing groundwater and the riparian buffer is extremely critical. Denitrifying microorganisms require an energy source, such as carbon, for this nitrogen transformation to occur. Riparian vegetation provides the denitrifying microorganisms a source of carbon, which becomes available from plant or root decomposition. Groundwater that flows too deep in the soil profile may bypass the strategic zones where riparian soils and vegetation exist, thus eliminating the possibility of the occurrence of denitrification. Researchers agree that there is a complex interaction between hydrology, vegetation, and soil processes with regard to denitrification.

Controlled Drainage

In Eastern North Carolina, over 2,000,000 acres of cropland are grown on soils that are poorly drained (Evans *et al.* 1991). Consequently, drainage is a critical component to successful crop production in Eastern North Carolina. Much of this acreage is located near sensitive lakes, estuaries, and streams. Pollutants, such as nitrogen, phosphorus, and sediment are easily transported into these bodies of water through surface or subsurface flow. Water table management, specifically controlled drainage, has been shown to improve water quality and improve crop production (Thomas *et al.* 1992; Thompson *et al.* 1998). Controlled drainage consists of installing a structure, such as a flashboard riser, in a drainage outlet. As boards are added to the riser, the water level rises in the drainage ditch, and subsequently, in the adjacent fields. Boards can also be removed during wet periods to encourage more rapid drainage, which improves trafficability in agricultural fields. However, controlled drainage is most effective when the topography is nearly level. With regard to water quality, controlled drainage reduces the amount of N through reduced flow and higher denitrification rates due to favorable conditions provided by a higher water table. Compared to conventional drainage, controlled drainage has been shown to reduce total outflow by up to 30% during some periods, but may vary based on the amount of rainfall, soil type, drainage system, management intensity, and season (Evans *et al.* 1995).

Redox Potential

Redox potential is one of the most important electrochemical properties that distinguish a well-drained soil from soils in wetter drainage classes. A high redox potential indicates aerobic soil conditions, while a lower redox potential reflects a more reduced state. It is commonly accepted that a redox potential value of 350 mV is the critical level for denitrification. Monitoring the state of reduction of a soil provides evidence as to whether or not conditions are favorable for biological reductions, such as denitrification. Denitrification is important because it efficiently removes nitrate from a soil system. Nitrate is very mobile and easily leaches into groundwater, which can potentially lead to human health hazards and environmental problems. Measuring redox potential in situ to determine the oxidation or reduction status of the soil, is one of the parameters that researchers are using to further substantiate the conditions at which nitrate disappears. Griffith *et al.* (1997) studied the loss of nitrate from groundwater as it moved from a cultivated field through a riparian buffer. Soil redox potentials measured at a depth of 25 cm and 45 cm in the riparian buffer (soil pH ranged from 4.9 to 5.5) averaged -200 mV to –100 mV which are clearly low enough for denitrification. All sampling dates showed that nitrate concentrations were higher in the field compared to nearly undetectable levels in the riparian buffer. Their data collectively attributed to riparian processes as one of the mechanisms through which nitrate was removed. The reducing status of the soil in the riparian forest is further evidence of nitrate losses that can be attributed to denitrification. Researchers in North Carolina studying the effects of controlled drainage on nitrate losses showed that in moderately well drained soils, Eh values were well above the critical value of 325 mV for denitrification. High nitrate concentrations at this location confirmed this. While there appeared to be no differences resulting from drainage control in poorly drained soils, low nitrate concentrations associated with low Eh values below 1.0 m in the soil profile were most likely a result of denitrification (Gilliam *et al.* 1979). Similar research by Jacobs and Gilliam (1985) and Gambrell *et al.* (1975) related nitrate losses, decreases in nitrate/chloride ratios, and low Eh values to denitrification. Riparian buffers and controlled drainage are two best management practices that are effective in removing nitrates, but individually, may not be practical for all landscape positions. The purpose of this study was to determine whether or not combining these practices could create conditions favorable for denitrification. Redox potential, as related to the absence or presence of nitrate in groundwater and nitrate/chloride ratios, was the indicator of this desirable soil condition.

Methods

Study site

The study site is in the Middle Coastal Plain of North Carolina which is characterized as a moderately dissected landscape that has gentle undulating, nearly level to level sloping uplands and gentle to steep valley slopes (Daniels *et al.* 1999). Adjacent forested riparian buffers protect many of the larger streams and rivers. However, smaller drainageways, to which most agricultural subsurface waters flow, are formerly natural streams that have been channelized with their natural riparian vegetation removed. The soils at this location are terrace and flood plain soils. Because of their location next to the Neuse River, which frequently floods, the area is geologically complex. Soils series of importance in this study include Roanoke (fine, mixed, semiactive, thermic Typic Endoaquults), Tomotley (fine-loamy, mixed thermic Typic Endoaquults), Tarboro (mixed, thermic Typic Udipsamments), and Wickham (fine-loamy, thermic Typic Hapludults). The Roanoke and Tomotley soils located next to the ditches are very poorly drained and have slopes from 0 to 2 percent. The Tarboro and Wickham soils, located on slightly higher landscape positions, are somewhat excessively drained and well drained, respectively. Slopes on these soils range from 1 to 6 percent. It is important to note that all delineated soil types have inclusions. Soil investigations at this site indicate that restrictive layers are present at varying depths in the better-drained soils.

Two buffers were established along different segments of two ditches. Each buffer was divided into two widths, 7.6 m and 15.2 m. Within each buffer width are five vegetative treatments that are 25 m in length. The treatments in the buffers include fescue (commonly used for grass buffers in North Carolina), pine trees, switch grass (a deep-rooted grass), natural vegetation and the crop that is planted in the adjacent field to simulate no buffer (planting to the ditch, i.e., the control). A water control structure was installed at the mouth of the ditch. It included a flashboard riser and an adjustable V-notch weir. Well nests consisting of wells at three depths were installed in each of the treatments. Well nests were located immediately next to the ditch and at the field edge of the treatment. Also, four well nests were located outside of each buffer in the adjacent cropped field. Well depths were determined by a detailed soil investigation that ascertained the depths to restrictive layers within the profile and the expected depth to the water table. Wells were screened within the most transmissive zones, which were generally 0.6 to 1.2 m for the shallow wells, 1.8 to 2.4 m for the medium deep wells, and 3.0 to 3.7 m for the deep wells. Wells were sampled monthly, or more, during periods when leaching would possibly occur. Redox electrodes were installed at two depths, 76 cm and 152 cm, and placed in line with the adjacent well nests in vegetative treatments except switch grass. Five electrodes were placed 76 cm below the soil surface and three electrodes were placed 152 cm below the soil surface.

Results

Under normal conditions, redox potentials recorded on the buffer with no water control structure (R1) at the field edge and along the ditch were generally too high to indicate denitrification. The average Eh value for the electrodes installed to 76 cm was 667 mV. The Eh values ranged from a low of –53 mV to a high of 833 mV. Initially there was a wide range of variability at this depth that continued through late spring. However, a period of warm temperatures and little rainfall resulted in a narrower range of variability**.** The deep electrodes had an average Eh value of 757 mV and had a range of 429 mV to 859 mV**.** Low redox potentials recorded on the buffer with controlled drainage (R2N) indicated that conditions favoring denitrification existed depending on soil texture. Throughout this study, Eh values for the shallow electrodes followed a general trend of having higher values during warm and dry periods, dropping briefly following rainfall events, and rebounding shortly thereafter. Electrodes installed at 152 cm had lower redox potential values and exhibited more variability, which is consistent with the extreme variable conditions that may exist within the soil. A notable pattern difference observed at locations in the middle of the buffer may be attributed to soil texture differences observed during the soils investigation.

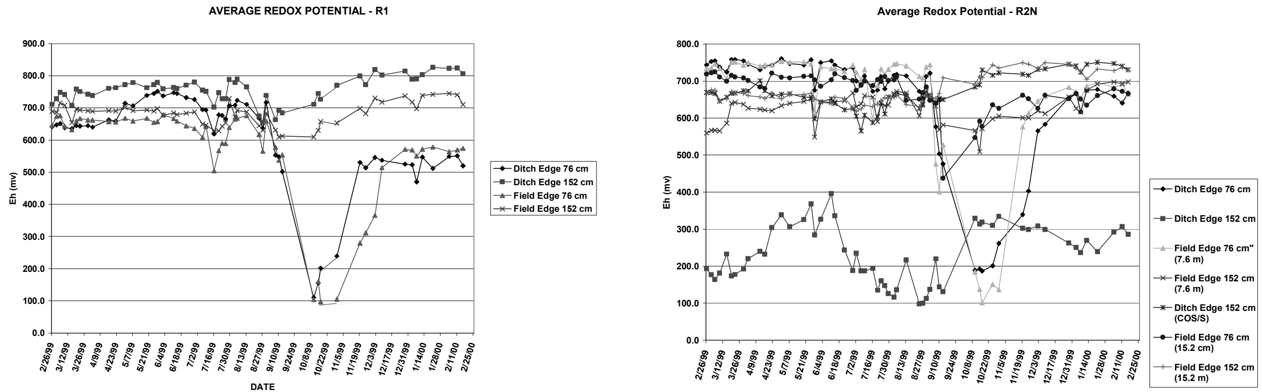

Figure 1. Average redox potential on buffers adjacent to ditches with (R2N) and without (R1) controlled drainage. Conditions were favorable for denitrification at the ditch edge with controlled drainage at the deeper depth.

Conclusion

The successful use of riparian buffers and controlled drainage is dependent on many factors, including soil type, hydrology, slope, vegetation, climate, etc. Each of these factors comes with variability. Therefore, predicting the successful use of these Best Management Practices is complicated. The 7.6-m and 15.2 m buffers with controlled drainage showed that conditions were favorable for denitrification in the vicinity of the water table or when soils restricted groundwater flow. The interaction between hydrology and the soils at this site was critical in attaining redox potential values suitable for denitrification. While there were no significant differences in nitrate concentrations with regard to buffer width, there were significant differences from the 7.6 m and 15.2 m field edges to the ditch edge. As expected, the 15.2-m buffer provided the largest decreases of 69% and 98% in nitrate concentrations from the field edge to the ditch edge in the medium and deep wells, respectively. Low soil redox potential values and decreasing nitrate/chloride ratios provide further documentation that losses were most likely attributed to denitrification. At R1 where no water control structure was present, nitrate concentration decreases in the medium wells were minimal and were significantly different than those at R2N. However, nitrate concentration losses in the deep wells on R1 were tremendous and comparable to the deep wells on R2N. This is probably a result of the presence of reducing conditions located deeper in the profile. Soil redox potential measurements at 152-cm indicated that conditions were not favourable for denitrification, which reflected the higher nitrate concentrations in the medium wells. It is clear that the interactions between soil and hydrology is critical for attaining conditions conducive to denitrification. A combination of riparian buffers with controlled drainage provided the most favorable conditions for this important nitrogen transformation at this location and understanding the relationship between the factors that influenced their effectiveness is key.

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