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

Jörg Prietzel[A], Sandra Spielvogel[A], Anna Botzaki[A], Mareike Bretthole[B] and Wantana Klysubun[C]

[A]Lehrstuhl für Bodenkunde, Technische Universität München, D-85350 Freising-Weihenstephan, Germany, Email prietzel@wzw.tum.de, spielvogel@wzw.tum.de, botzakianna@hotmail.com
[B]Institut für Röntgenphysik, Universität Göttingen, Göttingen, Germany, Email Mareike.Brettholle@phys.uni-goettingen.de
[C]Synchrotron Light Research Institute, Nakhon Ratchasima, Thailand, Email wantana@slri.or.th

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.

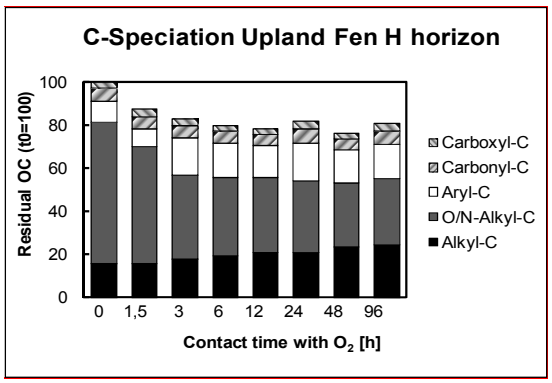

Figure 1: Pool changes of different OC species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±5%).

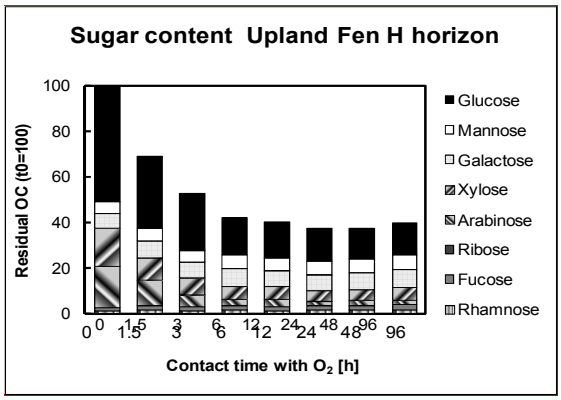

Figure 2: Pool changes of different neutral sugar species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±2%).

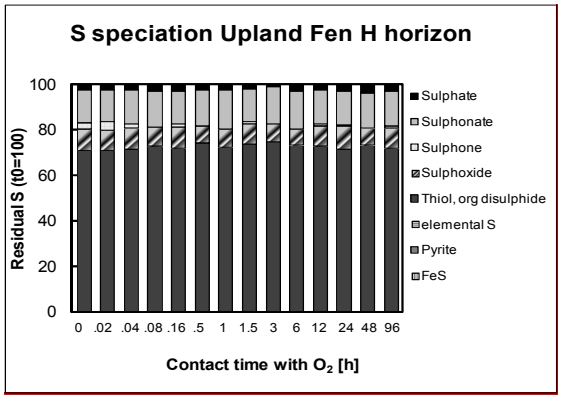

Figure 3: Pool changes of different sulfur species during incubation of an H horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±10%).

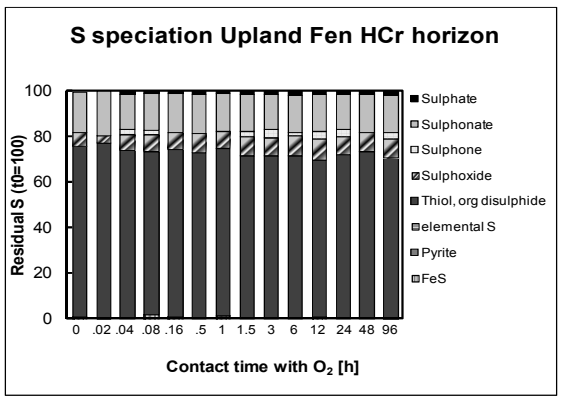

Figure 4: Pool changes of different sulfur species during incubation of an HCr horizon sample of the acidic Histosol Schlöppnerbrunnen (standard error of mean values ±10%).

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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