



Anoxic versus oxic sample pretreatment: Effects on the speciation of sulfur and iron in well-aerated and wetland soils as assessed by X-ray absorption near-edge spectroscopy (XANES)

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ABSTRACT

For a topequence with increasing groundwater influence (Cambisol, Stagnosol, Histosol) and with different groundwater regimes (Histosols 1 and 2) in a forested watershed in the Fichtelgebirge (Germany), the speciation of sulfur (S) and iron (Fe) in the soils was assessed by X-ray absorption near-edge spectroscopy (XANES) after anoxic and conventional oxic sample pretreatments. For samples with anoxic pretreatment, the contribution of reduced inorganic S compounds (monosulfide, pyrite) to total S increased with soil depth for the Cambisol and the Stagnosol, but decreased for the Histosols; the opposite trend was noticed for the contribution of reduced organic S (organic mono- and disulfides, thiols). The contribution of reduced S to the soil S pool increased and the contribution of oxidized S compounds decreased in the sequence Cambisol–Stagnosol–Histosol 1 (permanently anoxic). Histosol 2 (seasonally oxic) showed a markedly larger contribution of oxidized and intermediate S compounds to total S than Histosol 1. The dominating Fe-bearing phases in the Cambisol were Fe(III) oxyhydroxides; the contribution of sulfide-bound Fe was <5% of total Fe in all horizons. In Histosol 1, the contribution of sulfide-bound Fe increased with soil depth up to 50% in the Cr horizon, whereas in Histosol 2 Fe(III) phases strongly dominated in all horizons. After conventional oxic sample pretreatment, the contribution of reduced inorganic S to total S was markedly decreased in all soils. In the organic surface horizons, the contribution of reduced organic S was increased to the same extent; the contribution of oxidized S (sulfate) remained more or less unchanged. In the mineral soil, the contribution of sulfate and the mean oxidation state of sulfur (MOS) were strongly increased after oxic sample preparation. In Histosol 1, oxic sample pretreatment resulted in oxidation of labile Fe(II) compounds, probably sulfides or Fe(II)–S-org-complexes, to Fe(III). Our study shows that for anoxic wetland soils which contain inorganic sulfide and/or divalent Fe, the exclusion of O₂ during the entire period between sampling and analysis is crucial for a correct S and Fe speciation. Only after appropriate sample preparation, clear relationships between the mean oxidation states of S and Fe (MOFe) on one hand and soil hydrological conditions on the other become evident: a concomitant systematic decrease of MOS and MOFe from the well-aerated Cambisol to the permanently anoxic Histosol 1, and larger MOS and MOFe in the seasonally oxic Histosol 2 than in Histosol 1 indicate a close coupling of S and Fe cycling in the soils. Finally, the results of our study suggest that in organic horizons of wetland soils inorganic sulfide S is overestimated and reduced organic S is underestimated by S K-edge XANES, if a significant portion of the thiol groups in reduced organic S is complex-bound to Fe²⁺ or other chalcophilic metal cations. This is supported by the observation that synthetic organic compounds (cysteine; 1,3,5-trimer-captotriazine [TMT]; ferredoxin) after addition of Fe show spectra with pre-edge peaks at energies <2472 eV that are typical for inorganic sulfide.

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1. Introduction

Sulfur and iron in marsh (Xia et al., 1998), freshwater wetland (Novák and Wieder, 1992; Skyllberg et al., 2003; Prietzel et al., 2007, 2009), and forest soils (Prietzel et al., 2003, 2007, 2009) are bound in a variety of organic and inorganic compounds with different oxidation states. The

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speciation of sulfur and iron in well-aerated and wetland soils is relevant for many biogeochemical processes, including the cycling of nutrients (Reuss and Johnson, 1986) and toxic elements (e.g. Di Toro et al., 1996; Martínez et al., 2002; Barrett and McBride, 2007). It determines the possibility and intensity of sorption and precipitation processes (Alewell and Novák, 2001), and ultimately plays a major role in the regulation of soil and freshwater acidification (Reuss and Johnson, 1986; Alewell et al., 2006; Bottrell et al., 2007). Understanding the biogeochemical S and Fe cycling in ecosystems and soils as well as predicting long-term watershed acidification thus require an accurate and precise speciation of S and Fe. Whereas traditional wet chemical methods of S and Fe speciation allow only a rough quantification of operationally-defined fractions of these elements, synchrotron-based X-ray absorption spectroscopy has emerged as a powerful tool for an accurate and precise quantification of different S and Fe species in soils, which is based on specific physico-chemical properties, such as the electronic oxidation state, coordination type, and binding energy (Xia et al., 1998; Martínez et al., 2002; Prietzel et al., 2003, 2007, 2009).

The relations of cause and effect between the redox potential in a soil or sediment and the speciation of S and Fe are bidirectional: on one hand, the presence or absence of certain S and Fe species influence the redox potential of the surrounding soil and soil solution; on the other hand, changes in the redox potential result in changes of S and Fe speciation (e.g. Engler and Patrick, 1973; Novák and Wieder, 1992; Kostka and Luther, 1995; Paul et al., 2006; Bottrell et al., 2007). Particularly reduced inorganic S and Fe compounds formed under anoxic conditions are suggested to be labile in the presence of oxygen (Engler and Patrick, 1973; Buckley and Woods, 1985, 1987; Kostka and Luther, 1995; Di Toro et al., 1996; Barrett and McBride, 2007), whereas reduced organic S compounds are considered to be more stable (Novák and Wieder, 1992; Alewell et al., 2006; Paul et al., 2006). However, only little information is available about (i) the effects of the changes of oxygen availability or redox potential on the S and Fe speciation in soils in detail, and particularly (ii) about the kinetics of any resulting changes in S and Fe speciation. This deficit in knowledge is partly caused by the circumstance that until recently accurate analytical techniques for the speciation of S and Fe in soil and sediment samples were unavailable. An additional problem is the fact that the S and Fe speciation of anoxic soils and sediments may change rapidly during the period between sampling and analysis, unless anoxic conditions are permanently maintained during sample storage and all stages of sample preparation prior to analysis. Some earlier studies of S and Fe speciation in anoxic soils and sediments acknowledged this problem, and excluded the presence of O₂ at least during sample transport and storage (e.g. Novák and Wieder, 1992; Wieder et al., 1996; Johnston et al., 2009), whereas others (e.g. Alewell and Novák, 2001; Martínez et al., 2002; Jokic et al., 2003; Skjellberg et al., 2003) did not.

In the present study the effect of different sample pretreatments on the speciation of S and Fe in samples taken from well-aerated soils and wetland soils of a Cambisol–Stagnosol–Histosol catena in a forested watershed in Southern Germany was investigated by S and Fe K-edge X-ray absorption near-edge spectroscopy (XANES). One subsample of each soil horizon was sampled and prepared for XANES analysis in the traditional way (sampling, transport, drying, grinding under the presence of O₂); for another subsample the presence of O₂ was excluded during all steps of sample preparation. The study intends to (i) identify those soils and soil horizons for which the more complicated, labor-intensive, and expensive anoxic sample preparation technique is required to obtain unbiased analysis results. Moreover, (ii) the artifacts occurring when such samples are pretreated traditionally under the presence of O₂ should be identified and quantified. Besides contributing to the development of appropriate methods for the assessment of S and Fe speciation in anoxic or suboxic soils, our study should help to reveal the direction, intensity, and kinetics of major biogeochemical processes of S and Fe turnover in wetland soils which occur when anoxic or suboxic soil environments become oxygenated, e.g. due to increased drainage or climate change.

2. Material and methods

2.1. Site and soils

The study was conducted in the Lehstenbach watershed (Fichtelgebirge, Germany). The 4.2-hectare catchment has been described in detail in earlier publications (Alewell and Novák, 2001; Alewell et al., 2006; Paul et al., 2006; Prietzel et al., 2007); therefore only a short summary is given here. The elevation of the catchment is 690 to 880 m a.s.l.; its parent bedrock is granite. The annual precipitation varies between 900 and 1160 mm; 20–30% of it precipitates as snow. The mean annual temperature is 5 °C. Ninety percent of the watershed is stocked with Norway spruce (*Picea abies* L. [Karst.]) forest of different age classes and 30% is covered by intermittent seeps or wetland. The mean atmospheric S deposition between 1988 and 2001 was 30 kg ha⁻¹ yr⁻¹; between 1993 and 2000 it decreased by 70% (Paul et al., 2006).

Soil samples from four locations at two different sites in the catchment were studied. At site *Schlöppnerbrunnen 1* (50°08'14"N, 11°53'07"E), we investigated an Endostagnic Leptic Cambisol (aluminic), a Histic Stagnosol (albic, aluminic), and a Leptic Rheic Hemic Histosol (dystric) "Histosol 1" (Table 2). The three soils are located at different positions of a slope (inclination: 9%) with SSW aspect. They are subject to a hydrological gradient with increasing groundwater influence from the Cambisol to the Histosol. The Cambisol is stocked with medium-aged (50–70 yr) Norway spruce and has no groundwater influence; its topsoil is oxic throughout the year. The Stagnosol is also stocked with medium-aged Norway spruce. The site is an intermittent seep which is seasonally (winter, spring) affected by shallow ground-water up to the soil surface, but is completely aerated during summer. The Rheic Histosol is located at the lower edge of a small clearing, where a fen has developed. At that edge, patches of *Sphagnum* mosses alternate with Norway spruce trees. Throughout the year, the Histosol is strongly influenced by Fe-poor groundwater and characterized by anoxic conditions up to 10 cm below the soil surface (Küsel and Alewell, 2004; Paul et al., 2006). Another Rheic Histosol ("Histosol 2") was investigated at site *Schlöppnerbrunnen 2* downslope the catchment (50°08'38"N, 11°51'41"E). This Histosol is located at the southern edge of a larger fen, which is completely overgrown with *Molinia caerulea*, *Eriophorum vaginatum*, *Carex schanescens*, and *Juncus effusus* (Paul et al., 2006). At the site *Schlöppnerbrunnen 2* anoxic Fe(II)-rich ground-water emerges, resulting in oxidation of dissolved Fe²⁺ (Küsel and Alewell, 2004). The soil is characterized by alternating oxidation–reduction cycles and large contents of pedogenic Fe oxides (Paul et al., 2006).

2.2. Sampling and sample pretreatment

In March 2004, samples were taken from the organic surface layers (O, H horizons), mineral topsoil and subsoil horizons of each profile as indicated in Table 1.

For one subsample of each horizon, we strictly maintained anoxic conditions throughout the entire process of sampling, transport, and sample pretreatment. To minimize artificial changes of the samples by oxidation or microbial transformation, the soil samples were taken with a steel auger and quickly (within less than 1 s) loaded into 500-ml glass vessels used for freeze-drying which previously had been filled with 10 g solid CO₂ to keep the sample frozen and maintain it anoxic during transportation. Immediately after sampling, the vessels were closed with an air-tight rubber lid and flushed with pure argon (Ar) gas through a hole (diameter 1.5 cm) in the lid. Then the lid opening was closed with a polythene stopper with a centered hole (diameter 0.4 cm). A polythene hose (length 0.3 m) with the same diameter was attached, air-tight, to the stopper with one end, and connected to a Wolff bottle filled with O₂-free water. During the entire transport procedure, sublimation of solid CO₂ in the glass vessel resulted in a permanent CO₂ flux out of the vessel through the hose, thus preventing any contact of the sample with air. Within 24 h

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