

Sulfur K-edge XANES spectroscopy reveals differences in sulfur speciation of bulk soils, humic acid, fulvic acid, and particle size separates

Jörg Prietzel^{a,*}, Jürgen Thieme^b, Murielle Salomé^c, Heike Knicker^a

^aLehrstuhl für Bodenkunde, Technische Universität München, D-85350 Freising-Weihenstephan, Germany

^bInstitut für Röntgenphysik, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

^cX-ray Microscopy Beamline ID 21, European Synchrotron Radiation Facility, POB 220, 38043 Grenoble Cedex, France

Received 6 July 2006; received in revised form 17 October 2006; accepted 20 October 2006

Available online 27 November 2006

Abstract

X-ray absorption near edge structure (XANES) spectra at the sulfur (S) K-edge ($E = 2472$ eV) were compared for bulk soil material, humic and fulvic acid fractions, and different particle size separates from Ah horizons of two arable Luvisols, from an O and a Bs horizon of a Podzol under Norway spruce forest, and from an H horizon of a Histosol (peat bog). In the bulk soil samples, the contribution of reduced organic S (organic mono- and disulfides) to total sulfur increased from 27% to 52%, and the contribution of ester sulfate and SO_4^{2-} -S decreased from 39% to 14% of total S in the following order: arable Luvisols Ah—forested Podzol O—Histosol H. This sequence reflects the increasing organic carbon content and the decreasing O_2 availability in that order. Neither sulfonate nor inorganic sulfide was detected in any of the bulk soil samples. For all samples except the Podzol Bs, the XANES spectra of the bulk soils differed considerably from the spectra of the humic and acid fractions of the respective soils, with the latter containing less reduced S (16–44% of total S) and more oxidized S (sulfone S: 19–35%; ester sulfate S: 14–38% of total S). Also the S speciation of most particle size fractions extracted from the Ah horizon of the Viehhausen Luvisol and the Bs horizon of the Podzol was different from that of the bulk soil. For both soils, the contribution of oxidized S species to total S increased and the contribution of sulfoxides and organic mono- and disulfides decreased with decreasing particle size. Thus, sulfur K-edge XANES spectra of alkaline soil extracts, including humic and fulvic acids or of particle size separates are not representative for the S speciation of the original soil sample they are derived from. The differences can be attributed to (i) artificial changes of the sulfur speciation during alkaline extraction (conversion of reduced S into oxidized S, loss of SO_4^{2-} during purification of the extracts by dialysis) or particle size separation (carry-over of water-soluble S, such as SO_4^{2-}), but also to (ii) preferential enrichment of oxidized S in hydrophilic water-soluble soil organic matter (ester sulfate) and in the clay fraction of soils (ester sulfate, adsorbed SO_4^{2-}).

© 2006 Elsevier Ltd. All rights reserved.

Keywords: XANES; S speciation; Alkaline extraction; Particle size fractionation

1. Introduction

Sulfur (S) is an essential macronutrient for microorganisms, plants, and animals. Depending on the specific environment, it exists in soils in a great variety of organic and inorganic species with oxidation states ranging from -2 to $+6$, with organic S species comprising $>90\%$ of total S in most soils (Frenay, 1967; Likens et al., 2002).

Recently, the use of synchrotron-based X-ray Absorption Near Edge Fine Structure Spectroscopy (XANES) at the K absorption edge of sulfur ($E = 2472$ eV) has emerged as a new tool for the speciation of S in soil (Xia et al., 1998; Prietzel et al., 2003; Solomon et al., 2005). In contrast to the conventional methods, S K-edge XANES does not provide information on operationally defined fractions, but is based on a “hard” chemical property of the sample of interest, namely the electronic oxidation state. Results of studies where fine-ground soil particles have been investigated with XANES showed good agreement with results of

*Corresponding author. Tel.: +49 8161 71 4734; fax: +49 8161 71 4466.

E-mail address: prietzel@wzw.tum.de (J. Prietzel).

wet chemical S speciation conducted on the same samples, and yielded additional information that could not be revealed with the wet-chemical methods (Prietzel et al., 2003). Most studies, in which S K-edge XANES has been applied to soils to obtain information about their S speciation (Morra et al., 1997; Xia et al., 1998; Hundal et al., 2000; Hutchison et al., 2001; Solomon et al., 2003, 2005; Zhao et al., 2006), have not been conducted on original soils, but on their alkaline humic extracts after treatment with 0.1 M NaOH/0.4 M NaF under N₂ atmosphere at pH values of 12.4 (Zhao et al., 2006) to 12.9 (Solomon et al., 2005). However, Schoenau and Bettany (1987) as well as Strehl and Prietzel (1998) have demonstrated that alkaline extracts of soils are enriched in ester sulfate and SO₄²⁻ compared to the material they originate from. These findings made us skeptical, whether the assumption that the S speciation obtained by XANES analyses conducted on alkaline soil extracts represents the S speciation of the bulk soil from which the extracts originate from (cf. Solomon et al., 2003; Zhao et al., 2006) is really true. Similar problems are present when the S speciation of soil particle size separates is taken as proxy for the S speciation of the respective bulk soil (Solomon et al., 2001, 2003). Three major effects may confound the assumed representativeness. First, the particle size separates typically are isolated by wet sieving and/or sedimentation in aqueous solution. During these procedures, easily-soluble S compounds, such as inorganic SO₄²⁻, but also water-soluble organic S compounds are dissolved and removed from the sample, when the aqueous phase is discarded (Maynard et al., 1987; Prietzel et al., 1996). Second, the clay fraction comprises most of the minerals responsible for the sorption capacity of a soil such as clay minerals and iron oxides. It thus is enriched in organic and inorganic sulfates which have a high sorption affinity to charged mineral particles (Bettany et al., 1980; Anderson et al., 1981; Watwood and Fitzgerald, 1988; Stanko-Golden et al., 1992). Finally, soil organic matter bound in particles of different size classes is characterized by a different age and state of diagenesis (Kaiser et al., 2002; Schöning et al., 2005). Each single effect and also their combination make it unlikely that sulfur speciation conducted on distinct particle size separates, such as the silt or clay fraction (Solomon et al., 2001, 2003) is representative for the S speciation of the bulk soil from

which the particles were derived. In this study we compare the S speciation of bulk soil samples taken from two A horizons of arable soils, the O and the Bs horizon of a forest soil, and an H horizon of a peat bog with the S speciation of humic and fulvic acid fractions and selected particle size separates of the respective soil horizons. The aim of the study was to investigate whether the S speciation of humic and fulvic acid fractions and of particle size separates across a range of soil types with different organic carbon (OC) contents due to different land-use and O₂ availability were identical with that of the respective bulk soil sample.

2. Material and methods

2.1. Sites and soils

We analyzed soil samples taken from the Ah horizons of two arable Luvisols used as cropland (Viehhausen, Pfaffenhofen), from an O and a Bs horizon of a Podzol (Freisinger Forst) stocked with mature Norway spruce (*Picea abies*) forest, and from an H horizon of a Histosol located in a peat bog (Großer Bolchow). The two arable Luvisols Viehhausen and Pfaffenhofen are located 35 and 50 km north of Munich, Germany, respectively, and formed from loess. The Podzol is located in the vicinity of the Viehhausen site on an E–W-oriented ridge consisting of tertiary quartz-rich fluvial sediments dominated by sand and pebbles. For all soils, the climate is characterized by a mean annual temperature of 7.5 °C and a mean annual precipitation of about 800 mm. The Histosol Großer Bolchow is located 60 km SW of Berlin in a mesotrophic peat bog surrounded by Scots pine (*Pinus sylvestris*) forest and pasture land. Here, the mean annual temperature is 9.5 °C and the mean annual precipitation is 580 mm. The vegetation is dominated by *Eriophorum vaginatum*, *Molinia caerulea* and *Oxycoccus palustris*; the dominating peat-forming moss is *Sphagnum recurvum*. Basic properties of the sampled horizons are given in Table 1.

2.2. Chemical fractionation of soil organic matter

Subsamples of all samples were separated according to their solubility in aqueous solutions at different pH according to Fründ and Lüdemann (1991). Eighty gram

Table 1
Basic properties of the studied soils (arithmetic mean value ± standard error)

Soil/Horizon	Texture	Organic carbon (g kg ⁻¹)	Total nitrogen (g kg ⁻¹)	Total sulfur (g kg ⁻¹)	C:S mass ratio (kg kg ⁻¹)
Viehhausen A	Silt Loam	13.0 ± 0.0	1.39 ± 0.01	0.245 ± 0.001	53 ± 0
Pfaffenhofen A	Silt Loam	8.0 ± 0.2	0.79 ± 0.01	0.188 ± 0.017	43 ± 3
Freisinger Forst O	NA	388.4 ± 2.0	15.1 ± 0.07	2.543 ± 0.048	153 ± 2
Freisinger Forst Bs	Sand	32.3 ± 0.9	1.23 ± 0.03	0.197 ± 0.009	164 ± 3
Großer Bolchow H	NA	442.3 ± 2.2	16.7 ± 0.21	2.410 ± 0.070	184 ± 6

NA: not applicable.

Download English Version:

<https://daneshyari.com/en/article/2026359>

Download Persian Version:

<https://daneshyari.com/article/2026359>

[Daneshyari.com](https://daneshyari.com)