As is a ubiquitous, toxic contaminant threatening water resources worldwide. In soils and sediments, As is known to be predominantly associated with iron-(hydr)oxides [1,2] and clay minerals [3] under oxidizing, and with sulfide minerals [4] under strongly reducing conditions. Remarkably high concentrations of As in environments rich in organic matter (OM) and poor in metal-(hydr)oxides have recently raised the question whether natural OM can be regarded as an important sorbent for As [5-8]. For this reason, we started to investigate the speciation of both As (ESRF, Grenoble, France) and Fe (Hasylab, Hamburg, Germany) in the As-enriched, groundwaters-fed peatland Gola di Lago in canton Ticino, Switzerland. This peatland is characterized by a variable As content, partially reaching threshold values of environmental concern, and a variable composition in organic and mineral matter (Table 1).

Table 1. Laboratory and linear combination fit (LCF) results for two exemplarily selected peat samples (B3-1 and B1-23) collected at different depths.

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<tr>
<th>ID</th>
<th>Laboratory results:</th>
<th>Linear combination fits:</th>
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<tbody>
<tr>
<td></td>
<td>Eh [mV]</td>
<td>pH</td>
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<tr>
<td>B3-1(^b)</td>
<td>-108</td>
<td>6.2</td>
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<tr>
<td>B1-23(^i)</td>
<td>133</td>
<td>5.5</td>
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</table>

\(^a\)total concentration (dry weight basis) measured by XRF; \(^b\)determined using a high-temperature combustion CHNS-analyzer (Leco); \(^c\)natural; \(^d\)synthetic [9]; \(^e\)synthetic [10]; \(^f\)synthetic (Alfa Aesar 220-951-7); \(^i\)synthetic (Fluka 44941); \(^i\)sampling depth 0.00-0.12 m; \(^j\)sampling depth 1.92-2.00 m.

Peat samples were collected during the snow-melt period in spring 2009. Core holes were drilled up to a depth of 3.50 m and the retrieved core material was cut into slices of 8 cm, each slice split into two halves. One half was used for on-site measurements like redox potential and the determination of mineralogy by X-ray diffraction (XRD) analysis, and of total element contents by X-ray fluorescence (XRF) analysis. The other half, intended for X-ray absorption spectroscopy (XAS) measurements, was immediately shock-frozen in liquid N\(_2\) in the field, transported on dry ice to the laboratory, freeze-dried, and homogenized in an anoxic glove box. Based on XRD and XRF results, we selected a subset of 10 peat samples offering a wide range of As concentrations (130-1416 mg/kg) for XAS analysis. The samples were prepared in aluminum powder holders sealed with Kapton tape in an anoxic glovebox and stored under anoxic conditions until analysis at beamline C (CEMO) of the Hamburger Synchrotronstrahlungslabor (Hasylab) at Deutsches Elektronen-Synchrotron (DESY). The speciation and bonding environment of Fe were investigated by Fe K-edge (7,112 eV) X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Sample spectra were recorded in fluorescence mode at about 80 K using a 7-cell Si-drift-detector (SDD) and a cryostat. In addition, we collected XAS spectra of 21 reference materials in transmission mode including organic and inorganic Fe compounds. The reference spectra were used for Fe speciation in the peat samples by means of LCF analysis.

Samples chosen for XAS measurements derived from two different peat cores differing in the depth of As concentration maxima (B1 >1.6 m and B3 <0.4 m) (Table 1). X-ray diffraction analyses showed that peat samples mainly contained quartz and muscovite as mineral constituents. Pyrite was only detected by XRD in profile B1. Best fit results of the LCF analysis of two representative peat samples are shown in Table 1 and Figure 1.
Figure 1. Fe K-edge EXAFS spectra of selected peat samples (B3-1 and B1-23) and reference samples. Linear combination fits are indicated as dotted lines. (a) peat sample B3-1, (b) peat sample B1-23, (c) pyrite, (d) lepidocrocite, (e) ferrihydrite, (f) iron(III) oxalate, (g) iron(III) citrate.

We found significant differences in Fe K-edge EXAFS spectra between anoxic/suboxic peat samples as a function of sampling depth. While in the upper parts of the peat profile Fe(III)-(hydr)oxides were the major Fe species, the deeper peat layers were dominated by pyrite (FeS$_2$). Speciation analyses of As at ESRF (Grenoble, France) indicated that in the uppermost parts As was mainly present in the form of realgar ($\alpha$-As$_4$S$_4$), partly in association with As(III, V) sorbed to ferrihydrite, whereas in the lower parts As(III) was predominantly bound to S atoms of soil OM. The As K-edge EXAFS spectra closely resembled those of As(III) bound to cysteine residues in which As is coordinated to three S atoms at a distance of between 2.2 and 2.25 Å [11-13]. Our results document that the geochemical As cycle is not entirely linked to that of Fe in such OM-rich soil environments. In addition, sorption of As by particulate soil OM via a $S_N$ reaction and/or redox-sorption process can be regarded as a potent sequestration mechanism. These observations represent a great step forward in our understandings of the potential mobility and toxicity of As in OM-rich environments. Our next step is to investigate (i) annual speciation changes of Fe (and As) caused by seasonal changes in microbial activity, water table fluctuations, and thus changes in redox potential at our study site, and (ii) changes in Fe (and As) speciation during re-oxidation of the peat samples under controlled laboratory conditions.

References