



	<b>Experiment title:</b> Binding form of arsenic in arsenic-contaminated peatlands	<b>Experiment number:</b> EC-489
<b>Beamline: BM 29</b>	<b>Date of experiment:</b> From 29.04. to 04.05.2009	<b>Date of report:</b> 21 July 2009
<b>Shifts: 17</b>	<b>Local contact(s):</b> Dr. Matthieu Chorro	<i>Received at ESRF:</i>
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## Report:

### 1. Introduction

Arsenic (As) is a ubiquitous toxic contaminant threatening water resources and thus the life of millions of people worldwide. In soils and sediments, As is known to be associated predominantly 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). However, direct spectroscopic evidence for As-binding to OM in natural systems is still lacking. For this reason, we investigated the speciation of As in the As-enriched *Gola di Lago* peatland 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).

### 2. Materials and Methods

Peat samples were collected in spring 2009. Retrieved core material was cut into slices of 8 cm; each slice was 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 total element content by X-ray fluorescence (XRF) analysis. The other half intended for X-ray absorption spectroscopy (XAS) measurements was immediately inserted into liquid nitrogen in the field, transported on dry ice in 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 Plexiglas powder holders sealed with Kapton tape in an anoxic glovebox and stored under anoxic conditions until analysis at beamline BM29 of the European Synchrotron Radiation Facility (ESRF). The speciation and bonding environment of As was investigated by As K-edge (11,867 eV) X-ray absorption near edge structure (XANES) and extended X-ray fine structure (EXAFS) spectroscopy. Sample spectra were recorded in fluorescence mode at about 80 K using a 13-element Ge-detector and a cryostream. In addition, we collected XAS spectra of 15 reference materials in transmission mode including organic and inorganic As compounds. These reference spectra were used for As speciation in the peat samples by means of linear combination fit (LCF) analysis.

**Table 1. Range of soil properties at the Gola di Lago site analyzed in our laboratory and in the field. Element contents are given on dry-weight basis. Redox potentials are expressed relative to SHE.**

pH	Redox potential	Fe	Mn	S	C	As
	[mV]					
4.7-6.7	>-160	5-29	0.0-0.3	1-70	1-474	15-1416

### 3. Results and Discussion

Samples chosen for XAS measurements derived from two different peat profiles which differed in the depth of maximal As concentration (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. Comparison of the white line energy positions of the peat samples with reference materials indicated that As was mainly present in the trivalent oxidation state. As K-edge EXAFS spectra of selected peat (B1-23 and B3-1) and reference samples are shown in Figure 1. Best fit results of the LCF analysis of two representative peat samples are shown in Table 1 and as dotted lines in Figure 1.

**Table 2. Laboratory results and parameters for linear combination fits for two selected peat samples (B3-1 and B1-23) collected at different depths.**

ID	Laboratory results:					Linear combination fits:			
	Eh	As <sup>a</sup>	S <sup>a</sup>	Fe <sup>a</sup>	C <sup>b</sup>	As(III)-(GS) <sub>3</sub> <sup>c</sup>	Realgar <sup>d</sup>	As(V)-Fh <sup>e</sup>	As(III)-Fh <sup>e</sup>
	[mV]	— [mg/kg] —	— [g/kg] —	— [g/kg] —	— [g/kg] —	[%]			
B1- 23 <sup>f</sup>	130	425	7131	24	463	90	10	-	-
B3- 1 <sup>g</sup>	-108	1416	18	28	325	-	63	15	22

<sup>a</sup>total concentration (dry weight basis) measured by XRF; <sup>b</sup>determined using a high-temperature combustion CHNS-analyzer (Leco); <sup>c</sup>tri(glutamylcysteinylglycyl)trithioarsenite (9); <sup>d</sup>natural; <sup>e</sup>arsenite/arsenate sorbed to synthetic ferrihydrite (Fh) (10); <sup>f</sup>sampling depth: 1.92-2.00 m; <sup>g</sup>sampling depth: 0.00-0.12 m.

We found significant differences in As speciation within peat profiles as a function of sampling depth. While in the upper part of the peat profiles realgar ( $\alpha$ -As<sub>4</sub>S<sub>4</sub>) was the dominant As species, the deeper peat layers were dominated by As(III) bound to thiol groups of soil OM (Table 2). Our results suggest that particulate soil OM rich in reduced S-groups can be considered as an important sorbent for As. Our spectroscopy data thus corroborate earlier sequential extraction experiments (5) indicating that in the *Gola di Lago* peatland As is partly associated with OM. Noteworthy, by analyzing the speciation of Fe of the same peat samples by means of XAS, we found a general decoupling of both element cycles at *Gola di*

*Lago*. In other words, except for a few samples, no association between Fe mineral phases and As was detected within the limit of detection.

#### 4. Conclusion and Outlook

Our results document, for the first time, the quantitative relevance of natural particulate soil OM for the immobilization of As. Especially redox-active S-groups of natural OM appear to play an important role in As sequestration in organic-rich soils and sediments. The identification of the bonding scheme in the *Gola di Lago* peatland is a great step forward in our understanding of the potential mobility and toxicity of As in such environments. The next step in understanding the dynamics of As at our study site is to investigate the seasonal dynamics of As (and Fe). We are interested in the question whether the speciation of As analyzed in early spring is persistent or only transient during the year given significant seasonal changes in microbial activity, water table fluctuations, and hence redox potential changes. For this reason, we will sample the peat again in late summer (September) and re-analyze the speciation of As (and Fe) in order to estimate potential As hazards induced by seasonal changes in geochemical boundary conditions. A reasonable assessment of the potential mobility and bioavailability of As in the peatland without medium-term speciation analyses of As (Fe) is currently still impossible.

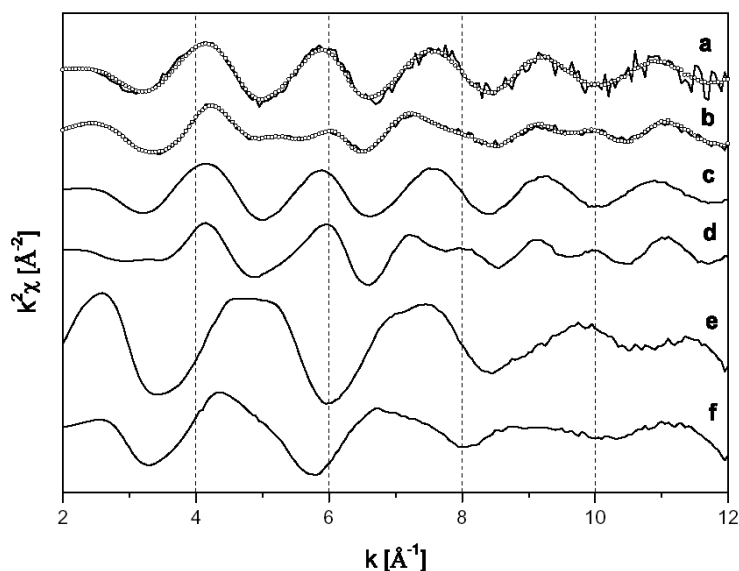


Figure 1. As K-edge EXAFS spectra of selected peat (B3-1 and B1-23) and reference samples. Linear combination fits are indicated as dotted lines. (a) peat sample B1-23, (b) peat sample B3-1, (c) tri(glutamylcysteinylglycyl)-trithioarenite, (d) realgar, (e) arsenate sorbed to ferrihydrite, and (f) arsenite sorbed to ferrihydrite.

#### 5. References

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#### Acknowledgements

We thank the ESRF for the allocation of beamtime as well as Dr. Matthieu Chorro and the technical staff of BM29 for the excellent support during the measurements. Furthermore, the provision of reference minerals from the TU Bergakademie Freiberg (Germany) and the ETH Zürich (Switzerland) is greatly acknowledged.