



	<b>Experiment title:</b> Seasonal speciation changes of arsenic in an arsenic-enriched peatland <sup>1</sup>	<b>Experiment number:</b> EC-574
<b>Beamline:</b> BM 29	<b>Date of experiment:</b> From 25.11. to 01.12.2009	<b>Date of report:</b> 17 September 2010
<b>Shifts: 18</b>	<b>Local contact(s):</b> Matthieu Chorro	<i>Received at ESRF:</i>
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<sup>1</sup> Due to the shutdown of beamline BM29 at the time of our experiment, we decided - in agreement with the responsible beamline scientist Dr. Matthieu Chorro - to continue and finish our previous work of session EC-489 ("Binding form of arsenic in arsenic-contaminated peatlands"). As a result, we did not pursue the original aim of session EC-574 ("Coprecipitates of iron oxides and natural organic matter: Structure and reactivity").

## Report:

### 1. Introduction

In soils and sediments, arsenic (As) is known to be effectively immobilized by adsorption to or coprecipitation with metal-(hydr)oxides (1, 2) under oxic conditions, or the formation of sulfide minerals (3) under strongly reducing conditions. Remarkably high concentrations of As in environments rich in natural organic matter (NOM) and depleted in metal-(hydr)oxides recently raised the question whether NOM can also be considered an important sorbent for As (4-6).

Our previous work on As (EC-489, ESRF, France) and iron (Fe) speciation (Hasylab, Germany) in peat samples collected in an As-enriched minerotrophic peatland (*Gola di Lago*, Ticino, Switzerland) revealed that As is not predominately associated with Fe mineral phases (7). Instead, the As speciation was dominated by realgar ( $\alpha$ -As<sub>4</sub>S<sub>4</sub>) close to the peat surface. In the lower part of the peat profiles, As was mainly present as As-NOM complexes in which As(III) is coordinated to sulfur (S) atoms of NOM. These results documented that the sorption of As by particulate NOM can be regarded as a potent sequestration mechanism. Because the peat samples analyzed so far were collected in early spring, our speciation results may only represent a transient situation in the peatland. In order to substantiate our preliminary conclusion that fixation of As by NOM can be considered an important sequestration mechanism of As in soil environments rich in NOM, our next step involved an As and Fe speciation analysis of peat samples collected in late summer. We hypothesized significant speciation changes of both elements, especially in the uppermost peat layers due to seasonal changes in microbial activity, water table fluctuations, and hence changes in the redox potential. In order to investigate As

(and Fe) speciation changes upon re-oxidation of anoxic peat samples, we also performed controlled re-oxidation experiment in the laboratory.

## 2. Materials and Methods

To address annual variations in the solid-phase speciation of As (and Fe), peat samples were additionally collected September 2009. These 'late-summer' samples were taken less than ~25 cm away from the original 'early-spring' sampling spots. We used an identical sample treatment procedure as in spring 2009 (8), which involved immediate shock-freezing of the samples in the field by insertion into liquid nitrogen, freeze-drying, and subsequent storage of the dried samples under anoxic conditions. In addition, anoxic peat samples from spring, which have been analyzed by bulk As and Fe K-edge X-ray absorption spectroscopy (XAS), were oxidized at 35°C and 99% humidity in a desiccator for five months in the laboratory. For XAS analyses at beamline BM29 of the European Synchrotron Radiation Facility (ESRF), both types of samples were prepared in Plexiglas powder holders and sealed with Kapton® tape. The oxidation state 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 absorption fine structure (EXAFS) spectroscopy. Sample spectra were recorded in fluorescence mode at about 80 K using a 13-element Ge detector and a cryostream. For quantitative As speciation in the peat samples by means of linear combination fit (LCF) analysis, we resorted to reference spectra already collected at BM29 (EC-489) under identical conditions.

## 3. Results and Discussion

Table 1 summarizes basic characteristics of representative peat samples collected in early spring and late summer at the same sampling positions (Table 1). Apparently, redox potentials did not vary significantly in deep peat layers (~2 m depth). Close to the peat surface, however, we recorded pronounced redox oscillations (Table 1).

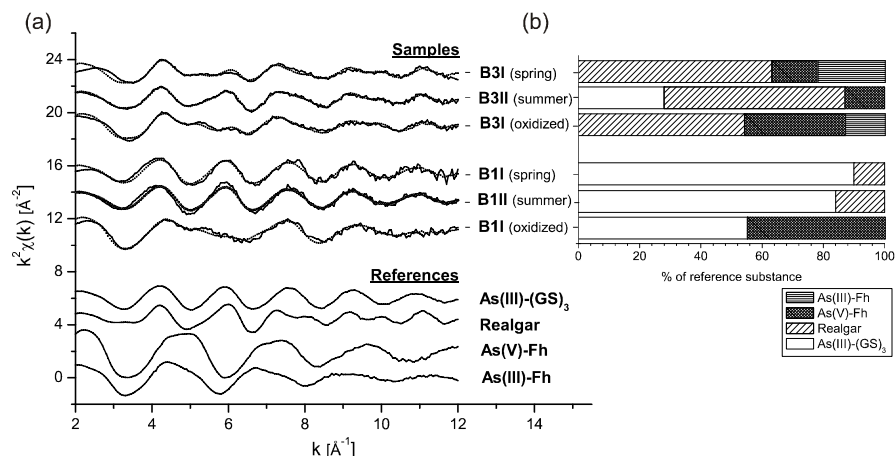
**Table 1. Laboratory results of selected peat samples collected at different depths in spring (I) and summer (II) 2009.**

ID	Description:	Laboratory results:				
		E <sub>h</sub> [mV]	As <sup>a</sup> [mg/kg]	S <sup>a</sup> [g/kg]	Fe <sup>a</sup> [g/kg]	C <sup>b</sup> [g/kg]
B1I <sup>c</sup>	spring	130	426	21	7	463
B1II <sup>c</sup>	summer	98	323	17	4	463
B3I <sup>d</sup>	spring	-108	1416	8	29	326
B3II <sup>d</sup>	summer	77	355	7	10	345

<sup>a</sup>total concentration measured by X-ray fluorescence spectrometry (dry weight basis); <sup>b</sup>determined with a Leco CHNS-analyzer; <sup>c</sup>sampling depth: 1.9-2.0 m; <sup>d</sup>sampling depth: 0.0-0.1 m.

A comparison of the white line energy positions of the summer and re-oxidized spring peat samples with those of appropriate As references indicated that As was still mainly present in its trivalent oxidation state. However, in the re-oxidized samples about 30% of As(III) was converted to As(V). For the B1 sample, for example, we calculated an average As(III)-As(V) transformation rate of 0.74 μmol/kg/h in our five-month re-oxidation experiment. Linear combination fit results of two representative peat samples collected at different depths (B1: 1.9-2.0 m and B3: 0.0 - 0.1 m) during spring (I) and summer (II) as well as of the re-oxidized samples analyzed are displayed in Figure 1. We detected pronounced speciation changes of As in the uppermost peat layers, where the fraction of As associated with Fe(III)-(hydr)oxides decreased and the fraction of As bound to NOM increased (Fig. 1b). Re-oxidation of B3 spring samples led to a significant increase in the fraction of As(V) sorbed to Fe(III)-(hydr)oxides, mainly at the expense of As(III) associated with Fe(III)-(hydr)oxides. In contrast, we observed minor As speciation changes in samples originating from deep peat layers (B1 profile). Here, As-NOM complexes in which As(III) forms covalent bonds with S-containing

functional groups of NOM are still dominating (Fig. 1b). Upon re-oxidation of these samples, however, we noticed a distinct shift in As speciation towards As(V) associated with Fe(III)-(hydr)oxides (Fig. 1b), implying the decomposition of As-NOM complexes. Our results indicate that seasonal changes of geochemical conditions in the peatland studied may have a significant effect on the As speciation, especially in the upper part of the peat profiles.



**Figure 1. Results from the LCF analysis of six selected peat samples (B1 and B3) collected within different seasons. Previously analyzed anoxic spring peat samples (EC-489) were oxygenated under controlled conditions in the laboratory for five months. (a) As K-edge EXAFS spectra of peat and reference samples (solid lines). Linear combination fits are indicated as dotted lines. (b) Normalized LCF fractions of arsenite sorbed to ferrihydrite (As(III)-Fh), arsenate sorbed to ferrihydrite (As(V)-Fh), realgar, and tri(glutamylcysteinylglycyl)trithioarsenite (As(III)-(GS)<sub>3</sub>). Note that Fh served as a proxy for poorly crystalline Fe(III)-(hydr)oxides, whereas As(III)-(GS)<sub>3</sub> was taken as a proxy for As associated with reduced S-groups of NOM.**

#### 4. Conclusions

Our results imply that there are hardly any speciation changes of As in deep peat layers within the time-frame of our field study (March-September). However, in the top ~30 cm of the peat, where changes in microbial activity, production of below-ground plant biomass, and hence redox gradients are most pronounced, we detected As speciation changes that might be related to (i) the re-oxidation of As(III) in sulfide minerals, (ii) the reduction of Fe(III)-(hydr)oxides upon microbial dissimilatory Fe reduction, (iii) the spatial peat inhomogeneity on a decimeter scale, or (iv) a combination of these factors. Our spectroscopy results of the samples analyzed so far also suggest that the re-oxidation kinetics of As(III) bound to NOM via S-groups are relatively slow and that As released from NOM becomes subsequently immobilized by Fe(III)-(hydr)oxide phases.

#### 5. References

- (1) Dixit, S.; Hering, J. G. *Environ. Sci. Technol.* 2003, 37: 4182; (2) Howell, R. J. *Appl. Geochem.* 1994, 9: 279; (3) O'Day, P. A. et al. *Proc. Natl. Acad. Sci. U.S.A.* 2004, 101: 13703; (4) Gonzalez A., Z. I. et al. *Environ. Sci. Technol.* 2006, 40: 6568; (5) Bauer, M. et al. *Sci. Total Environ.* 2008, 401: 109; (6) Rothwell, J. J. et al. *Sci. Total Environ.* 2009, 407: 1405; (7) Langner, P. et al. *Geochim. Cosmochim. Acta* 2010, 74: A559; (8) Langner, P. et al. *ESRF* 2009, EC-489;

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