



	<b>Experiment title:</b> Effect of natural organic matter on the Fe(II)-induced release of trace metals from Fe(III)-oxyhydroxides	<b>Experiment number:</b> EV-11
<b>Beamline:</b> BM23	<b>Date of experiment:</b> 03.-07.04.2013	<b>Date of report:</b> 26 June 2013
<b>Shifts: 12</b>	<b>Local contact(s):</b> Carlo Marini	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): Christian Mikutta* Laurel ThomasArrigo* Ruben Kretzschmar  <u>All:</u> Institute of Biogeochemistry and Pollutant Dynamics (Soil Chemistry) Swiss Federal Institute of Technology Zurich (ETH Zürich) ETH Zentrum, Universitätstrasse 16, CH-8092 Zurich, Switzerland		

## 1. Introduction

In order to explore the role organic ligands play in Fe(II)-activated trace metal release, we planned to study the Fe(II)-induced Zn(II) release from Zn(II)-substituted Fe(III)-oxyhydroxides in the presence of natural organic matter. We were particularly interested in the bulk-surface transfer of Zn(II) contained in the structure of goethite ( $\alpha$ -FeOOH). Extensive laboratory research conducted prior to our synchrotron experiments (C. Münch, master thesis, ETH Zurich, 2013), however, revealed a lacking effect of Fe(II) on the release of Zn(II) from goethite, which unexpectedly contrasted earlier findings on the Fe(II)-induced trace metal release from Fe(III)-oxyhydroxides [1, 2] and hence rendered the intended Zn K-edge (9659 eV) X-ray absorption spectroscopy (XAS) measurements unnecessary. Therefore, we decided to use our EV-11 beamtime for another project in which we examine the role of mineral-organic associations on the dynamics of pollutants in wetlands. In freshwater ecosystems suspended associations of natural organic matter (NOM) and mineral phases ('flocs') significantly impact fluxes of organic C, nutrients, and contaminants. These flocs, often dominated by NOM, are frequently enriched in trace elements (e.g., Ag, As, Cu, Co, Ni, Pb) when compared to trace element contents of the bed sediments [3-5]. Several studies implied that the ability of suspended freshwater flocs to sequester trace elements depends on the content of floc-associated amorphous Fe-oxyhydroxides [3-5]. The reactivity of these phases was speculated to be closely linked to floc NOM (predominantly microbial cells and exopolymeric substances), which acts as organic framework for trapping and/or precipitating amorphous Fe-oxyhydroxides [4]. Since knowledge about the composition of freshwater flocs is crucial to understand and predict trace element behavior in aquatic systems, we have collected Fe-rich organic freshwater flocs from surface waters of a naturally As-enriched minerotrophic peatland (*Gola di Lago*, canton Ticino, Switzerland) [6]. The flocs were shock-frozen in liquid N<sub>2</sub> after centrifugation, freeze-dried, and transferred into an anoxic glove box where they were sieved (500  $\mu$ m), homogenized, and stored until use. The samples were analyzed for their total C content, the content of major and trace elements after microwave digestion, and for their mineralogy using synchrotron-X-ray diffractometry (SXRD). These analyses revealed that the flocs were significantly enriched in As (<2615 mg/kg) and other trace elements (Pb, Zn) and that ferrihydrite – a nanocrystalline Fe(III)-oxyhydroxide – was the dominating mineral Fe phase in all samples. We found no significant correlation between all major elements and As, suggesting that several As immobilization mechanisms are

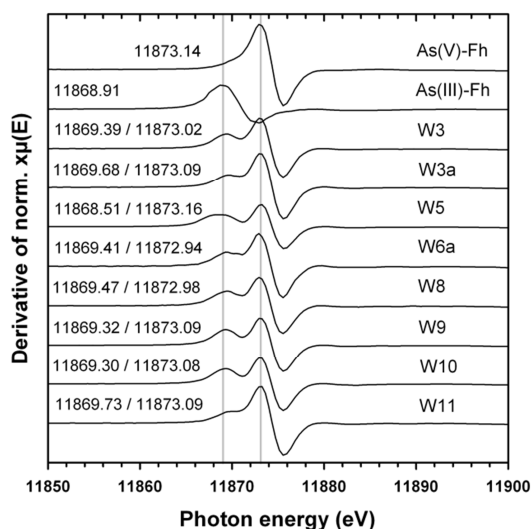
operating simultaneously. Two As sequestration mechanisms linked to Fe were conceivable for these freshwater flocs: (i) binding of both arsenite (As(III)) and arsenate (As(V)) – the dominating inorganic As species in the *Gola di Lago* peatland – to organic Fe(III) complexes and (ii) complexation of As(III/V) on surfaces of Fe-bearing minerals, notably Fe(III)-oxyhydroxides [e.g., 7-9]. In order to provide novel information on the speciation of As in freshwater flocs, we examined the oxidation state and local coordination environment of As in eight floc samples using As K-edge (11868 eV) XAS.

## 2. Experimental

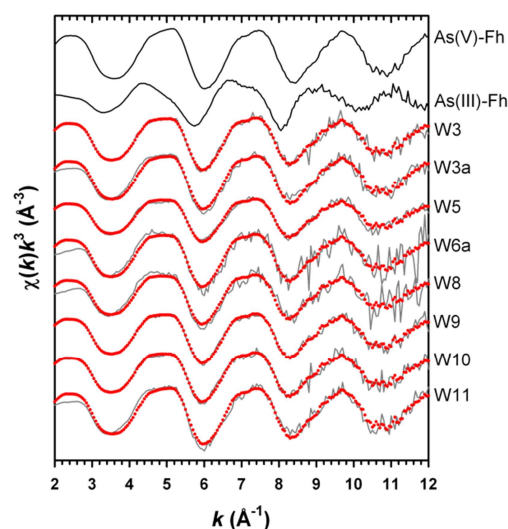
For As K-edge XAS measurements, freeze-dried floc material was filled into Al sample holders and sealed with Kapton<sup>®</sup> tape. The samples were kept under anoxic conditions until the end of the measurements. Arsenic K-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra were recorded in fluorescence mode at ~20 K using a 13-element Ge detector and a He(I) cryostat. The monochromator was calibrated to the first maximum in the first derivative of the absorption spectrum of a metallic Au foil (11919 eV), which was continuously monitored to account for slight energy shifts (<1 eV) during the sample measurements. For each sample 11-19 scans had to be averaged for a decent signal-to-noise ratio. Spectral processing and data analyses were done according to standard procedures using the IFEFIT program suite [10].

## 3. Results and Discussion

First derivatives of As K-edge XANES spectra of the As-rich freshwater flocs are shown in Figure 1. They exhibit two maxima at ~11869 and ~11873 eV, consistent with As(III) and As(V) reference compounds. Accordingly, the flocs contained appreciable amounts of trivalent As, which points towards a slow oxidation kinetics of As(III) in oxic surface waters due to adsorption reactions [11]. Principal component analysis and target transform testing revealed that all spectra could be described by a linear combination of only two reference spectra: As(III) and As(V) adsorbed to ferrihydrite. Linear combination fit (LCF) analysis of  $k^3$ -weighted EXAFS spectra ( $k$ -range: 2-12 Å<sup>-1</sup>) were conducted in Athena. For this analysis, the edge energy,  $E_0$ , was set to 11969 eV for all sample and reference spectra. Figure 2 illustrates the EXAFS spectra of the flocs along with the corresponding LCFs, and Table 1 summarizes the LCF results.



**Figure 1.** First derivatives of normalized As K-edge XANES spectra of As(III/V) adsorbed to ferrihydrite (Fh) and freshwater flocs from the *Gola di Lago* peatland. Figures indicate energy values (eV) of the first derivative maxima corresponding to trivalent and pentavalent As, respectively.



**Figure 2.**  $k^3$ -weighted As K-edge EXAFS spectra of As-rich freshwater flocs and linear combination fits using As(III/V) adsorbed to ferrihydrite as fit references. Experimental data is shown as solid and linear combination fits as dotted lines.

**Table 1.** Linear combination fit results obtained from As K-edge EXAFS spectra using As(III/V) adsorbed to ferrihydrite (Fh) as fit references.<sup>a</sup>

Sample	As(V)-Fh	As(III)-Fh	Initial Sum	R-factor	red. $\chi^2$
W3	0.75	0.25	1.04	0.052	1.2
W3a	0.80	0.20	1.04	0.044	1.1
W5	0.71	0.29	0.87	0.045	0.7
W6a	0.71	0.29	1.07	0.223	6.2
W8	0.68	0.32	1.02	0.184	4.2
W9	0.72	0.28	1.01	0.033	0.7
W10	0.71	0.29	1.02	0.061	1.3
W11	0.84	0.16	1.05	0.044	1.2

<sup>a</sup>fit results rescaled to a sum of unity.

Our LCF results imply that the flocs contained between 16 and 32% As(III) (average: 26%) and indicate that the entire As was associated with poorly crystalline Fe(III)-oxyhydroxides and/or present in ternary Fe(III)-NOM complexes. Preliminary shell-fit analyses showed that both As(III) and As(V) are coordinated to Fe in a monodentate binuclear fashion ( $r_{\text{As-Fe}} \sim 3.3 \text{ \AA}$ ;  $^2\text{C}$  complex). Additionally, we fitted Fe atoms at a distance of  $\sim 2.9 \text{ \AA}$ , the typical interatomic As-Fe distance in  $^1\text{E}$  complexes of As(III) adsorbed to Fe(III)-oxyhydroxides. Currently, we are performing shell fits with various alternative fit models in order to test for the presence of weak low-Z backscatterers such as S and C in the first and second coordination shell of As, respectively. So far, our analyses document that freshwater flocs of the *Gola di Lago* peatland are significantly enriched in As and that multiple As coordination environments exist. These findings have important implications for the fate of As in wetlands. Since freshwater flocs are highly mobile and dynamic in composition, they exert an important control on the mobility and bioavailability of As and other trace elements in freshwater systems. In order to better understand the composition and dynamics of freshwater flocs in wetlands, particularly with respect to the coupled dissimilatory Fe(III) reduction and trace element release, we plan to use Fe K-edge EXAFS spectroscopy to additionally characterize the local Fe coordination in our flocs. These analyses are crucial to infer the structure of the nanocrystalline Fe(III)-oxyhydroxides formed in the presence of abundant biopolymers. These phases are expected to possess a much lower extent of octahedral linkages in their structure, making them more vulnerable to bacterial Fe(III) reduction and trace element release as compared to Fe(III)-oxyhydroxides formed in the absence of biopolymers.

#### 4. References

- [1] Frierdich A. J. and Catalano J. G. (2012) Controls on Fe(II)-activated trace element release from goethite and hematite. *Environ. Sci. Technol.* **46**, 1519-1526.
- [2] Frierdich A. J., Luo Y., Catalano J. G. (2011) Trace element cycling through iron oxide minerals during redox-driven dynamic recrystallization. *Geology* **39**, 1083-1086.
- [3] Plach J. M., Elliott A. V. C., Droppo I. G., Warren L. A. (2011) Physical and ecological controls on freshwater floc trace metal dynamics. *Environ. Sci. Technol.* **45**, 2157-2164.
- [4] Plach J. M. and Warren L. A. (2012) Differentiating natural organic matter roles in freshwater floc and bed sediment lead dynamics. *Chem. Geol.* **304-305**, 97-105.
- [5] Elliott A. V. C., Plach J. M., Droppo I. G., Warren L. A. (2012) Comparative floc-bed sediment trace element partitioning across variably contaminated aquatic ecosystems. *Environ. Sci. Technol.* **45**, 209-216.
- [6] Langner P., Mikutta C., Kretzschmar R. (2012) Arsenic sequestration by organic sulphur in peat. *Nat. Geosci.* **5**, 66-73.
- [7] Mikutta C., Frommer J., Voegelin A., Kaegi R., Kretzschmar R. (2010) Effect of citrate on the local Fe coordination in ferrihydrite, arsenate binding, and ternary complex formation. *Geochim. Cosmochim. Acta* **74**, 5574-5592.
- [8] Mikutta C. and Kretzschmar R. (2011) Spectroscopic evidence for ternary complex formation between arsenate and ferric iron complexes of humic substances. *Environ. Sci. Technol.* **45**, 9550-9557
- [9] Hoffmann M., Mikutta C., Kretzschmar R. (2013) Arsenite binding to natural organic matter: Spectroscopic evidence for ternary complex formation and ligand exchange (*submitted*)
- [10] Ravel B. and Newville M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFIT. *J. Synchrotron Radiat.* **12**, 537-541.
- [11] Manning B. A. and Goldberg S. (1997) Arsenic(III) and arsenic(V) adsorption on three California soils. *Soil Sci.* **162**, 886-895.