ESRF	**Experiment title:** Arsenic speciation in flooded soils heavily impacted by Acid Mine Drainage, Gard, France	**Experiment number:** 30-02 1021
Beamline:	**Date of experiment:** from: 28-09-2011 at 8 am to: 05-10-2011 at 8 am	**Date of report:** Mar 26, 2012
Shifts:	**Local contact(s):** **Olivier Proux, Jean-Louis-Hazemann**	*Received at ESRF:*

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Report:

The objective of this proposal was to determine the molecular-scale mechanisms of As retention and dissolution in flooded soils (up to 4000 mg/kg As) impacted by a heavily contaminated acid mine drainage (AMD) in the Gard department, France. Beyond the natural attenuation processes related to As and Fe biomineralization in this AMD, little is known on the evolution of As-rich iron-oxide colloids deposited on riverbank soils upon large flooding events. Evaluating the mobility and toxicity of arsenic in these soils over which housing and local agriculture has developed is of prime importance for soil and water management.
As K-XANES indicated changes in As oxidation state from topsoil to deep horizons and As K-EXAFS analysis of the investigated soil samples was expected to reveal As bearing phases. Unfortunately, severe difficulties were encountered for recording EXAFS data on these impacted but natural soil samples (Figure 1). Data were recorded using 220 Si monochromator with saggital focusing of the second crystal. Sample fluorescence was measured using a 30 elts Ge detector.

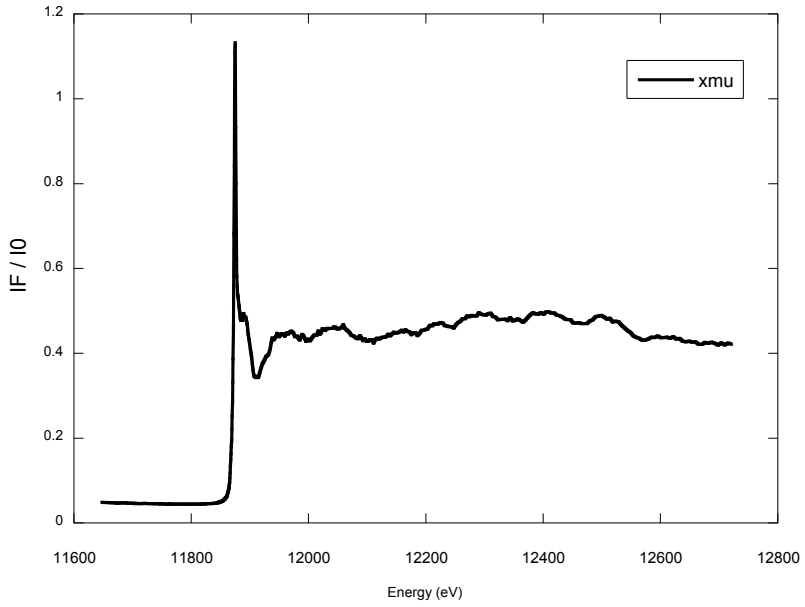

Figure 1. Example of an EXAFS scan collected at the As K-edge in fluorescence mode at 10K on finely ground natural soil sample containing 0.197 wt% As. Data are not usable for EXAFS, which might be related to the difficulty of recording EXAFS data on natural heterogeneous samples with grain size of few tens of microns, using a small heterogeneous focused X-ray beam of a few hundred micron width.

Similar difficulties were encountered in obtaining EXAFS data on river sediments from the same and other localities (Figure 2).

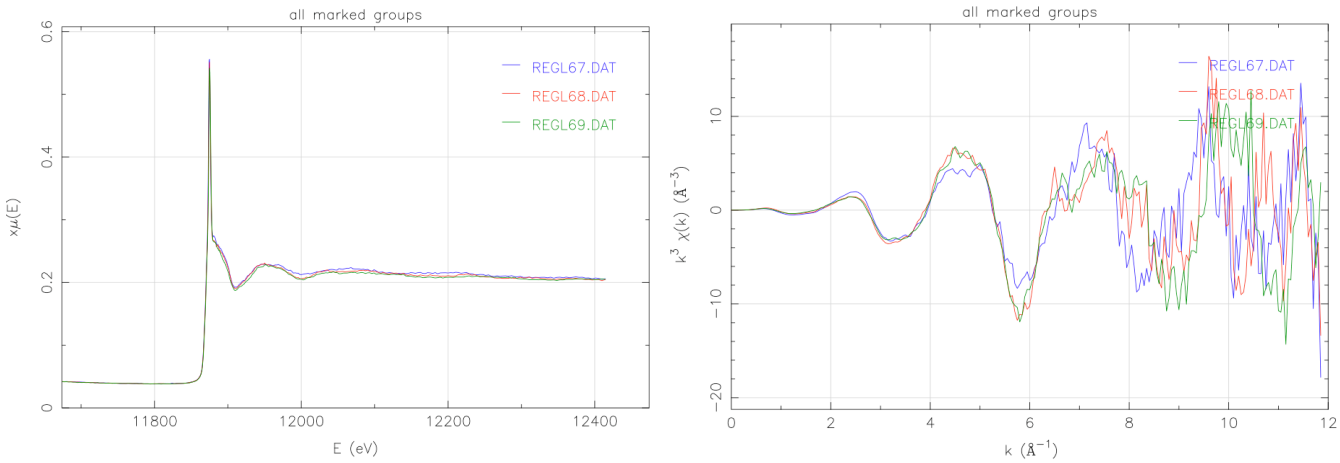

Figure 2. Examples of EXAFS data collected at the As K-edge in fluorescence mode at 10K on finely ground natural AMD sediments containing 400 ppm wt. As(V). Although the three scans are collected at the same spot position, data are not reproducible, which might be related to the difficulty of recording EXAFS data on natural heterogeneous samples with grain size of few tens of microns, using a small heterogeneous focused X-ray beam of a few hundred micron width.

In order to optimize the beamtime, As K-edge data were recorded on laboratory samples consisting of As-sorbed pure iron minerals obtained from abiotic as well as biogenic pathways and containg 0.1 to 3 wt% As. On these homogeneous samples, good quality data could obtained by merging 3 to 10 scans (Figure 3).

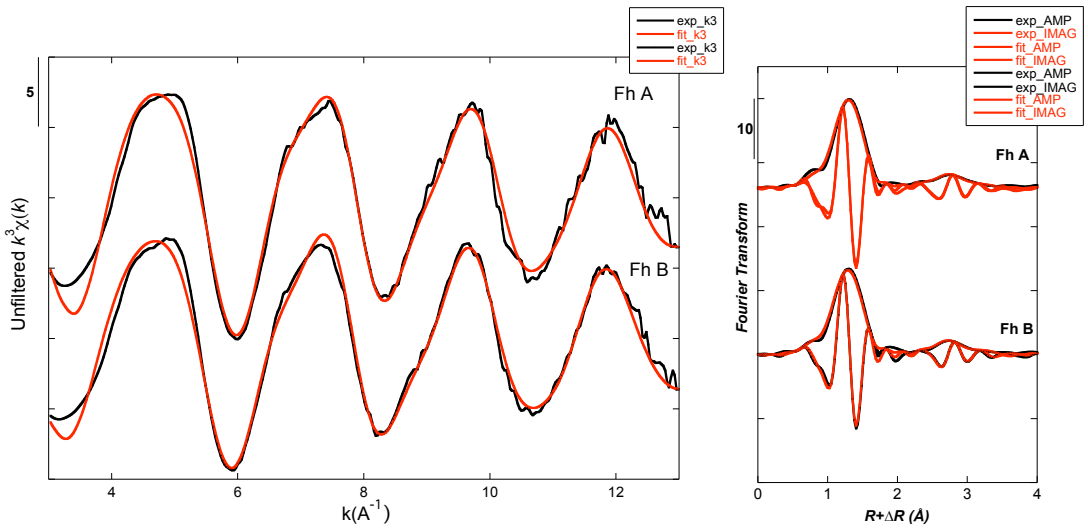

Figure 3. Examples of good quality EXAFS data collected at the As K-edge in fluorescence mode at 10K on pure As(V)-sorbed hydrated iron-oxyhydroxide samples prepared in the laboratory. Shell-by-shell fitting confirm the presence of inner-shere surface complexes with As(V)-Fe(III) distance at 3.3Å. These samples will be used as model compounds for interpreting As K-edge data of natural AMD sediments.

In addition, Fe K-edge data were also recorded on natural sediments and on laboratory samples in transmission mode (40 wt% Fe) and were of very good quality for both types of samples (Figure 4 and 5 , respectively). Data collected on AMD sediments samples are used to comlete an already existing data set and are thus already included in a manuscript in preparation.

Besides, data at the As and Fe K-edge for the flooded soils samples are still missing and are the goal of the resubmission of this proposal for experiments at the SAMBA beamline.

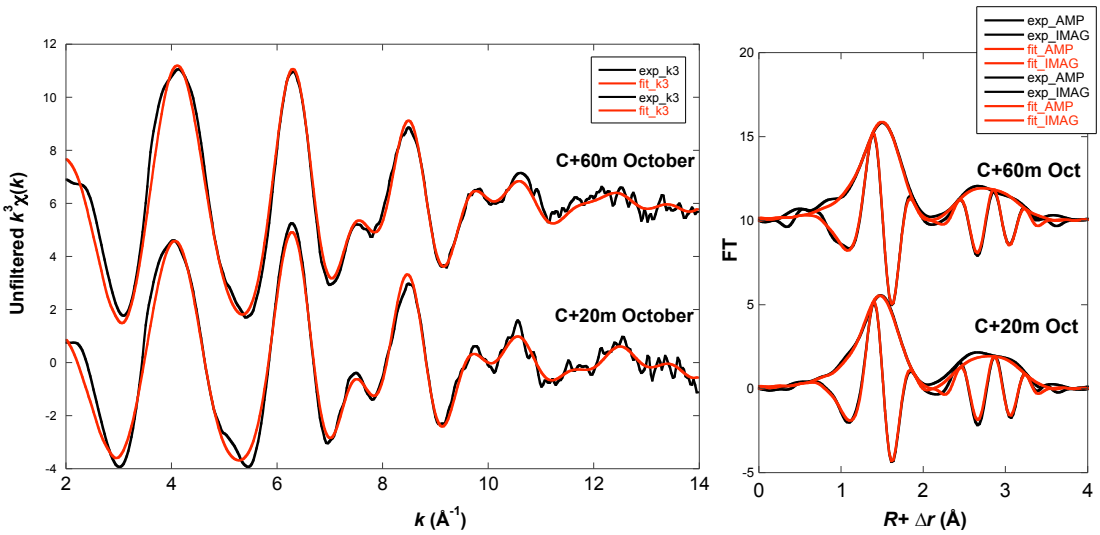

Figure 4. Examples of good quality EXAFS data collected at the Fe K-edge in transmission mode at 10K on natural AMD sediment samples containing 1 to 3 wt% As(V). Shell-by-shell fitting indicate local structures close to that of ferrihydrite (see Figure 4) but with differring number of neighbors, which can be related to different and less ordered local structure.

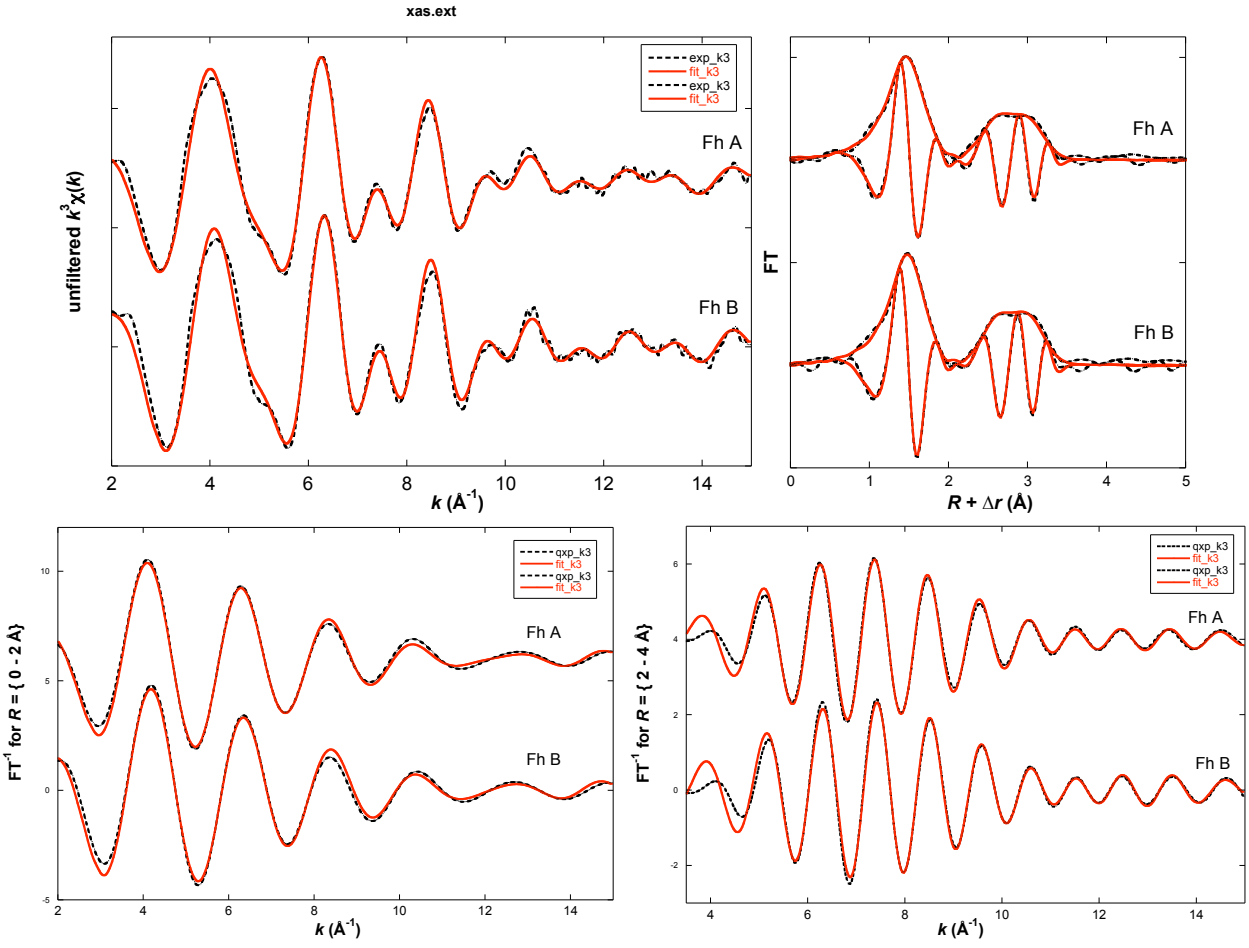

Figure 5. Examples of high quality EXAFS data collected at the Fe K-edge in transmission mode at 10K on As-sorbed hydrated iron-oxyhydroxide samples prepared in the laboratory. Shell-by-shell fitting confirm local structures close to that of ferrihydrite with distorted Fe-O shell and two Fe-Fe distances at 3.0Å and 3.45Å. These samples are used as model compounds for interpreting Fe K-edge data of natural AMD sediments (Figure 5).