



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Role of natural colloids as environmental nanovectors of As in contaminated soils	<b>Experiment number:</b> EC822
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 06/05/2011 at 08:00 to 10/05/2011 at 08:00	<b>Date of report:</b>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Jon Ander GALLASTEGUI	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b>  <b>Susana Serrano*</b> , <b>Martin Helmhart*</b> and <b>Fernando Garrido*</b> Instituto de Ciencias Agrarias, CSIC, Spain  <b>Peggy A. O'Day*</b> , University of California, Merced, US  <b>Eduardo Bolea and Francisco Laborda</b> , Departamento Química Analítica, Universidad de Zaragoza, Spain.		

### Remarks:

During our experiment period, we have studied the molecular-scale speciation of As in selected natural colloids samples obtained from metal(loid)s contaminated soil samples aiming to assess the role of soil natural colloidal particles as nanovectores of toxic elements in the contamination process of the soil-water system (Report 1). In addition, we could perform supplementary studies of As speciation in two bulk soil samples aiming to complete our previous study (EC649 and corresponding experimental report) on the geochemical behaviour and distribution of As in contaminated soils and to elucidate the role of preferential water flow phenomena on their sorption mechanisms in the soil (Report 2).

### Report 1:

Arsenic associated with colloidal particles is an important vector for As migration in contaminated soils. Using Asymmetric-Flow Field-Flow Fractionation (AsFIFFF) coupled to an inductively coupled plasma-mass spectrometer (ICP-MS), we determined the As distribution as a function of the particle size of the colloidal fraction of soils samples. The samples were collected from stained preferential flow paths and bulk soil samples, impacted by a mine waste. Physical and chemical properties of the colloids were also determined using X-ray-diffraction, SEM and TEM. Arsenic and Fe speciation in the colloidal fraction was characterized using X-ray absorption (XAS) spectroscopy techniques. Preliminary results indicated that more than 47% of the As mobilized in the preferential flow paths (70.5 mg/L) was associated with the colloidal fraction of the soil. Instead, 5% (2 mg/L) of the mobile As in the bulk samples of the soil was colloidal As. Common to both samples, a similar fractogram (1-1000 nm) was obtained for As, Fe and Al, suggesting an association of As with Fe and/or Al colloidal particles. As XAS analysis of the colloidal fractions (>10 nm) of the soil samples, indicated As adsorption on ferrihydrite as the main As-colloid retention mechanism. The presence of Fe oxyhydroxides in addition to phyllosilicates was also showed by Fe X-ray absorption analysis. These results show the important role of Fe-oxyhydroxides as nanovectors of colloidal As in preferential flow paths and bulk samples of a contaminated soil.

During our experiment, As and Fe k-edge XANES spectra were measured on bending-magnet BM25A beamline (SpLine) (6 GeV, 100 mA, Si(111) monochromator crystals) in fluorescence model using a Vortex, one-element solid detector (RT) and an He-cryostat in quench-frozen samples. The samples corresponded to selected natural colloidal soil samples obtained from a contaminated scenario located in Madrid province (Spain). The SpLine X-ray energy range (5 - 35 keV) allowed determination of both Fe and As edges. The average of all the spectra for each samples was performed using the computer package Athena.

However, unconvulsive XANES spectra were obtained due to the low As concentration in the samples and the use of a Vortex, one-element solid detector (Figure 1). In order to confirm our results, additional beamtime were allocated under the CRG Spline proposal 25-01-828 (see report Cod. 25-01-828) and preliminary results have been presented as:

Garrido, F., Laborda, F., Bolea, E., Helmhart, M., O'Day, P., and Serrano, S. 2011. Colloidal arsenic distribution and speciation in mine soils. *Goldschmidt Conference Abstracts*. p 895.

Serrano, S., O'Day, P., Gómez-González, MA., Laborda, F., Bolea, E., Helmhart, M., and Garrido, F. Colloidal arsenic distribution and speciation in mine soils. *In preparation*

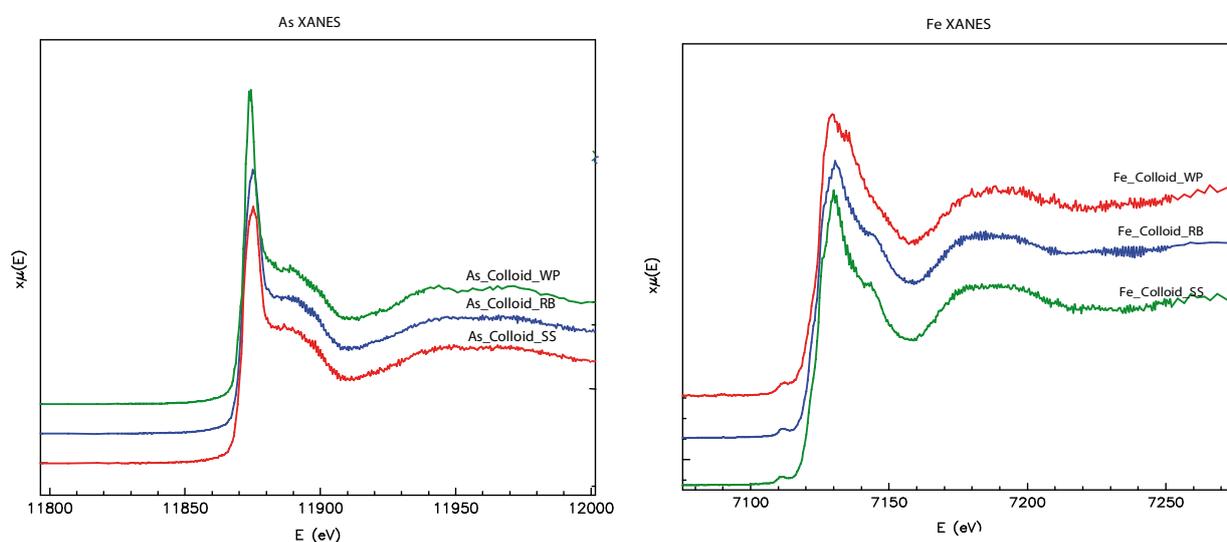


Figure 1. Arsenic and Fe XANES of the colloidal samples corresponded to the samples Wastepile (WP), Riberbed (RB) and Subsoil (SS) (mean spectra out of 25 scans each).

This research is currently in progress within the frame of the research project CGL2010-17434 supported by the Spanish National Research Plan and a related new proposal for beam time at the BM25A Spanish beamline will be submitted.

## Report 2.

The effect of preferential flow on the spatial distribution and chemical speciation of As, Cu and Zn in a metal(loid) polluted soil was studied within the river bed of a small stream that collects surface runoff from an arsenic-bearing, mainly as scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), waste pile near an abandoned mine. Water flow domains, either preferential or matrix, were identified by staining techniques, a detailed soil sampling procedure, and statistical analysis. General soil properties were studied in each flow domain. In addition, total metal(loid) content and chemical distribution by means of sequential extraction procedure were done within each flow domain. Lastly, As speciation was studied by X-ray absorption spectroscopic (XAS) methods. An upper river bed and its underlying subsoil were distinguished, and both were characterized by low pH and high As, Cu, Zn and Fe concentrations as compared to the adjacent soil. Metal(oid) concentrations were higher in the river bed than in the subsoil due to the accumulation of incoming material from the waste pile. In the river bed, higher metal(oid) concentrations were found in the preferential flow domain compared to matrix flow. Instead in the subsoil, preferential flow paths were characterized by a lower ion exchange capacity and lower Cu and Zn concentrations from acidic leaching, and higher concentrations of total organic matter attributed to high root content, compared to the soil matrix. Arsenic was mainly concentrated in the preferential flow paths as As(V). XAS analysis indicated As sorption on iron hydroxide phases as the primary retention mechanism in

the subsoil, which may be a reversible process if geochemical conditions change. Preferential flow, acting as a by-pass connecting the highly contaminated river bed layer with deeper soil, has an impact on the distribution of metal(oids) at the study site and may increase the risk for groundwater contamination.

Overall, our results have been presented in:

Helmhart, H., O'Day, P.A., Garcia-Guinea, J., Serrano, S., and Garrido, F. 2011. Arsenic, copper, and zinc leaching through preferential flow in mining-impacted soils. Goldschmidt Conference Abstracts. p 1004.

Helmhart, H., O'Day, P.A., Garcia-Guinea, J., Serrano, S., and Garrido, F. Arsenic, copper, and zinc leaching through preferential flow in mining-impacted soils. Soil Science Society of America Journal (*In review* – July 2011, S11-0269)