EUROPEAN SYNCHROTRON RADIATION FACILITY

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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.

ESRF	**Experiment title:** **Arsenic transport an speciation along the course of stream in a abandoned silver mine nearby Madrid**	**Experiment number**: CRG 25-01 944
Beamline: BM25A	**Date of experiment**: from: 27/11/2014 at 08:00 to 02/12/2013 at 08:00	**Date of report**: 07/05/2015
Shifts: 15	**Local contact(s)**: Dr. Eduardo Salas	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Natural colloids formed by weathering of mine-contaminated soils may transport hazardous elements such as As in surface waters reaching areas situated at long distances from the contaminant source. The important role of inorganic colloids as metal(oid)s carriers in natural systems has already been documented. Colloids may behave as nanovectors of toxic elements between environmental compartments of the soil-water system in contaminated sites. The nature of the colloid-arsenic interactions determines metal mobility and bioavailability and thus need to be characterized to prevent and evaluate the pollution process. However, the colloid stability and the nature of the chemical bonding of As in colloidal nanovectors depends on the inorganic or organic nature of the nanoparticle and the geochemical conditions which may be highly variable within the natural travel path potentially covered.

It is necessary to know the occurrence of mobile colloids in natural systems, their organic or inorganic nature and the physical and chemical conditions that induce their release to the soil solution as well as the nature of the interaction contaminant-colloids in soils. In addition, it is also important to compare these colloids with the As-bearing phases which cause the As spread in mine-impacted soil. Our project has a two-fold objective: (1) to study the role of soil natural colloids as nanovectors of toxic elements in the contamination process of the soil-water system and (2) to evaluate possible changes in the As speciation between leaching dispersible colloids and bulk soil samples.

Experimental methods

In the Mónica mine, nearby Bustarviejo (NW Madrid, Spain), silver was extracted since the XV century until it was close in 1980. Pyritic dumps remain close to Bustarviejo village along the La Mina stream gorge. Large amounts of metal(oid)s are released to the media but there is just a few studies on metal(oid) spreading from this area and no spectroscopic information is available to the best of our knowledge. Further research is thus needed to reveal whether stable metal-colloid particles may effectively control metal distribution and retention mechanisms in the soil and to elucidate the mechanisms behind the transport of metals through the soil especially in locations like this, affected by large amount of metals released due to the acid mine drainage and close to urban areas.

Undisturbed soil cores (0-15 cm depth) were collected along the natural stream from the pyritic waste pile (source point of As pollution) until approximately one kilometer far away. Samples were immediately frozen after collect them, and later vacuum-dried, sieved (2-nm mesh) and homogenized in a glove box. Leaching batch experiments were performed at solid/solution ratio equal to 1:10 under anoxic conditions and the dispersible colloidal fraction ≤ 1000 nm was isolated by centrifugation (ω=800 rpm, 10 min). Subsequently, solid colloids with sizes ranging 1000-10 nm were deposited on ultrafiltration membranes (10 nm membrane pore size). These membranes were placed on peek holders and sealed with Kapton tape for XAS analyses.

Additionally, bulk samples were powdered, diluted 9:10 with cellulose and pressed into 13-mm pellets inside the glove box, and subsequently measured by XAS.

Samples and spectra collected

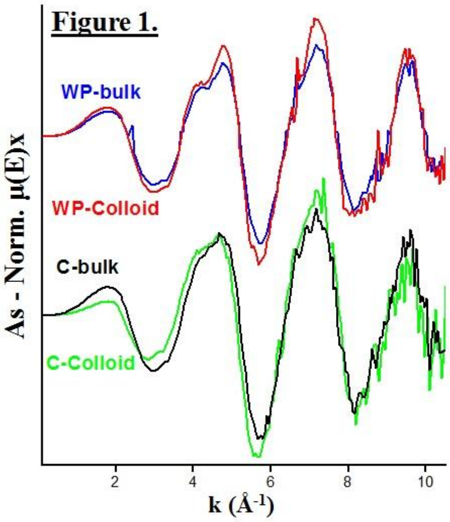
During our experiment, one soil core collected from the processing waste-pile (WP) and three soil core samples collected along the stream (A-B-C) together with their corresponding dispersible colloids (1000-10 nm) were measured under anoxic conditions (using a vacuum reactor) in order to evaluate both the As and Fe speciation by K-edge EXAFS analysis. A total of 96 EXAFS (7 As-spectra + 5 Fe-spectra per sample) were collected in fluorescence mode on bending-magnet BM25A beamline (SpLine) using a 13-element Si(Li) solid state detector, at room temperature.

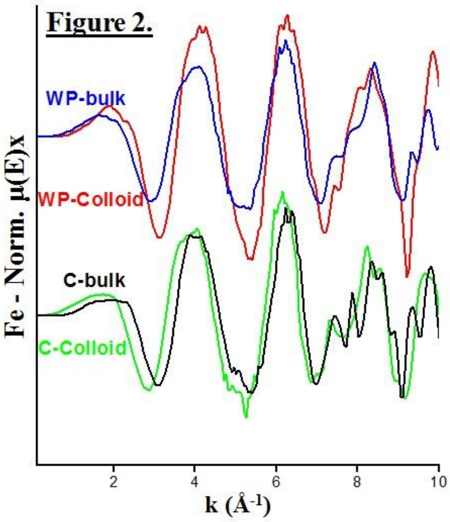
In addition, thallium pure compounds ($TlNO_3$, TlS, TlAc, Tl_2O_3) and thallium absorbed to synthetic standards (smectite, illite and Na-birnessite) as well as lorendite (thallium arsenic sulfosalt) were measured by Tl L3-edge EXAFS analysis in order to get a library reference spectrum for later studies involving thallium. A total of 23 EXAFS were collected in transmission mode.

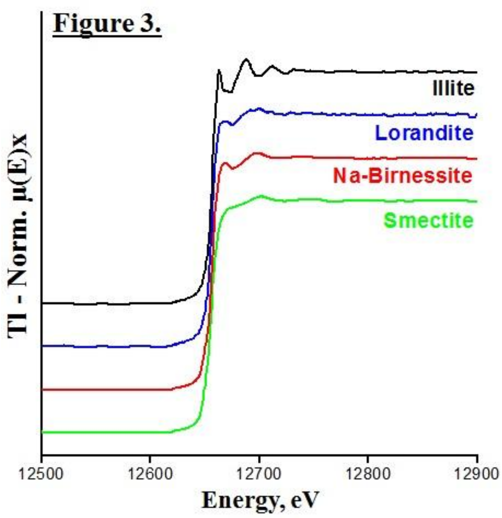
Results

Preliminary As and Fe XANES analysis of both the colloidal fraction and the bulk samples indicated only the presence of As(V) and Fe(III) along the stream. The As and Fe K-edge EXAFS spectra of the point-source of As (WP) and the furthest experimental location (C) are presented in Figure 1 (As) and Figure 2 (Fe), for both the colloidal and bulk samples. Samples from WP clearly showed a different As and Fe speciation of samples collected in C zone, and interestingly, the K-edge EXAFS spectra presented significant variations between bulk and colloidal samples, which should be properly analyzed by *Linear combination fits* (Athena) and by *shell-by-shell fittings* (Artemis).

In addition, thallium reference spectra collected during this beamtime are shown in Figure 3. These reference EXAFS data are expected to be extremely useful in our future Tl speciation studies.







Conclusions

The EXAFS analyses confirmed the expected differences on As and Fe speciation between the point-source of As contamination (WP) and the other samples collected along the stream reaching up to 1 km of distance (A-B-C). The comparison between bulk and colloidal samples also established significant unexpected variations, which should be carefully analyzed.

We expect that the processing of the data collected during this beamtime could provide evidence that colloids are effectively acting as contaminant carriers and represented a rapid transport pathway for element pollutants such as has been previously found by our research group in other polluted areas [1].

This work has been performed within the project CGL2010-17434 supported by the Spanish National Research Plan.

Those results are in preparation as:

M.A. Gómez-González, J. García-Guinea, J.F. Marco, F. Laborda and F. Garrido. Colloidal and bulk arsenic contamination in mining-impacted areas: Differences in transport and speciation along the stream. *In preparation*

[1] Serrano S, Gomez-Gonzalez MA, O'Day PA, Laborda F, Bolea E, Garrido F. Arsenic speciation in the dispersible colloidal fraction of soils from a mine-impacted creek. Journal of Hazardous Materials 2015; 286: 30-40