



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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.



	Experiment title: Colloidal arsenic transport and speciation in mine sediments along the course of a stream	Experiment number: 25-01 830
Beamline: BM25A	Date of experiment: from: 01-03-2013 to: 5-03-2013	Date of report: 13-12-2013
Shifts: 12	Local contact(s): Eduardo Salas	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): S. Serrano¹, F. Garrido^{1*}, P.A. O'Day², M.A. Gómez-Gonzalez^{3*}, E. Bolea³, F. Laborda³. ¹ Instituto de Ciencias Agrarias, CSIC, Spain; ² University of California – Merced, USA; ³ Universidad de Zaragoza, Spain		

Report:

Colloid-size scorodite is an As natural attenuation form in a range of environments. It minimizes As release when dumped on site. However, long-term stability of this mineral is uncertain and their potential transport makes As attenuation capacity of scorodite unclear. Our project aims to study the role of soil colloids as nanovectors of As in the soil-water system and to evaluate the nanosize scorodite stability to assess its potential transport capacity under natural conditions.

Experimental site, sample collection, and analyses

Mining As-rich wastes from an abandoned smelting factory remain on the soil subjected to erosion and weathering processes in a sub-catchment of the Guadalix River (Madrid, Spain) feeding the Madrid Tertiary Detrital Aquifer. Undisturbed soil cores were taken from the As-bearing waste pile (WP) [A], along the riverbed (RB) of a stream (~1 m wide) that collects runoff from the WP [B and C], from sediments downstream accumulated in an artificial pond (SP) [D] and from an adjacent farm that receives runoff that overflows the pond during rain events [E] (Fig. 1). All columns were cut at 15-cm intervals, air-dried, homogenized, and sieved (2-mm mesh) prior to analysis. SEM-EDX was used to collect images and spot semi-quantitative elemental analyses. Mineralogical composition of the ≤ 2 mm fraction of samples was identified by XRD. Samples from core sections were subjected to a sequential As and Fe extractions (Root et al. 2007).

Synchrotron X-ray absorption spectroscopy

Arsenic and Fe K-edge spectra were collected from ultrafiltrated colloid-size samples (A₁, A₄, B₁, B₃, D₁ and E₁) at room temperature on BM25A beamline in fluorescence mode using a Si(111) monochromator and a 13-element Si-Li solid-state detector. Beam energy was calibrated for As on KH₂AsO₄(s) by setting the maximum absorbance to 11,875 eV and for Fe by setting the first inflection of the absorption edge of metallic Fe foil to 7112 eV. Between 10 and 22 XANES and 12 EXAFS (sample A₁, spectra for the rest of samples too noisy due to low As mass) spectra were collected and averaged for each sample and element. XANES spectra were analyzed (ATHENA, Ravel and Newville, 2005) by linear least-squares combination fits using a reference compound library (O'Day et al., 2004) consisting of phyllosilicate and Fe(III) oxide minerals, fit with all combinations of 2 or 3 spectral components, and ranked by statistical best fit. Sensitivity tests of the fit to the number of reference components were performed, treating energy as a variable parameter, and changing the spectral fit range. Sum of the reference components was not forced to 100 %. EXAFS data were analyzed by shell-by-shell method (k-range = 2.0 to 12 Å⁻¹) with theoretical reference functions (FEFF 8.0 {Ankudinov, 1998 #216}) based on atomic clusters from crystalline reference compounds (ATOMS {Ravel, 2001 #217}). A triangular multiple scattering path among bonded As and O atoms, resulting from the high symmetry of arsenate tetrahedral, was included in the fit model in addition to single-scattering paths {Root, 2009 #56}. Interatomic distance (R), and either N (number of backscattering atoms) or σ^2 (Debye-waller factor), was treated as a variable parameter for each atomic shell. Threshold energy (E₀) was treated as a single variable for all shells and scale factor (S₀²) was fixed (= 1). Estimated errors based on empirical fits to reference compounds are: first shell: R \pm 0.01 Å; σ^2 \pm 10% (N fixed); greater than first shell: R \pm 0.02 Å; N \pm 25% (σ^2 fixed).

Conclusions

Mining wastes, rich in scorodite and dumped on the soil surface from an abandoned smelting factory have been characterized as a point source of As and metals pollution in the surrounding media. Erosion and weathering processes results in a continuous release of As to soils. Microscopic and spectroscopic analysis show that As is present mainly as As(V) and associated with Fe phases along the transect from an As-rich waste pile downward to a shallow soil in both adsorbed and co-precipitated species. No role of scorodite as As nanovector could be detected and only arsenic sulfide minerals were detected in the shallow soil due to seasonal reducing conditions at the sampling time. While both scorodite and Fe(III) oxyhydroxides minerals where As is adsorbed present in the waste hamper As vertical leaching through the waste pile, the effect of natural rainfall and the resulting runoff downhill boost seasonal lateral spreading of As either as dissolved anions or bound to suspended particles within the runoff. Neither the low solubility of scorodite nor other natural As attenuation phenomena such as As(V) sorption onto ferrihydrite should be considered as a desired secondary phases for remediation of As-rich mine waste materials as they do not limit natural spreading of As and companions metals when they are exposed to natural conditions. Both chemical extractions and XAS (Figure 2 and table 1) analyses highlight the important role of ferrihydrite as As scavenger in natural systems and confirms the strong association of As(V) with Fe(III) oxide phases. In this dynamic and seasonally variable system, however, other trapping systems such as jarosite-like minerals play a role in the attenuation of As and companion metals released to the medium. However, either due to partial dissolution of these phases or due to the excess of As released, an important amount of As reaches land soils in which temporal hydromorphic and reducing conditions induces the formation of arsenic sulfides phases. Overall, our results highlight the importance of runoff as driving force for As dispersion in the environment. On the basis of our results, it becomes urgent to remediate this mine site as otherwise continuous spreading of As through surface runoff may produce groundwater pollution in Madrid province. The results of this project are included the following manuscript close to be sent for publication: Gomez-Gonzalez, MA., O'Day, P., Serrano, S., Laborda, F., Garrido, F. Downstream spreading and partitioning of Arsenic from a mine waste pile in Madrid (Spain).

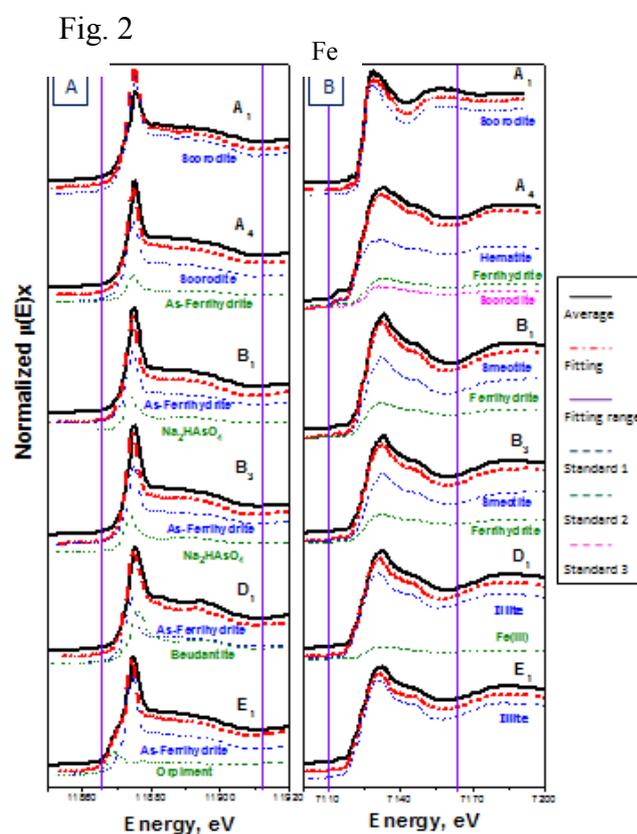
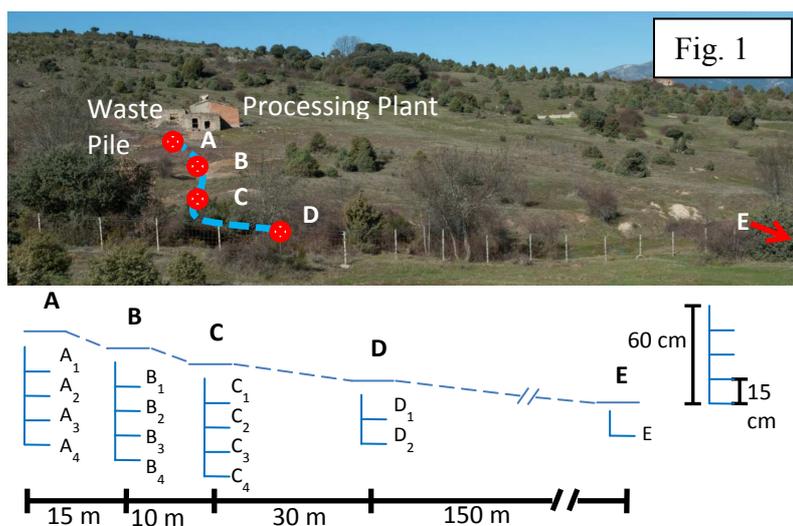


Table 1. Shell-by-shell fit analyses of As and Fe K-edge EXAFS spectra of colloidal samples ($\geq 1 \mu\text{m}$) with Artemis.

As	^a Path	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	Fit range (Å)	R-factor	red χ^2
	As-O	4 /	1.68 ^b	0.0019 ^b	- 8.05	2-13	0.0730	$2.98 \cdot 10^7$
A_1	As-Fe	3.2 ^b	3.35 ^b	0.0049 ^b				
	As-O-O ^c	3 /	3.36 ^b	0.0029 ^b				
Fe	^a Path	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	Fit range (Å)	R-factor	red χ^2
	^d Fe-O (eq)	4 /	1.96 ^b	0.0042 ^b	2.05	2-13	0.0544	$1.02 \cdot 10^6$
A_1	Fe-O (ax)	2 /	2.08 ^b	0.0048 ^b				
	Fe-As	2.5 ^b	3.35 ^b	0.0034 ^b				

^a Path is the A-B absorber-backscatterer pair; N is the number of backscattering atoms at distance (R); σ^2 (Debye Waller term) is the absorber-backscatterer mean-square relative displacement; ΔE_0 is the energy shift in the least-squares fit; χ^2 is a reduced least-squares goodness-of-fit parameter ($=\text{F-factor}/(\# \text{ of points} - \# \text{ of variables})$); scale factor (S^2_0) fixed

^b Parameter allowed to vary during fit; / parameter linked in fit to the parameter directly above

^c Spectrum fit with a multiple scattering path that is a composite of 6 triangular paths (O→O→As)

^d Fe-O spectra are divided in equatorial and axial according to their octahedra configuration