



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.



	Experiment title: Spatial distribution and chemical speciation of As and Pb in contaminated soils: influence of preferential flow paths	Experiment number: EC649
Beamline: BM25A	Date of experiment: from: 16/06/2010 (8H00) to: 19/06/2010 (8H00)	Date of report:
Shifts: 9	Local contact(s): Dr. Jon Ander GALLASTEGUI	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Martin Helmhart* and Fernando Garrido* Instituto de Ciencias Agrarias, CSIC, Spain Peggy A. O'Day* , University of California, Merced, US		

Remarks:

During our experiment period, we have studied the molecular-scale speciation of As and Pb in 8 selected contaminated bulk soil samples aiming to assess differences in metal sorption mechanisms resulting from water flow domains through the soil (Report 1). In addition, we could perform preliminar studies of As speciation in two samples of colloidal particles isolated from bulk contaminated soil on the basis of the application of Field-Flow Fractionation methods. This research will center a new proposal for beamtime in Spline (BM25A beamline) (Report 2).

Report 1:

Preferential flow is the rapid non-equilibrium movement of water and solutes through soils that bypasses a large portion of the soil matrix thus affecting a small portion of the soil volume. These phenomena limit the sorbing and buffering capacity of the soil and reduce the residence time of solutes accounting for a significant, increased risk of groundwater contamination from soil. Although preferential flow has been proved to enhance the transport of reactive agrochemicals, little research on the effects of macropore flow on trace metals leaching has been conducted. The main objective of the project in which frame our XAS experiments were planned was to study the geochemical behaviour and distribution of As and Pb in contaminated soils and to elucidate the role of preferential water flow phenomena on their sorption mechanisms in the soil. By means of dye tracer experiments to stain preferential flow paths in natural soils, an intensive soil sampling procedure and proper statistical analysis, previous investigations included the macroscopic description of the spatial distribution and chemical speciation of the elements in soils through total metal content quantification and a sequential chemical extraction protocol. In the last step of our research, XAS analysis were performed on selected soil samples representing bulk soil matrix and preferential flow domains to identify differences in the molecular-scale sorption mechanisms of the elements between these two flow domains taking advantage of the technical characteristics of BM25A beamline.

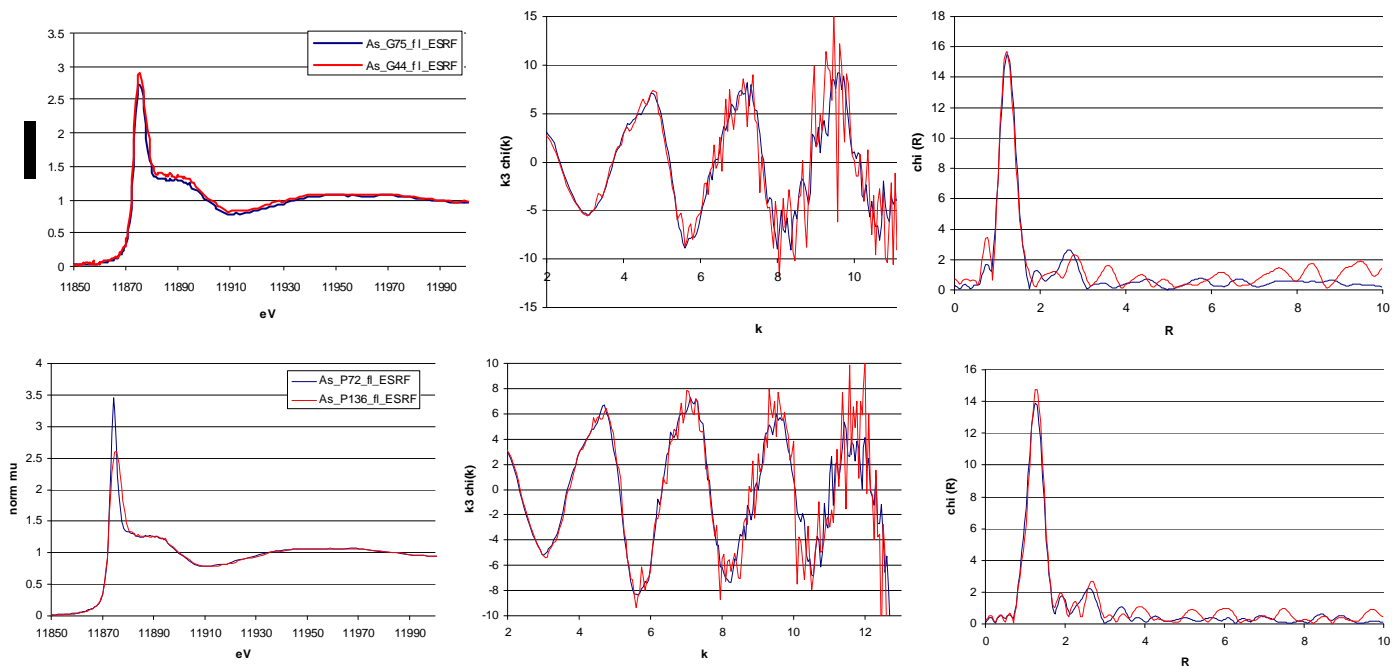


Fig. 1: Arsenic K-edge XANES, EXAFS and Fourier transforms (FT) Up: Guadalix; Down: Sao Domingos

During our experiment, XAS measurements were performed in fluorescence mode and at room temperature at the Pb L_{III} and As K, adsorption edges on four selected soil samples obtained from two contaminated scenarios chosen for the purpose of the project. The SpLine X-ray energy range (5 - 35 keV) allowed determination of both Pb and As edges, obtaining high quality spectra data (on the basis of collecting enough scans from each experimental case), even more with the recently acquired new 13 elements solid state detector at SpLine. Further data collection for Pb was abandoned after running the first sample for 17 scans as we were unable to optimize an efficient signal/noise ratio. All As spectra are currently being analyzed using the computer packages Sixpack and EXAFSPAK (SSRL), together with *ab initio* reference phase shift and amplitude functions for EXAFS calculated with the program FEFF and calibrated against experimental reference compound data.

Our preliminary results show that within a given soil horizon and at the pedon scale, metal concentration as well as reactive soil solid phases such as organic matter and Fe oxi-hydroxide particles are not evenly distributed but it is significantly affected by water flow domains. Thus, preferential flow domains have significantly higher metal concentration as compared to matrix flow domains. However, first ad-hoc analysis of the spectra obtained from samples of both characterized flow domains indicates that differences in mass of metals retained in the soil do not induce sizable differences in the main molecular-scale sorption mechanisms responsible for their retention (Figure 1). In spite of it, as preferential patterns at large scales result from local preferential phenomena, the effect of these non-equilibrium water transport on water contamination must be further studied.

Report 2.

One of the main limitations for the development and application of models for description and prevention of pollution processes is the lack of knowledge on natural phenomena such as the association of toxic elements on colloids and their mobilisation as nanovectors of contaminants as well as on the potential effect of non-equilibrium physical processes in solute and water movement on the leaching of these nanovectors through preferential water flowpaths in the soil. Within this research line, we have a two-fold objective: (1) to study the role of soil natural colloidal particles as nanovectores of toxic elements in the contamination process of the soil-water system and (2) to evaluate the possible influence of water and solute preferential pathways as fundamental mechanism that leads to nanovector transport in contaminated soils. By means of an experimental plan including advanced techniques such as field-flow fractionation to characterize the soil colloidal fraction and X-ray absorption spectroscopy for element speciation in colloidal surfaces, the scientific team of the project aims to investigate the fundamental mechanisms that determine the transport, retention and distribution of toxic elements in soils affected by toxic dumping, abandoned mine soils or agricultural soils.

With these purposes, we had the chance of analyzing two colloidal samples obtained from a contaminated soil to test the feasibility of a specific method to isolate the colloidal fraction and study the metal solid phase speciation on them. By means of an Asymmetrical Flow Field-Flow Fractionation (AsFIFFF) system coupled to an ICP-mass spectrometer, the colloidal fraction of two contaminated soil samples were characterized (Figure 2). The colloidal size range with greatest concentration in As was isolated onto an ultrafiltration membrane which was transported to the beamline for XAS measurement. Following the same experimental conditions as explained before, EXAFS spectra were obtained and are currently analyzed (Fig 3).

These results indicate that an experimental protocol to transfer samples from AsFIFFF-ICP-MS to XAS and other techniques such as Transmission Electron Microscopy is possible and will provide an advance in the current knowledge on the sorption and transport of toxic elements in contaminated soil materials. This investigations are currently in progress within the frame of the research project CGL2010-17434 financed by the Spanish National Research Plan and is object of a new proposal for beam time at the BM25A Spanish beamline.

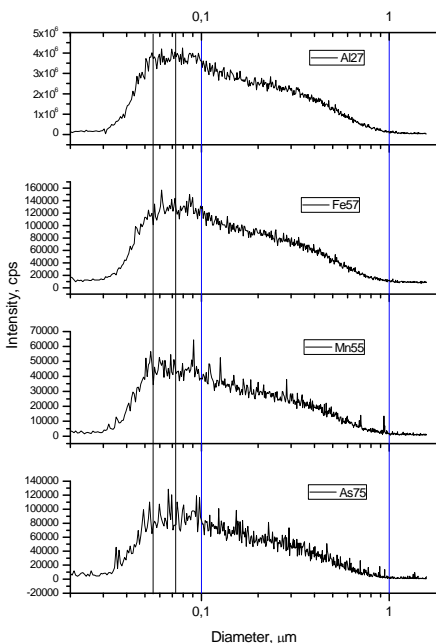


Fig. 2. Element composition and colloidal particle size distribution for sample 47.

Fig 3: Arsenic K-edge XANES, EXAFS and Fourier transforms (FT) on colloid samples

