ESRF	**Experiment title:** Effects of soil composition and mineralogy on the bioaccessibility of arsenic in heavily contaminated Ogosta river floodplain soils, NW-Bulgaria.	**Experiment number**: 01-01-848
Beamline: BM01B	**Date of experiment**: from: 06.04.2011 to: 12.04.2011	**Date of report**: 09.09.2011 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Hermann Emerich	

Names and affiliations of applicants (* indicates experimentalists):

Dr. Petar Mandaliev[*,1], Dr. Christian Mikutta[*,1], Prof. Dr. Ruben Kretzschmar[1]

[1]Department of Environmental Sciences, ETH Zurich, CH-8092 Zurich, Switzerland

Report:

Arsenic (As) is an toxic and carcinogenic trace element, which commonly occurs as contaminant in river floodplains and associated wetlands affected by mining of metal sulfide ores [1]. High arsenic concentrations in mining affected river floodplain soils are usually a result of oxidative weathering of primary As bearing minerals, such as arsenopyrite (FeSAs). The floodplain of the Ogosta river in NW-Bulgaria is extremely contaminated with As by effluent waters issued from several closed mine facilities and three tailing impoundments containing 3.5 million tones mill tailings [2]. Soil samples collected from the lower Ogosta river floodplain have As concentrations ranging from 0.04 to 37.4 g/kg, exceeding the local regulatory level of 50 mg/kg [3] by up to ~750 times. The presence of a contaminant in excess of these guidelines poses a significant threat to the river ecosystem and the health of the local population using these soils for settlements, gardening, horticulture, cattle grazing, and agricultural crop production [2].

In this work we investigated the mineralogical and chemical speciation of As in the lower and upper floodplains of Ogosta river. Our goal was to identify and quantify the major As species and their distribution among different grain-size fractions (<2 mm and <50 µm) in Ogosta river floodplain soils differing in soil moisture regime and sedimentation age (e.g., lower vs. upper floodplain).

Our study area is located at the Ogosta river in Northwest Bulgaria (Fig. 1a). Tailing impoundments are situated ~10 km upstream from the soil sampling area. The three soil profiles studied, herafter labelled P1, P2, and P3, are situated at Lat. 43°24'33.1"N and Long. 23°02'29.2"E along a transect through the lower and higher floodplains and at a distance from the river bed of 0, 7, and 49 m, respectively (Fig. 1b). Soil samples were collected in June and July 2011 up to a depth of 120 cm.

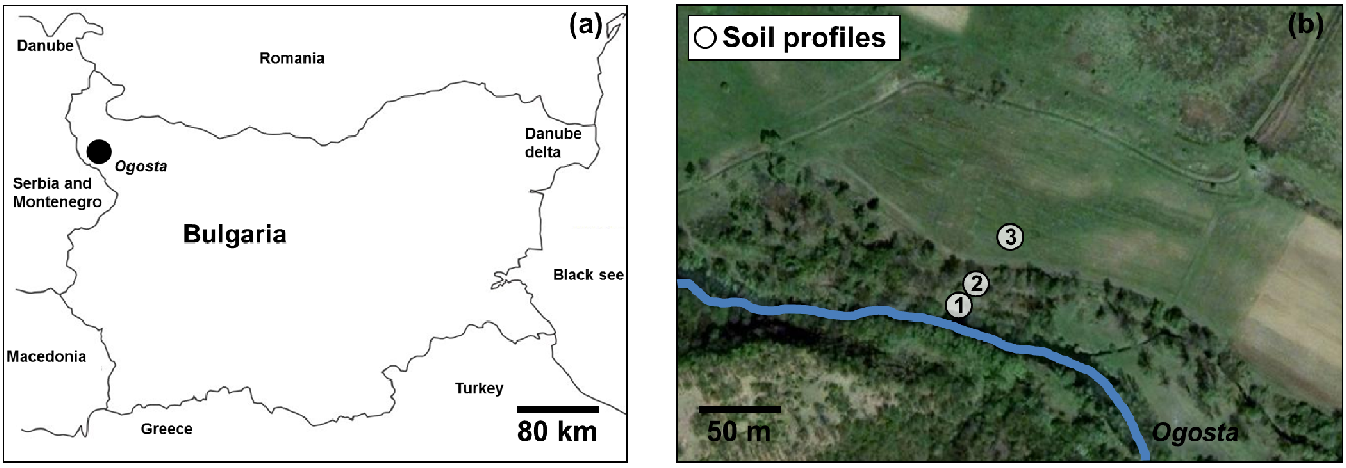

Figure 1. (a) Location of the Ogosta river in Northwest Bulgaria, and (b) aerial view of the soil transect.

X-ray absorption spectroscopy (XAS) experiments at the As K-edge edge (11’867 eV) were carried out at the bending magnet beamline BM01B (SNBL) at the ESRF using the energy resolution of the Si(111) monochromator. The measurements were conducted at liquid N_2 temperature (~77 K) in both transmission (ionic chambers) and fluorescence modes (13-element Ge solid-state detector). The XAS spectra were energy-calibrated to the first inflection points of the L_{III}-absorption edge of Au (11`919 eV). Between three and ten scans were averaged to obtain a satisfactory data statistics. Data reduction and modelling was performed with the ATHENA/ARTEMIS package [4, 5].

For a quantitative estimation of As species in the <2 mm and <50 µm soil fractions, linear combination fits (LCF) of As K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) were performed over the k-range 3–10.4 $Å^{-1}$ using selected reference samples. Reference samples were selected based on soil X-ray diffraction analysis and theoretical considerations. All spectra were properly fitted with only two references: As(V) sorbed to ferrihydrite (As(V)/Fh) and arsenopyrite. The LCF fits are shown in Fig. 2 and fit parameters are provided in Table 1. Our EXAFS data revealed that in the lower floodplain As is mainly present as As(V) associated with Fe(III)-(hydr)oxides. For example, in profile P1 between 47% and 83% of As is associated as pentavalent As with Fe(III)-hydroxides in the <2-mm size fraction (Table 1).

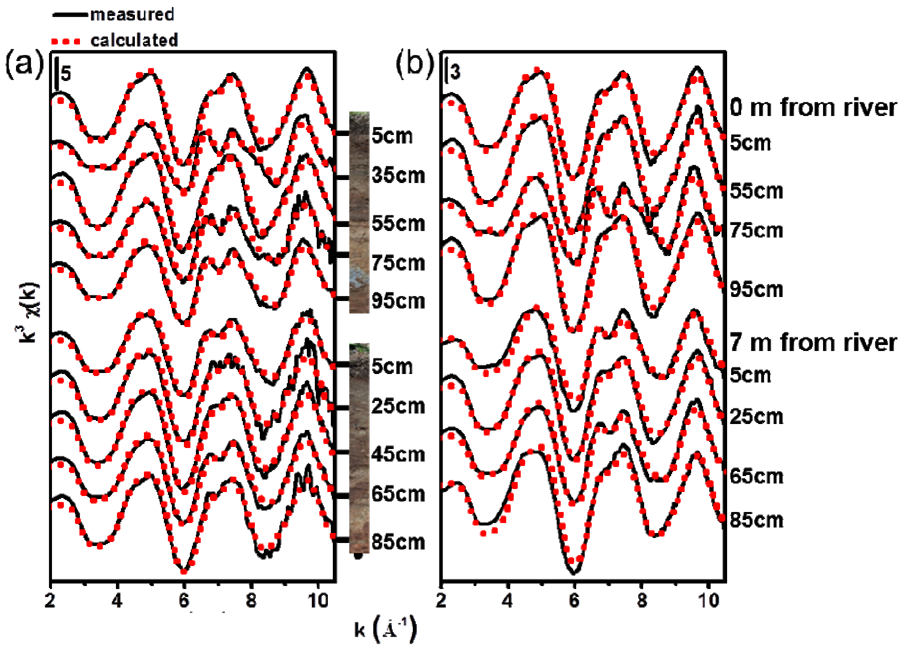

Figure 2. Linear combination fits (LCF) of As K-edge EXAFS spectra of selected (a) bulk (<2 mm) and (b) <50-µm soil size separates collected from the lower Ogosta river floodplain (black solid line = data, red dotted line = fit)

The amount of As(V) sorbed to Fe(III)-(hydr)oxides generally decreased with soil depth, but was significantly higher in the fine size separates compared to the bulk soil (Table 1). A particularly high fraction of As(V) sorbed to Fe(III)-(hydr)oxides was found in a soil sample from 97 cm depth of profile P1 (Table 1), which agrees well with the high As concentrations measured by XRF spectrometry and the predominance of ferrihydrite in the sample as inferred from Fe K-edge XAS analysis (data not shown). Our data further show that the abundance of primary As-bearing minerals (arsenopyrite) relative to secondary As species formed by weathering of primary minerals (As(V)/Fh) decreases with increasing distance from the river (Table 1). Additionally, the EXAFS results revealed that As in the Ogosta floodplain soils is not associated with carbonate phases, for example, calcite or siderite. Secondary As(V) minerals such as pharmakosiderite ($Fe_4(AsO_4)_3(OH)_3 \cdot 6H_2O$), Ca-As(V) (pharmacolite, $CaHAsO_4$; weilite, $CaHAsO_4$), or Ca-Fe(III)-As(V) mineral phases (arseniosiderite, $Ca_2Fe_3O_2(AsO_4)_3.3H_2O$; yukonite, $Ca_7Fe_{12}(AsO_4)_{10}(OH)_{20}.nH_2O$), which are commonly formed at high As(V) concentrations and circumneutral pH [6, 7], were also absent. Likewise, the precipitation of amorphous Fe(III) arsenates [8] was not observed in our soil samples.

Our XAS data collected at ESRF provide valuable information on the speciation of As under oxidizing conditions in the Ogosta river floodplain soils. Unfortunately, we were unable to evaluate our fluorescence EXAFS data set because the software necessary for data transformation was not available at the beamline. This data would have been important for the quantitative speciation of As at low soil As concentrations. Our next goal is the identification of major and minor As species in Ogosta occurring under reducing conditions. This information, in conjunction with the data collected on oxic soil samples, will be an important step towards developing appropriate remediation strategies for the Ogosta river area.

Table 1. Distribution of main As species (%) in the two soil size fractions (<2 mm and <50 μm) of the lower floodplain soils determined by LCF of As K-edge EXAFS spectra.

Depth (cm)	As(V) on Ferrihydrite(1)	Arsenopyrite(1)	Sum (%)	$\chi^{2(3)}$	*R*-factor (%)(4)
Lower floodplain		**0 m from river**			
<2 mm					
5	78	18	96	0.61	0.03
35	47	52	99	0.74	0.07
58	83	5	89	0.74	0.03
78	58	40	98	1.28	0.09
97	60	39	99	0.46	0.03
<50 μm					
5	77	14	91	0.57	0.03
58	86	7	93	0.89	0.04
78	49	55	104	0.81	0.07
97	86	9	95	0.64	0.03
		7 m from river			
<2 mm					
5	65	33	98	0.57	0.04
25	79	16	95	2.31	0.10
45	85	15	100	0.91	0.04
65	70	26	96	0.58	0.03
85	81	16	97	1.07	0.05
<50 μm					
5	59	34	93	1.27	0.09
25	75	16	91	0.52	0.03
65	66	32	98	0.39	0.03
85	81	18	99	1.42	0.06

(1) Synthetic ferrihydrite according to ref. [11]

(2) Natural arsenopyrite, ICSD#042508, SG: P-1, a = 5.744 Å, b = 5.675 Å, c = 5.785 Å, γ = 112.17 Å

References

1. Smedley, P. L.; Kinniburgh, D. G., *Applied Geochemistry* **2002,** *17,* (5), 517-568.
2. Bird, G.; Brewer, P. A.; Macklin, M. G., *International Journal of River Basin Management* **2010,** *8,* (1), 63 - 78.
3. Atanassov, I., *Bulgarian Journal of Agricultural Science* **2008,** *14,* 68-75.
4. Newville, M., *J. Synchrotron Rad.* **2001,** *8,* (2), 96-100.
5. Ravel, B.; Newville, M., *J. Synchrotron Rad.* **2005,** *12,* 537-541.
6. Paktunc, D.; Dutrizac, J.; Gertsman, V., *Geochimica Et Cosmochimica Acta* **2008,** *72,* (11), 2649-2672.
7. Pfeifer, H.-R.; Gueye-Girardet, A.; Reymond, D.; Schlegel, C.; Temgoua, E.; Hesterberg, D. L.; Chou, J. W., *Geoderma* **2004,** *122,* (2-4), 205-234.
8. Leblanc, M.; Achard, B.; Ben Othman, D.; Luck, J. M.; Bertrand-Sarfati, J.; Personné, J. C., *Applied Geochemistry* **1996,** *11,* (4), 541-554.
9. Raposo, J.; Olazábal, M.; Madariaga, J., *Journal of Solution Chemistry* **2006,** *35,* (1), 79-94.
10. Waychunas, G. A.; Rea, B. A.; Fuller, C. C.; Davis, J. A., *Geochimica Et Cosmochimica Acta* **1993,** *57,* (10), 2251-2269.
11. Mikutta, C.; Frommer, J.; Voegelin, A.; Kaegi, R.; Kretzschmar, R., *Geochimica Et Cosmochimica Acta* **2010,** *74,* (19), 5574-5592.