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REPORT

Aims of the experiment and scientific background

Arsenic concentrations above 10 µg/l (WHO Maximum Contamination Level), are found in over 50% of the wells of Bangladesh, placing an estimated 20 million people at risk of developing neurological, skin diseases and cancer[1,2]. Previous results indicate that Fe and As are strongly related in the control of As in the groundwater and that a majority of wells exhibit anoxic conditions[e.g. 1,3].

Recently new types of arsenic exposures are suspected to yield human diseases. There have been a number of conflicting reports[e.g.4-6] regarding the possibility of significant exposure to As through food, particularly the large quantities of rice grown throughout South Asia on paddies irrigated with groundwater contaminated with arsenic. In that context an international research project between Columbia University (New York-USA) and the CEREGE (Aix-en-P[ce]-France) started year 2004, funded by the NSF (National Science Foundation (USA)) and the French ministry of Research. We would like to characterize the bio-physico-chemical mechanisms of As transfer from irrigation water to rice plant via the rhizosphere.

First Results

Three weeks field experiments were conducted in January 2005 and 2006 (dry season) in the Araihazar thana district (30 km Est of DHAKA). The most striking result from this study is that concentrations of As in soil water (30-1500 µg/L) spanned almost two orders of magnitude in the 0-15 cm depth interval of 14 different rice paddies, and this for samples that all contain >1 mg/L dissolved Fe (unmistakably anoxic)[7]. The voltammetric measurements indicated that As in the soil water was essentially in the As[III] state, the most mobile form. Our first analysis of rice grains indicate that irrigation with groundwater high in dissolved As does not seems to significantly increase the exposure of the Bangladesh population to As[7]. The mechanism preventing As increase in rice grain could be related to particular properties of rice plant. Indeed rice plant roots can oxidize the immediate proximity (tens to hundreds of microns) of roots. Rice develops porous tissue that allows enhanced oxygen transport from leaves to roots for respiration. Sediment oxygenation at the root surface leads to iron oxidation and then precipitation. Since Fe[III] and As

exhibit high affinity, the ferric iron coating may reduce the arsenic mobility through Fe-As coprecipitation.

Experiments

The initial goal was to use the KB focussing set-up on the FAME beam line. Unfortunately, the device was not available at the time the samples were collected from Bangladesh. Anyway, raw EXAFS and XANES were performed on roots from plants that were sampled at various period of the growth season (january to march). Samples were scanned at the liquid He temperature using a He cryostat to prevent any beam damage. The samples were scanned at the As and Fe K edge. At the As K edge the fluorescence mode was selected.

The EXAFS session was successfull, no problem specific of the beamline are to be reported.
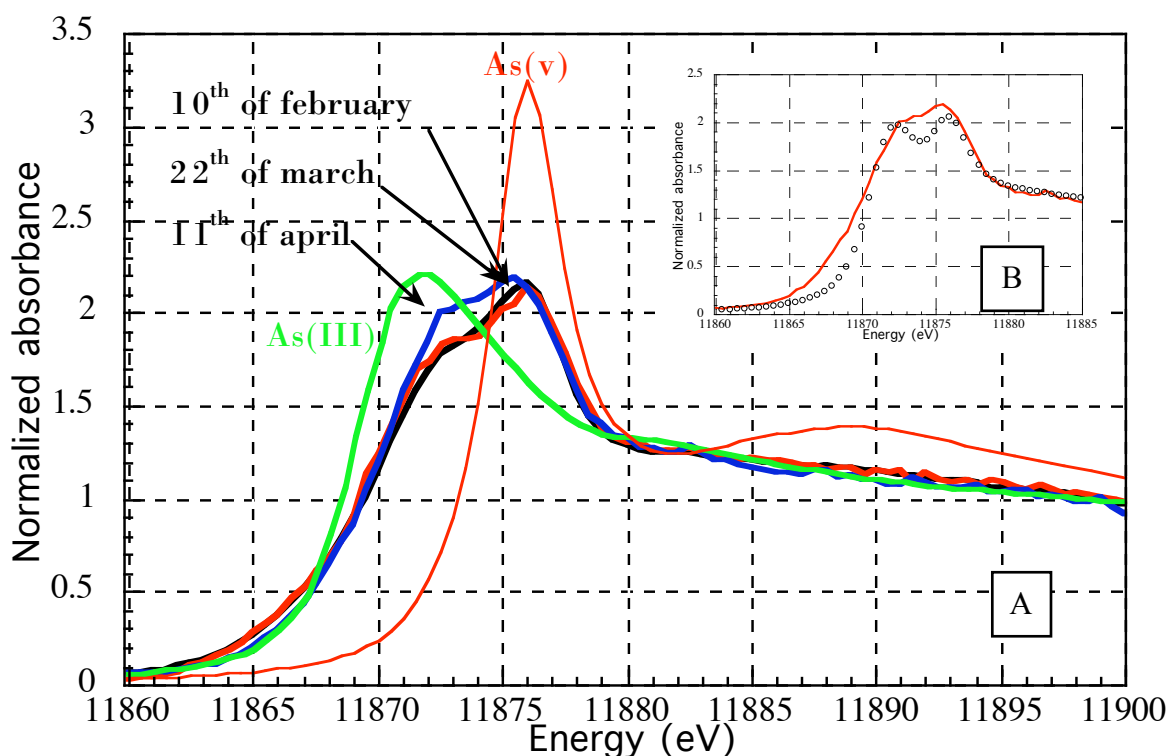

Figure 1: A) XANES of As at the K edge for various root iron plaque. B) Fit of the XANES of the 11-04

The xanes results of arsenic within the iron plaque around the roots indicated that a very low evolution of the As(III)/As(V) ratio appeard with time. It can be seen in figure 1 that the XANES spectra of As in the roots slightly evolved in april. The peak at low energy (11872 eV) is more prononced than in february and in march.
The XANES spectra were fitted with As(III) and As(V) reference spectra. The results indicated that samples were composed of 65-70% of As(III) (10-feb and 22-march) and 75% in april. This very low evolution of the arsenic redox state in the root can be related with the arsenic redox state in the pore water that is almost pure As(III) during all the period of rice growth. In contrast with the low evolution of the redox state of As, the total concentration of As in the root increased from 12 ppm in february, 18 ppm the 22th of march and then decreased again to 8 ppm in april. When compared with results from the field, they strongly suggest that the chemical composition of the iron plaque evolved with time as function of the composition of the pore water.

Concerning iron we have scanned EXAFS spectra at the Fe K edge of samples collected at various time during the growth season.

Figure 2: Pseudo-radial distribution function of EXAFS spectra at the Fe K edge
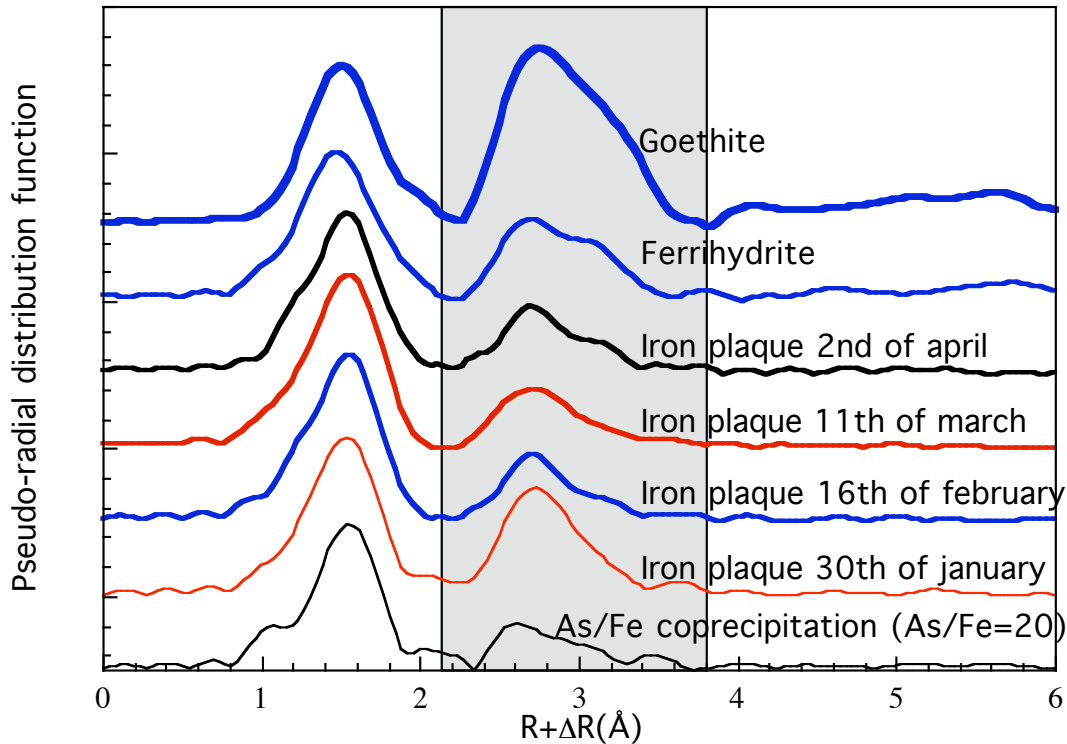
The EXAFS at the Fe K edge are difficult to interpret. The main point is that no Fe cristalline phase was detected within the plaque. All EXAFS spectra correspond to amorphous phases as it can be seen in the second coordination sphere of Fe. The low peaks intensity in the 2.2-3.8 Å range revealed a low iron polymerisation rate. The amorphous character of iron phases is certainly due to the coprecipitation of various elements present in the pore water (phosphate, arsenite...) with iron. The intensity of the peaks can be compared with the RDF of a synthetic As/Fe coprecipitation sample (As/Fe=20) and the RDF of the ferrihydrite. Nevertheless it is worth noting that the january sample is quite different. The intensity of the peak of the second coordination sphere is much higher that the other iron plaque. The <u>EXAFS spectra modeling are still under progress</u> but our first results tend to indicate that the iron in the january plaque is more 'ordered' than the other. The modeling of iron spectra are quite difficult since many atoms can be present in the second coordination sphere like Fe, of course, but also arsenic, phosphorous...

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