Dedicated to Professor Emil Cordoş
on the occasion of his 80th anniversary

PRELIMINARY INVESTIGATION ON ARSENIC FRACTIONATION IN SOIL FROM OGOSTA RIVER FLOODPLAIN USING A SEVEN-STEP EXTRACTION PROCEDURE

**MARIN SENILA[a,*], TSVETAN KOTSEV[b], ERIKA LEVEI[a],
MARIUS ROMAN[a], VASSILKA MLADENOV[c],
ZORNITSA CHOLAKOVA[c], LACRIMIOARA SENILA[a]**

ABSTRACT. Arsenic (As) is a toxic element which can occur in increased concentrations mainly in areas affected by mining and ore processing activities. To assess the As fractionation in soils from the Ogosta River floodplain, a seven-step sequential extraction procedure (SEP) followed by As determination using ultrasonic nebulization inductively coupled plasma optical emission spectrometry (USN-ICP-OES) was applied. The SEP fractionate between the *(1)* ionically bound As; *(2)* strongly adsorbed As; *(3)* As co-precipitated with acid volatile sulphide, carbonates, Mn oxides, very amorphous Fe oxyhydroxides; *(4)* As co-precipitated with amorphous Fe oxyhydroxides; *(5)* extraction in 0,2M NH_4-oxalate buffer + ascorbic acid; *(6)* As associated with crystalline Fe oxides; *(7)* orpiment and remaining recalcitrant As minerals. No significant differences were found between the pooled amount of As concentrations in each extraction step and the total As concentration measured using a XRF spectrometer (recoveries rate of 90 –110%). Total As concentration in soils varied widely, in the range of 36 - 72300 mg kg^{-1}. The partitioning of As among the seven fractions in the six soil samples (%, medians and ranges) was: *(1)* 0.97 (0–4.8); *(2)* 12 (0–36); *(3)* 25 (12–44); *(4)* 8.7 (2.5–31); *(5)* 4.0 (0.2–25); *(6)* 34 (3.6–84); *(7)* 0.15 (0.02–1.1). Significant differences on As distribution in contaminated and uncontaminated soils were observed, the fractions of mobile species, were found to be predominant in highly contaminated soils in contrast to the low-As soils, where As contents were bound to the matrix.

Keywords: *arsenic fractionation, floodplain soil, contamination, ICP-OES, sequential extraction procedure, Ogosta River*

[a] *INCDO-INOE2000, Research Institute for Analytical Instrumentation, 67 Donath, Cluj-Napoca, Romania*
[b] *National Institute of Geophysics, Geodesy and Geography, Bulgarian Academy of Sciences, Acad. Georgi Bonchev str., bl. 3, 1113 Sofia, Bulgaria*
[c] *Sofia University "St. Kliment Ohridski", 15 Tsar Osvoboditel bul., 1000 Sofia, Bulgaria*
* *Corresponding author: marin.senila@icia.ro*

M. SENILA, T. KOTSEV, E. LEVEI, M. ROMAN, V. MLADENOV, Z. CHOLAKOVA, L. SENILA

INTRODUCTION

Environment contamination with toxic metals and metalloids may pose risks for the ecosystems and for the human health, therefore the assessment of theirs concentration and possible mobilization in soils is required [1-6]. Arsenic (As) is a metalloid well-known for its high toxicity, being categorized as a group I carcinogen in humans [7,8]. It enter into the environment is both from anthropogenic and natural sources. Anthropogenic sources of As are represented by mining and smelting of ferrous and base metal minerals, manufacturing of As-based chemicals, use of pesticides in agriculture, industrial wastes discharging, burning of fossil fuels, landfilling of industrial and municipal wastes [9]. All these sources have led to the increase of the As concentration in soils from affected areas [10].

Although the soil quality standards are typically based on total metal content, it is generally recognized that includes both bioavailable and non-bioavailable fractions [11]. Knowledge on metals distribution in different soil fraction is very important both for the assessment of risks for human health and for elaboration of remediation strategies of contaminated soil [12]. To obtain this, procedures for distinguishing among various binding forms of metals and metalloids in soils are necessary. The identification and quantification of metals/metalloids associated with predefined phases or soil was defined by IUPAC as "fractionation analysis" [13]. Different sequential extraction procedures (SEPs) were developed and applied in order to obtain the fractionation of elements (or species) and to estimate the quantities of elements that could be mobilized due to changes in chemical properties of the soils [14]. Selective chemical extractants, used in the SEPs, intend to replicate the conditions found in soils under different environmental scenarios in order to find the fraction of metals that can be released [15]. Many extraction procedures are based on sequential extraction scheme developed by Tessier et. al in 1979 [16]. Another selective extraction protocol widely used in the last years is the three-step BCR protocol [17], created to distinguish between exchangeable, reducible, oxidizable and residual fractions.

The majority of SEPs found in literature were developed for trace metals fractionations. The anionic nature of As species in soil led to a different behaviour of this element and thus the necessity of different SEPs. The information of SEPs used for As fractionation is still limited [7,14,18,19]. These SEPs vary in terms of types of extraction solutions and conditions of extractions, number of fractions and their sequence, but an accepted standardized SEP was yet not established. Thus, there is a need for developing and studying of analytical performances for SEPs special designed for As fractionation in soils in order to find the most appropriate procedure for this purpose.

As a result of historic mining activities and also due to the failure of a large tailing dam in 1964, the floodplain soil from Ogosta River valley, Bulgaria was highly polluted with As [20,21], thus an evaluation of its possible mobilization is of a high interest.

The aims of this study were: *(1)* to evaluate the main figures of merit of a seven-step SEP for As fractionation in soil; *(2)* to accomplish a preliminary assessment of the As fractionation in floodplain soil from Ogosta River valley, Bulgaria.

RESULTS AND DISCUSSION

Sequential extraction procedure (SEP) validation

The applied procedure was based on a modified SEP from Keon and co-workers [22] and included the steps presented in detail in the Table 2 (Experimental section).

The validation of the analytical procedure for SEP in soil was performed by evaluating the main figures of merit: limit of detection (LoD), precision in term of repeatability for the each step of extraction procedure and accuracy in terms of recovery from the soil CRM and by comparing the amounts of As extracted in each step with the total As concentration measured directly in soil samples using a XRF spectrometer. *LoD* was calculated on the basis of 3 s criterion ($LoD=3s_B/m$), where m was the slope of calibration curve and s_B the standard deviation of 10 successive measurements of blank [23]. LoD was 0.005 mg L^{-1} in extraction solutions, which means, for an extraction ratio of 1:100, a method LoD of 0.5 mg kg^{-1}. *Accuracy* was studied by evaluating the recovery of the soil CRM SRM 2709 San Joaquin Soil, New York, USA. Also, the pooled amount of As recovered from all the fractions using the SEP was similar (90–110%) to the total As concentration measured directly in soil samples using a XRF spectrometer. The recovery for CRM was 96 ± 5 %. *Precision* was studied in term of repeatability by analysing 3 parallel samples by a single operator using the same equipment. The standard deviations of repeatability, in all the steps of the procedure, did not exceed 5% of the respective means.

Concentrations of total As and metals in soil samples

In the Table 1 are presented the total As and metal concentrations measured in soil samples by XRF spectrometry. For comparison, the typical ranges and common values present in unpolluted soils and the average abundance in the earth's crust [24] are also showed. With the exception of samples S3 and S6, the concentrations of total As were much higher than the maximum concentration in Earth's crust in unpolluted soil and also much

higher than the typical range reported in literature [25]. In a similar study [26] carried out on soils from Tamar, England, it was reported total As concentrations in the range of 3.8 – 848 mg kg^{-1}. In other study on soils from China [27], were reported total As concentration in the range of 36.0 – 4172 mg kg^{-1}. Increased As concentrations in sediments and mine waste samples in mining areas from NW Spain ranged between 310 – 67000 mg kg^{-1} were also reported [28].

Table 1. Total metal and As concentrations in soil samples,
typical range and the normal values in the unpolluted earth's crust
(mg kg^{-1}, mean ± s, n=3 parallel measurements)

Sample	As	Fe	Mn	Mg	Al	Ca
S1	2460 ± 120	103500 ± 3100	14000 ± 440	10800 ± 240	23300 ± 360	72500 ± 2400
S2	1350 ± 67	135500 ± 4300	32000 ± 1000	7300 ± 130	13900 ± 220	70900 ± 2520
S3	33 ± 2.0	42400 ± 1000	1250 ± 50	7200 ± 140	21400 ± 310	10000 ± 430
S4	72300 ± 2900	296500 ± 14700	41200 ± 2100	17400 ± 1300	6400 ± 700	102500 ± 5500
S5	12700 ± 640	144800 ± 4900	24300 ± 800	21500 ± 1200	12300 ± 800	209800 ± 7300
S6	41 ± 3.0	43100 ± 1100	1300 ± 50	6100 ± 110	26900 ± 280	13800 ± 540
Range	33 - 72300	42400 - 296500	1250 - 41200	6100 - 21500	6400 - 26900	13800 - 209800
Typical range	0.1 - 50	7000 - 42000	20 - 10000	-	-	-
Earth's crust	40	50000	1000	-	81300	-

The concentrations of Mn and Fe (with the exception of samples S3 and S6) were higher than the Earth's crust maximum concentration and generally above the typical ranges. The high concentrations of total metals are an indicator for a contamination of the floodplain soils in the investigated area with metals coming from mining activities.

Arsenic fractionation in soil

The percentages of metals in each fraction are presented in Figure 1. It must be accepted that these results are operationally defined and redistribution and adsorption of As can occur during extraction steps; however the partitioning of the As into the different fractions provides an indication of their mobility and availability to the environment and to the living organisms [29].
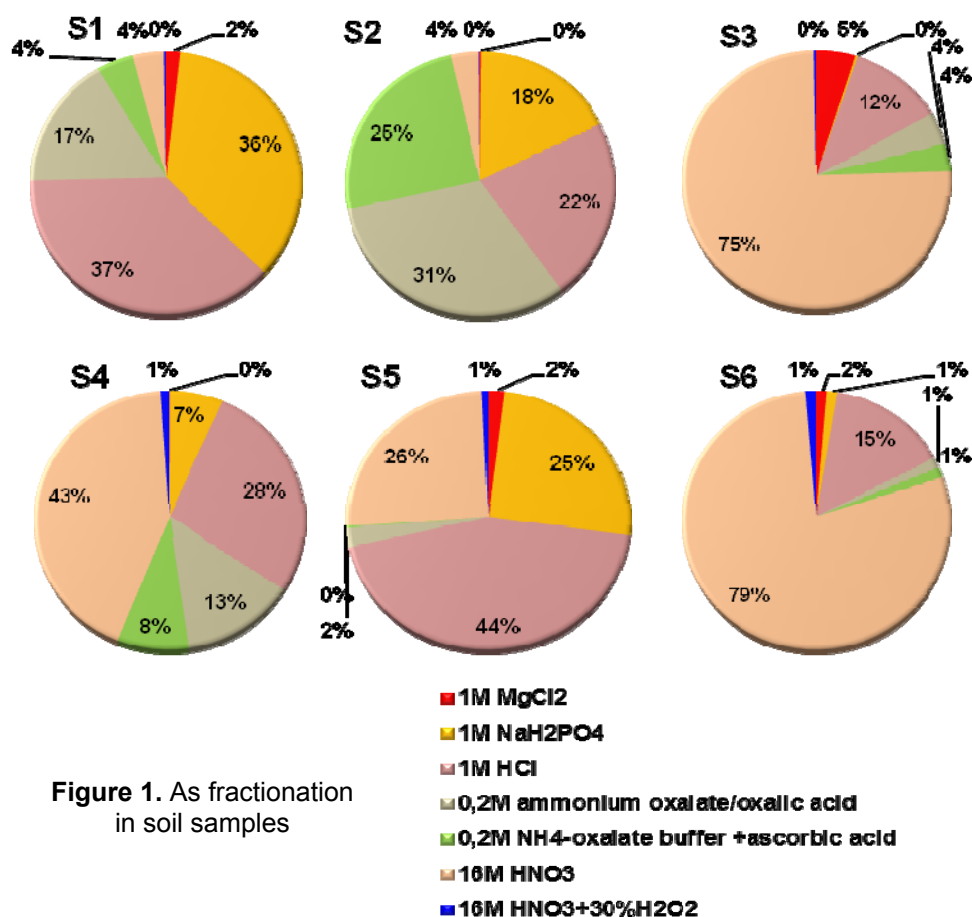
Figure 1. As fractionation in soil samples

- 1M MgCl2
- 1M NaH2PO4
- 1M HCl
- 0,2M ammonium oxalate/oxalic acid
- 0,2M NH4-oxalate buffer +ascorbic acid
- 16M HNO3
- 16M HNO3+30%H2O2

The first extractant used in SEP (1 M $MgCl_2$) is a very weak extractant and only dissolve the As weakly (ionically) bound to the matrix. The As concentration extracted in this step varied from below detection limit (*bdl*) in sample S6 and 251 mg kg^{-1} in sample S5, and represented less than 5 % from the total As concentration in all analysed samples. The amounts of As extracted in the second fraction (1 M NaH_2PO_4) estimates the strongly adsorbed As and was found to be generally high, in particular for samples containing high amount of total As (S1, S2, S4, S5). Percent of As extracted in this fraction ranged between 0 - 36 % (median 12%). Our results are in agreement with those reported by Javed who found high percentage of strongly adsorbed As (16-29%) in sediment samples [30]. In the third fraction, extracted using 1 M HCl, As was found in amounts ranging between 5.8 –

19700 mg kg^{-1} (12 – 44%, median 25%). This fraction was the most dominant one in all soils contaminated with As (S1, S2, S4, S5). The 1 M HCl extracts As co-precipitated with acid volatile sulphide, carbonates, Mn oxides and very amorphous Fe oxyhydroxides. The results of fraction F3 showed that high percentages of As associated to this extraction step were observed mainly in samples rich in Mn (S1, S2, S4, S5). The 0.2 M ammonium oxalate + oxalic acid (F4), which solubilize the As co-precipitated with amorphous Fe oxyhydroxides. The percent of As extracted in this fraction was 2.5 – 31% (median 8.7%). Good correlations were observed between the As extracted in F4 with the amounts of Fe measured in the respective samples (higher extraction rate being observed in the samples S1, S2, S4). The extractant used in step 5 (0.2 M NH$_4$-oxalate buffer + ascorbic acid) dissolves As associated with crystalline Fe oxides. The As concentrations found in F5 were in the range of *bdl* – 5800 mg kg^{-1}. Also in this case percentages of As were well related to the amounts of Fe measured in the respective samples (higher extraction rate in the samples S1, S2, S4). The solution used in step 6 (16 M HNO$_3$) extracts the As co-precipitated with pyrite and As strongly bound to the matrix. This fraction was the most dominant As pool in the soils with low As contents (75% and 79%, of the total As for the samples S3 and S6, respectively). Surprisingly, also in the sample with the highest amount of total As (S4) an important percent of As was found to be soluble in this step, probably due to the contamination of floodplain soil in this sampling point with minerals containing arsenopyrite. In the last step of the SEP were measured orpiment and remaining recalcitrant As minerals using a hot mixture of 16 M HNO$_3$ + 30% H$_2$O$_2$. Amounts of As extracted in this step were between *bdl* – 760 mg kg^{-1}, representing only 0 – 1.1 % of the total concentration of As found in the sample. Our results highlight the importance of testing soils with different sources and contamination degrees, confirming thus previous studies found in literature [4, 7, 20, 21, 27, 28, 31].

Multivariate statistics

The varimax rotated factor loadings of principal components (PCs) for the total As and metal concentrations and As fractions are presented in the Table 2. The loadings in bold face correspond to variables with dominantly influence the selected latent factor. Two PC's with eigenvalues higher than 1 explains about 95% of the total variance of the system. The first component (PC1) exhibits 74% of the total variance with positive loadings on total As, Fe and Mn and As fractions F2, F3, F4, F5, F6 and F7 and negative loading on Al. This behaviour is explained by the influence of total As concentration

on the level of As in different fractions and also by the influence of Fe and Mn on As retention mechanisms in soil. The second component (PC2) explains about 21% of the variability and contains the Ca and Mg concentrations correlated with the most mobile fraction of As (F1) and partially correlated with fraction F2. This can be explained by the influence of Ca and Mg on the exchange capacity of the soil and thus on As mobilization.

Table 2. Factor loadings after Varimax rotation

	PC1	PC2
Total Fe	**0.827**	0.334
Total Mn	**0.657**	0.406
Total Mg	0.381	**0.807**
Total Al	**-0.666**	-0.493
Total Ca	0.140	**0.898**
Total As	**0.892**	0.157
As F1	-0.128	**0.886**
As F2	**0.707**	***0.555***
As F3	**0.879**	0.211
As F4	**0.910**	0.027
As F5	**0.912**	0.001
As F6	**0.900**	0.098
As F7	**0.899**	0.107

The dendrogram resulting from Agglomerative Cluster Analysis (AHC), created by using Ward's method and Euclidian distance for dissimilarity, is presented in Figure 2. The studied parameters were grouped in 3 clusters: cluster 1 contains total Al and indicate the lack of influence of this parameter on As, cluster 2 groups Ca, Mg and mobile fractions of As, F1 and F2, respectively, while cluster 3 contains total As, Mn, Fe associated to the As fractions F3, F3, F5, F6, F7 and confirm the results obtained by the PCA.

The obtained results suggests that in anthropogenic contaminated soils the As is found predominantly in fractions that can be relatively easily mobilised, whereas in soils with low As content high amounts of As were found to be retained mainly as insoluble forms under natural environmental conditions. Our results are in agreement with other previous results on As fractionation that revealed that As natural occurred in soils is immobilised in soil [29, 32]. Other authors [33] showed that aging favor the immobilization of As in soils, while in case of recent anthropogenic As inputs in soils a high percentage of As in more mobile fractions. In a previous study using a similar SEP (6 steps) to our study for As fractionations in sediments and mine waste

samples [28] it was shown that important amounts of As is incorporated into amorphous Fe oxyhydroxides. As a conclusion of that study, it was shown that arsenic fractionation is very much influenced by the extent of mining and ore processing.
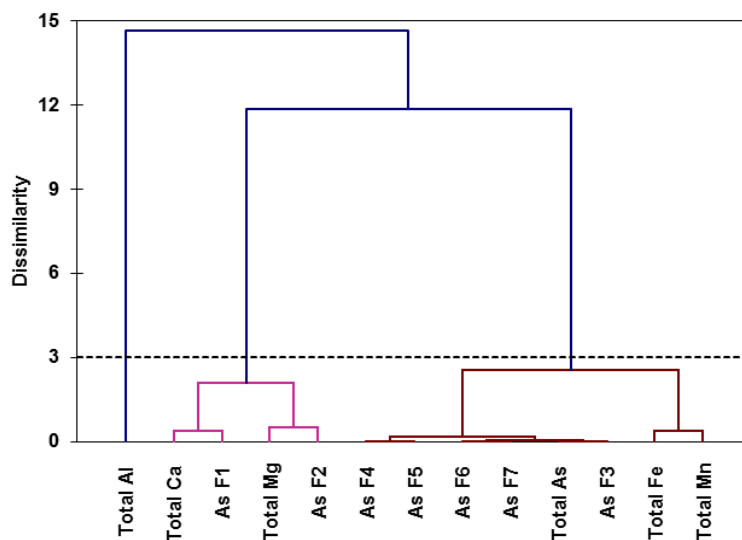

Figure 2. Dendrogram showing the clustering of total As, total metals concentration and As extracted in different fractions

CONCLUSIONS

A modified seven-step SEP was evaluated and applied for As fractionation in soil samples with total As concentrations varying between 36 - 72300 mg kg^{-1} collected in the Ogosta River floodplain. The results revealed that As distribution in the contaminated soils differs significantly from that of uncontaminated or soils with low As content. Thus, the fractions of mobile species, which are the most dangerous for the environment and biota, were found to be predominant in As contaminated soils in contrast to the percentages present in low-As soils, where As was to a high extent, strongly bound to the matrix. The most abundant fractions in contaminated soils were usually the F2 and F3 which represent the strongly adsorbed As and As co-precipitated with acid volatile sulphide, carbonates, Mn oxides and very amorphous Fe oxyhydroxides, respectively. However, As distribution showed significant differences between samples. Multivariate statistics (PCA and AHC) were used to find the correlations between As fractionation and the content of total As and other metals content in soil. Significant correlations

were found between total As concentration, Fe and Mn and the relatively immobile As fractions, while the most mobile As fractions (F1 and F2) were related to the content of Ca and Mg. The As fractionation in soils should be long-term monitored in order to assess if the aging and changes in soil properties will affect the As availability and its dynamics in natural ecosystem.

EXPERIMENTAL SECTION

Site description and sampling

The soil samples were collected from three sites in the Ogosta River basin upstream the "Ogosta" reservoir in 2009 (Figure 3). Site #1 N43°23.692', E23°06.338' and site #2 N43°24.557', E23°02.483' are located in highly contaminated sections of the Ogosta River floodplain close to the river banks. Samples S1, S2 and S3 are taken from prepared soil pit at site #1 from depths of 0-28 cm, 28-42 cm and 57-100 cm, respectively. The soil profile is well oxidized with no signs of Fe and Mn reduction. Samples S4 and S5 are from site #2 located at the river bank several kilometres upstream of the previous sampling area. The two samples were taken from the most contaminated layers of the floodplain sediments at depths 29-50 cm and 50-77 cm respectively. The upper part of the soil profile is well oxidized, but some ochre and grey-bluish spots in the lower part bellow 50 cm indicates frequently lowering of soil
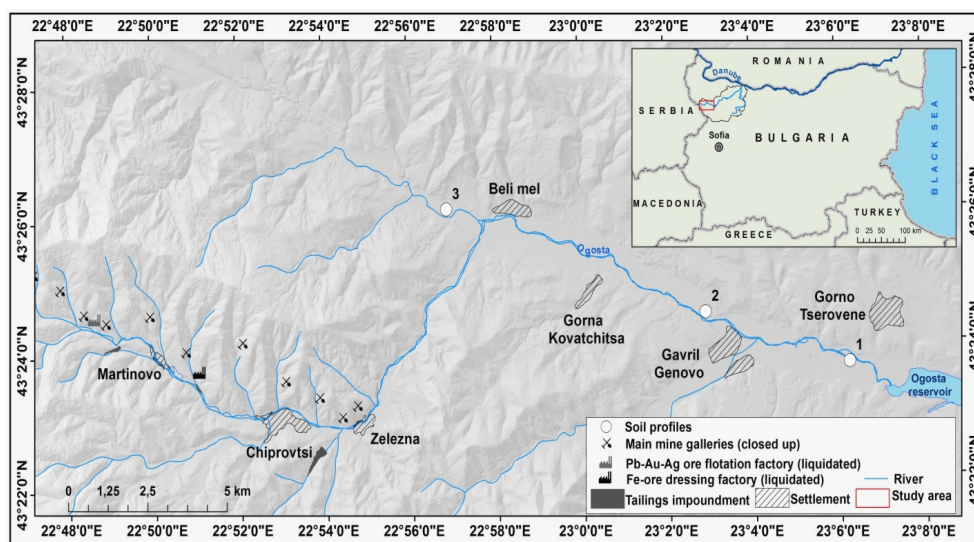

Figure 3. Study area and designation of soil sampling sites

redox potential. Sample S6 (well oxidized topsoil, 0-18 cm) is from the site #3 N43°26.028', E22°57.002' located in the floodplain of the Prevalska River. It is a tributary of the Ogosta River, which was not affected by the mining activities and where As levels and fractionation patterns in soil can be considered natural and serve as background.

For soil analyses, a representative part of each sample was air dried and then ground using a porcelain pestle and mortar. Fine fraction < 0.063 mm from each sample was obtained for chemical analyses.

Reagents and instrumentation

The solutions were prepared using reagents p.a. quality (Merck, Darmstadt, Germany) and ultrapure Milli-Q water provided by a Direct-Q purification system (resistivity > 18 MΩ cm^{-1}, Millipore, France). Stock multi-element standard solution containing Fe, Mn, Mg, Al, and Ca of 1000 µg mL^{-1} (Merck, Germany) and stock standard solution containing As 1000 µg mL^{-1} (Merck, Germany) were used to calibrate the ICP-OES for metals determination. All of the glassware was carefully cleaned, soaked in 10% (v:v) HNO_3 for 24 h and rinsed with ultrapure water prior to use. The reagents and operational conditions used in the SEP are summarized in Table 2. Three parallel sequential extractions were carried out using 1 g soil for each sample in order to separate the seven fractions. Soil was placed in 50 ml centrifugation tubes and 25 ml of the extraction reagents were added sequentially. After each extraction step, the slurry was centrifuged for 15 min at 4500 rpm using EBA 200 centrifuge (Hettich, Germany). Solution trapped in the remaining soil was collected in subsequent wash steps and combined with the corresponding extract.

Table 2 Reagents and operating conditions used in SEP (according to ref. [22]).

Step	Nominal target phase	Reagents	Shaking time and temperature
F1	*Ionically bound As*	Sample + 1M $MgCl_2$ pH=8 Residue + 1M $MgCl_2$ pH=8 Residue + Milli Q water	shaken 8h at 25 ºC shaken 8h at 25 ºC shaken 0.5 h
F2	*Strongly adsorbed As*	Residue +1M NaH_2PO_4 pH=5 Residue +1M NaH_2PO_4 pH=5 Residue + Milli Q water	shaken 16h at 25 ºC shaken 24h at 25 ºC shaken 0.5 h
F3	*As coprecipitated with acid volatile sulphide, carbonates, Mn oxides, very amorphous Fe oxyhydroxides*	Residue+1N HCl Residue + Milli Q water	shaken 1h at 25 ºC shaken 0.5 h

Step	Nominal target phase	Reagents	Shaking time and temperature
F4	*As coprecipitated with amorphous Fe oxyhydroxides*	Residue +0.2 M ammonium oxalate/oxalic acid, pH=3 Residue + Milli Q water	shaken 2h in dark (aluminium foil) at 25 °C shaken 0.5 h
F5	*As associated with crystalline Fe oxides*	Residue + NH_4-oxalate buffer (0.2M) + ascorbic acid (0.1 M) pH=3.25 Residue + Milli Q water	shaken for 0.5h at 96±3 °C at light shaken 0.5 h
F6	*As coprecipitated with pyrite and amorphous*	Residue +16 N HNO_3, Residue +16 N HNO_3, Residue + Milli Q water	shaken 2h at 25 °C shaken 2h at 25 °C shaken 0.5 h
F7	*Orpiment and remaining recalcitrant As minerals*	Residue +16 N HNO_3+30% H_2O_2	Boiling at least 2 h

ACKNOWLEDGMENTS

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