

## Arsenic Fractionation in Agricultural Soil in Vietnam using the Sequential Extraction Procedure

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**Abstract.** Given increasing awareness of As and its potential mobilization in soils, rigorous sequential extraction procedures have been developed and applied by researchers. A set of eight soil samples from the Red River Delta was examined in order to identify As distribution in agricultural soil. Sampled soils were characterized, As distribution was determined using the sequential extraction procedure, and the relationship between the sum of As fractions and total As content was analysed using the linear regression model. Five As fractions were extracted which appear to be associated with (1) non-specifically sorbed As; (2) specifically sorbed As; (3) amorphous and poorly crystalline hydrous oxides of iron and aluminium; (4) well-crystallized hydrous oxides of iron and aluminium; and (5) residual phases of As. The soil samples had a total As content ranging from 6.3 to 18.5 mg/kg in one sample, far exceeding the maximum allowed by Vietnamese legislation of 12 mg/kg. The distribution of As among five fractions was (% , range in mg/kg): (1) 0.09 (0–0.042); (2) 7.03 (0–1.016); (3) 30.99 (1.969–2.996); (4) 37.23 (1.173–12.993) and (5) 24.65 (1.222–3.559). The linear regression model proved a significant correlation between the sum of five As fractions and the total As content in the soil with  $R^2=0.98$ .

**Keywords:** sequential extraction, arsenic, soil analysis

### 1. Introduction

Arsenic-rich soil can affect human health by entering the food chain through plant uptake. Although measuring the total As content ( $As_t$ ) in soil is undoubtedly important, it should be borne in mind that permitted levels vary throughout the world. In Vietnam, the maximum level of As allowed in agricultural soil is 12 mg kg<sup>-1</sup>, in Germany the guidance value of As in soil is 50 mg kg<sup>-1</sup>, while in Spain,  $As_t$  in soil for agricultural use may not exceed 25–30 mg kg<sup>-1</sup>[1]. Another problem associated with the use of  $As_t$  as an indicator of toxicity is that it only gives a poor indication of arsenic availability and potential toxicity risks for living organisms. Due to the potential risks of arsenic-contaminated soil and water for public health, scientists' interest has grown in determining the potential mobilization of As in soil. A relatively simple method to estimate arsenic fractions of differential relative lability in soil is the chemical sequential extraction procedure (SEP). Various SEP schemes have been developed to fractionate As in sediments [2]; [3]; and [4].

The Red River Delta (RRD) is the social and economic centre of the northern part of Vietnam with the highest population density of 12,000 inhabitants km<sup>-2</sup> [5]. Geogenic arsenic contamination of groundwater in floodplain sediments from the RRD was documented in 2001 [9]. Inorganic arsenic concentrations of between 1 and 3050 µg/L (mean: 159 µg/L) have been reported in groundwater in the Red River Delta, while the level of arsenic in sediment ranged from 0.6 to 33 µg/g [6]. In addition, increased industrial activities and manufacturing in handicraft villages (such as metal processing and painting) might have become subsidiary

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pollution sources in the last few decades [7]. However, the risk assessment of arsenic-rich soils in Vietnam has not been systematically scrutinized.

Soil samples from eight paddy fields in the Red River Delta were examined in order to identify As distribution in agricultural soils in the RRD. Sampled soils were characterized, soil As distribution was estimated by means of the sequential extraction procedure, and the relationship between the sum of As fractions with the total As content were evaluated by using a linear regression model.

## 2. Materials and Methods

### 2.1. Sampling

The study site is located in Dai Lam village, Bac Ninh province, about 40 km northeast of the capital Hanoi. This region is part of the Red River Delta. Dai Lam is a food-processing village, which is located on the banks of the Cau River. Although the village is located in the zone of the RRD, which is less affected by As in the groundwater, the groundwater and some leafy vegetables have unexpectedly high As concentrations.<sup>1</sup> In early May 2014, eight samples were taken from a depth of 10–15 cm (the root zone).

### 2.2. Analytical methods

The pH of soil samples was measured using a glass electrode in suspensions of soil and distilled water with a ratio of 1:5 (w/v). For the other experiments, soil samples were dried by oven until their weight was stable and remained unchanged at 105°C over 24 hours. All the dried samples were placed in a desiccator to cool down for 1 hour before weighing. Gravimetric water content was defined by the ratio of the mass of water and the bulk mass over a range of 0–1 (0–100%). Then the soil samples were ground to a fine powder with an agate mortar and pestle and stored in zip plastic bags.

In this study, five-step sequential extraction was performed following the procedure described by Wenzel [2]. This method was chosen for this study because of its simplicity and high arsenic recovery rate, which has been confirmed by several recent studies [1] [8] and [9]. From each sample, 0.20–0.25 g of air-dried soil was weighed out and placed in a 50 ml plastic centrifuge tube. The method was applied in duplicate and is summarized in Table 1. The liquid was separated from the soil phase after each extraction step by centrifugation at 5000 rpm for 15 minutes, after which the liquid was filtered with filter paper. After filtration, the liquid was used to measure the concentrations of arsenic, iron and magnesium. Samples from step 4 were centrifuged and then air-dried at 105°C for 24 hours. After the homogenization process, 0.2g of each soil sample was used for microwave digestion in step 5.

Table 1: Sequential extraction procedure

Step	As fraction	Extractants	L/S	Extraction conditions
F1	Non-specifically sorbed	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 0.05M	1:25	4h shaking, 20°C
F2	Specifically sorbed	(NH <sub>4</sub> )HPO <sub>4</sub> 0.05M	1:25	16h shaking, 20°C
F3	Amorphous and poor crystalline hydrous oxides of Fe and Al	NH <sub>4</sub> – oxalate buffer 0.2M	1:25	4h shaking, 20°C, in the dark
F4	Well-crystallized hydrous oxides of Fe and Al	NH <sub>4</sub> – oxalate buffer 0.2M + ascorbic acid 0.1M, pH = 3.25	1:25	30 min in a water bath at 96°C
F5	Residual phases	HNO <sub>3</sub> /H <sub>2</sub> O <sub>2</sub>	1:50	Microwave digestion

The total As concentration in soil samples was determined by digesting 0.20–0.25 g of soil in a mixture of nitric acid and hydrogen peroxide. The samples were then digested in a MARS-5 microwave-accelerated reaction system (CEM Corporation, USA). After digesting, the samples were filtered through a 0.2 µm polytetrafluoroethylene (PTFE) membrane prior to analysis. All the microwave digestion experiments were carried out in triplicate. The concentration of arsenic and other elements in soil samples was measured using ICP-MS (Perkin Elmer-Sciex Elan DRC-e). All the chemicals used for analysis were of analytical grade quality.

<sup>1</sup> According to personal communication with Celia Hahn (Dipl. -Geol.)

### 3. Results and Discussion

#### 3.1. Soil properties

Table 2: pH, water content, total As, Fe and Mn of study soils

Soil sample	pH	Water content (Percentage)	Total As (mg/kg)	Total Fe (g/kg)	Total Mn (mg/kg)
1	5.85	26	6.336	24.66	89.49
2	4.78	53	7.888	21.42	81.78
3	6.13	36	8.082	26.19	130.92
4	5.41	29	7.436	21.77	148.69
5	6.92	31	18.514	21.66	155.19
6	6.28	27	7.138	26.55	149.02
7	6.68	24	7.705	32.22	212.21
8	7.16	23	7.073	28.08	136.75
Min	4.78	23	6.336	21.42	81.78
Max	7.16	53	18.514	32.22	212.21
Mean	6.15	31.13	8.775	25.32	138.01

Soil properties are presented in Table 2. With the pH varying from 4.78 to 7.16 (mean: 6.15), samples were mildly acidic to neutral. The soil water content ranged from 23 to 53% (mean: 31.13%). Total As content ranged from 6.3 to 18.5 mg/kg (mean: 8.8 mg/kg). Soil sample 5 was found to have the highest soil arsenic level (As concentration: 18.5 mg/kg). The total Fe level ranged from 21.42 to 32.22 g/kg (mean: 25.32 g/kg). The total Mn content ranged from 81.78 to 212.21 mg/kg (mean: 138.01 mg/kg). The findings of the soil arsenic content in this study are similar to previously reported values, and most samples have a total As concentration below 10 mg/kg. One of the eight samples exceeded 12 mg/kg, the maximum amount allowed in Vietnamese agricultural soils by law (TCVN 7209 2002). Then again, the As content of the analysed soil was much lower than in other regions of the RRD, such as Hanoi, Hung Yen and Hanam provinces, where levels range from 34.9 to 41.7 mg/kg [7].

#### 3.2. Arsenic distribution in soil samples

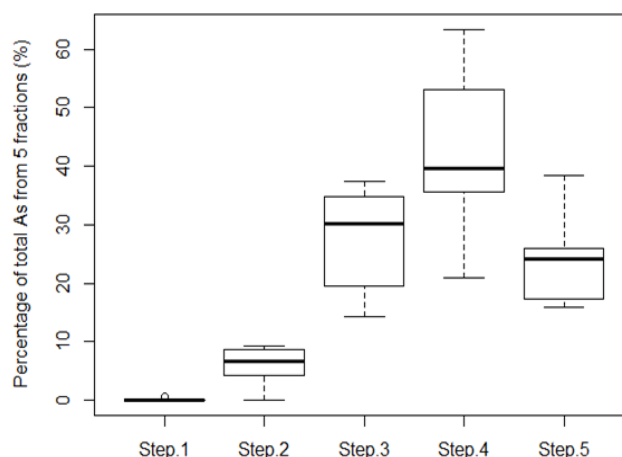


Fig. 1: The distribution of soil arsenic among five 5 steps

On average, the amount of As extracted by sequential reagents expressed as a percentage of the total decreased in the following extractant order: 0.2 M  $\text{NH}_4^-$ - oxalate + ascorbic acid > 0.2 M  $\text{NH}_4^-$ - oxalate > residual microwave digestion > 0.05 M  $\text{NH}_4\text{H}_2\text{PO}_4$  > 0.05 M  $(\text{NH}_4)_2\text{SO}_4$ . Fig. 1 shows the As distribution of

soil among five fractions. Corresponding to other studies of contaminated soils, the majority of soil As was associated with the Fe and Al oxide minerals (F3+F4) based on the partitioning of total soil As using an As specific sequential fraction scheme [2] [10]. This can be explained by the high iron content of soil in F3 and F4, which creates a large adsorption pool for As, as shown in Table 3. In particular, in this study, on average 37.2 % of total soil As was associated with the  $\text{NH}_4^+$  – oxalate buffer + ascorbic acid extraction targeting well-crystallized hydrous oxides of Fe and Al (F4), exhibiting a range of 20.3–63.4%. However, using the same fractionation scheme as in this project, Smith reported that the majority of soil As was associated with amorphous, poorly crystalline hydrous oxides of Fe and Al (F3) in a range of 13 –83% of total soil As in eleven long-term contaminated soils with different pollution histories [10]. Similarly, on average 42.3% of total soil As was extracted by  $\text{NH}_4^+$ - oxalate (F3) in twenty soil samples from As-contaminated sites in Austria [2]. In this study, the proportion of As associated with amorphous Al/Fe oxides (F3) was smaller than the pool of As adsorbed onto crystalline Fe/Al oxides (F4). On average, 31% of total soil As was F3 extractable As. Nevertheless, the difference between F3 and F4 extractable As was not statistically significant ( $P > 0.05$ ) and this could be due to the small quantity of soil samples. The two fractions of specifically adsorbed and non-specifically adsorbed As, which are considered the most mobile As fractions in soil, account for approximately 7% of the  $\text{As}_t$ . This value is lower than the result of Taggart’s study on a highly As-contaminated soil, where those two As fractions constituted up to 23% of  $\text{As}_t$  [9]. The proportion of total soil As that remained readily available was markedly high: on average 24% of total soil As. The probable reasons for this phenomenon may be the re-adsorption of As onto soil minerals during the extraction procedure.

Table 3: Results of the sequential extraction procedure for As, Fe and Mn. (F1) non-specifically sorbed As; (F2) specifically sorbed As; (F3) amorphous and poorly crystalline oxides of Fe and Al; (F4) well crystallized oxides of Fe and Al; and (F5) residual As phases (0\*: below detection level)

Soil	mg/kg										
	As					Fe			Mn		
	F1	F2	F3	F4	F5	F3	F4	F5	F3	F4	F5
1	0*	0.486	1.969	1.957	1.371	5,221.46	6,590.60	4,327.93	11.67	12.57	18.58
2	0.042	0.623	2.229	1.494	2.742	4,718.54	4,467.10	3,913.46	8.15	6.70	11.85
3	0.005	0.709	2.87	2.87	1.222	7,224.40	7,221.79	3,585.55	19.79	14.08	17.31
4	0.005	0.743	2.385	1.173	1.465	5,299.81	6,405.00	2,926.01	29.24	21.51	16.60
5	0.002	1.016	2.92	12.993	3.559	6,675.75	5,215.20	2,958.99	55.55	19.58	23.10
6	0*	0.687	2.013	3.173	2.197	5,599.11	7,552.65	4,104.20	26.43	22.59	19.80
7	0*	0*	2.996	3.37	2.067	9,850.67	11,594.54	10,395.05	75.72	43.30	58.91
8	0*	0.249	2.043	2.99	1.728	5,718.92	10,324.68	10,021.41	36.95	34.49	45.58
Min	0.000	0.000	1.969	1.173	1.222	4,718.54	4,467.10	2,926.01	8.15	6.70	11.85
Max	0.042	1.016	2.996	12.993	3.559	9,850.67	11,594.54	10,395.05	75.72	43.30	58.91
Mean	0.007	0.564	2.428	3.753	2.044	6,288.58	7,421.45	5,279.07	32.94	21.85	26.47

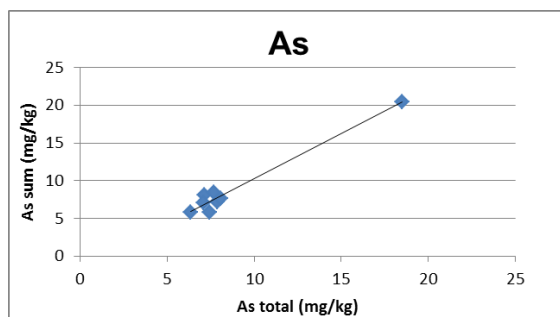


Fig. 2: Linear regression between  $\text{As}_{\text{sum}}$  and  $\text{As}_{\text{total}}$

The amount of As recovered from all five fractions matched (~ 78–113%) the total As extracted by acid digestion. The accuracy of the sequential extraction procedure was tested by comparing the sum of five As fractions ( $\text{As}_{\text{sum}}$ ) to  $\text{As}_t$ , which was measured independently in a single microwave digestion. The results of  $\text{As}_{\text{sum}}$  were linearly correlated ( $R^2 = 0.98$ ) with  $\text{As}_t$  ( $P < 0.0001$ ) for eight investigated soils. Fig. 2 clearly shows a significant linear relationship between  $\text{As}_{\text{sum}}$  and  $\text{As}_t$ . Three out of eight samples had > 100%

recovery. These recovery rates might be attributable to a cumulative error in each of the extraction measurements [11].

#### 4. Conclusion

The sequential extraction procedure is a relatively simple method to determine arsenic distribution in soil. Although the potentially mobile As fractions (F1+F2) were found to be quite low in this study, identifying contaminated areas in the Red River Delta and conducting risk assessment are still essential in order to prevent further As pollution in the agricultural soils in this region.

#### 5. Acknowledgement

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