SEQUENTIALLY EXTRACTED ARSENIC FROM DIFFERENT SIZE FRACTIONS OF CONTAMINATED SOILS

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Abstract. Five soils from Austria that have high contents of arsenic (As) due to anthropogenic and/or geogenic sources were separated into sand, silt, and clay fractions. The distribution of As among the particle-size fractions was clay >> silt > sand. The particle-size fractions were analysed according to an 8-step sequential extraction procedure (SEP) designed to assess the primary reservoirs and extractability of As. Steps 1 and 2, (i.e. NH_4NO_3 and $(NH_4)_2SO_4$) extracted the least As, while considerably greater amounts were extracted in steps 3, 4 and 5 (i.e. $NH_4H_2PO_4$, NH_2OH-HCl, and NH_4F). The greatest amounts of As were extracted in steps 6 and 7, both NH_4-oxalate extractants targeting the amorphous and crystalline oxide fractions. The residual fraction (step 8) was typically low. The extraction of the clays contained generally more As in steps 3 to 8, while As release in the first two steps was typically highest in the sand and silt fractions. These findings are in accord with factor analysis indicating that the extractants of the SEP are separated into weak (steps 1 and 2) and strong (steps 3 to 8) extractants. SEP data along with microprobe analyses (X-ray microanalyses) indicate that most As is associated with Fe and is therefore not readily mobile. Anyhow, As could be released upon changes in redox potential or pH. The greater extractability of As from sand fractions using weak extractants may explain the higher toxicity of As in coarse-textured soils, as found in previous studies.

Keywords: arsenic, sequential extraction, soil size fractions

1. Introduction

Arsenic has been long recognized to be a toxic element but recent greater awareness of its toxicity at very low concentrations has renewed our public welfare concern. Primary natural sources of this element in soils are parent materials containing arsenic sulphide minerals and input due to volcanic activity. Important anthropogenic sources are mining and smelter operations, coal burning, and arsenical pesticides. Natural versus anthropogenic sources of arsenic have been estimated at 60:40 (Buat-Menard *et al.*, 1987). The average content of arsenic in uncontaminated soil is 5–6 mg kg^{-1} (Adriano, 1986).

A series of studies have reported relations between mobility and total content of As in soil and soil texture. In soil, arsenic mobility and toxicity to plants are strongly influenced by Fe and Al oxides/hydroxides and clay minerals (Galba,

1972; Frost and Griffin, 1977; Holm *et al.*, 1979; Leckie *et al.*, 1980). Differential contents of oxides and clay minerals in different particle-size fractions suggest that the aresenic distribution also varies among soil texture fractions for a given soil (Wauchope, 1975). Because the chemical and physical characteristics of soils are strongly related to texture, the fate of arsenic could be affected by the particle-size distribution. Many soil properties are related to surface phenomena occurring at liquid–solid interface; the surface area of particle-size fractions increases in the order sand « silt « clay. A positive correlation between clay and arsenic content in the soil has been reported by various authors (Yang, 1983; Shen *et al.*, 1983). In contrast, in soils with a large content of sand, or enriched in silicon and aluminum, As concentrations are typically small (Koyama, 1975; Shen *et al.*, 1983). Therefore, in regions with soils derived from the same parent material, soil texture may be the dominant soil feature to affect the background levels of arsenic in soil (Huang, 1994). Jacobs and Keeny (1970) and Woolson *et al.* (1973) found that arsenic was less toxic in fine-textured soils.

To our knowledge, As distribution in sand, silt, and clay and its implication to As mobility has not been comprehensively investigated. The primary aim of this article is to assess the distribution and the major sink of arsenic among various particle size fractions (sand, silt, and clay) of the soil.

2. Materials

Representative bulk soil samples were collected from the B horizon of five Cambisols in Austria (Table I). These soils have been contaminated with arsenic from various geogenic and anthropogenic sources, with total As concentrations varying between 240 and 1900 mg kg^{-1} (Table I). The samples were air-dried and passed through a 2-mm sieve.

Particle size separation was performed according to Genrich and Bremner (1974). Size limits for the fractions were sand (2000–63 μm), silt (63–2 μm) and clay (<2 μm). One hundred gram of bulk soil samples were dispersed by ultrasonic vibration in water. The sand fraction was separated by wet sieving. Silt and clay fractions were isolated using a centrifuge technique. The separation procedure was repeated 5 times to minimize the amount of clay-size particles remaining in the silt fraction. All fractions were oven-dried at 40 °C. The effectiveness of the clay-silt separation was assessed using a Micrometrics Sedigraph 5000ET.

3. Methods

3.1. MINERALOGICAL AND CHEMICAL COMPOSITION

The mineralogical composition of sand and silt fractions was assessed by X-ray diffraction (Philips PW 1130). Clay mineralogy was determined using oriented

TABLE I

Soil characteristics and soil classification after FAO (1988)

Sample	Sample location and soil type	Horizon	pH (CaCl$_2$)	Total As (mg kg^{-1})	Note
951002	Mitterberg (Salzburg) Eutric Cambisol	Bw1	5.62	1520	Pasture/located near an abandoned smelter
951003	Mitterberg (Salsburg) Eutric Cambisol	Bw2	6.67	655	near abandoned smelter
960057	Lungau (Salsburg) Dystric Cambisol	Bw2	3.39	214	Forest/geogenic
960065	Brixlegg (Tirol) Dystric Cambisol	B1	3.98	581	Spruce forest/active smelter
960144	Kliening (Carinthia) Dystric Cambisol	Bw	4.20	335	Pasture, old mining deposit
960149	Lavantal (Carinthia) Calcaric Cambisol	Bw	7.30	1990	Grassland/geogenic

mounts prepared by aspirating a suspension of the clay-size fraction through a porous ceramic plate. Clay minerals were identified according to Riedmüller (1978), a semiquantitative estimate of their amount was made using the method of Johns *et al.* (1954).

Total carbon in each particle-size fraction was measured using a Carlo Erba CNS Analyzer NA 1500 Series 2. Organic carbon (OC) was measured using the same instrument after pre-treating the sample with 0.2 M HCl to remove carbonates; the carbonate content was calculated by difference.

Samples (500 mg) of each size fraction were digested HNO$_3$-H$_2$O$_2$ in a microwave (MLS Mega 2400). The digest was analyzed for total arsenic by atomic absorption spectrometry (AAS 2100 Perkin Elmer) equipped with a hydride generation system (FIAS 400, Perkin Elmer), and Al, Ca, Fe, Mn and Si were measured using inductive-coupled-plasma emission-spectrometry (ICP Plasmaquent 100, Zeiss).

3.2. SEQUENTIAL FRACTIONATION OF ARSENIC

A sequential extraction procedure was employed to chemically fractionate arsenic in each of the particle-size fractions (Table II). The extractant:soil ratio was 25 mL:1 g. Extracts from each step were analyzed for As, Al, Ca, Fe, K, Mg, Mn, Na, and Si as described above. Dissolved organic carbon (DOC) in the extracts from steps 2 to 5 was estimated by UV absorption at 254 nm (Brandstetter *et al.*, 1996).

TABLE II

Sequential soil extraction procedure utilised for arsenic fractionation

Step	Treatment	Fraction	Reference
1	NH_4NO_3 1 M – 24 hr shaking	Exchangeable	a
2	$(NH_4)_2SO_4$ 0.001 M – 24 hr shaking	Specifically sorbed I	b
3	$(NH_4)H_2PO_4$ 0.05 M – 24 hr shaking	Specifically sorbed II	b
4	NH_4F 0.5 M pH 7.0 – 1 hr shaking	Al – associated	c
5	NH_2OH-HCl 0.1 M + NH_4OAc 1 M – pH 6.0 30 min shaking 2 wash step: NH_4OAc 1 M – 10 min shaking	Mn – associated	a
6	NH_4-oxalate 0.2 M pH 3.25 – 4 hr shaking in the dark wash step: NH_4-oxalate 0.2 M – 10 min shaking	Amorphous Fe bound	a
7	NH_4-oxalate 0.2 M + Ascorbic ac. 0.1 M pH 3.25 – 30 min shaking in water bath at 96 °C wash step:NH_4-oxalate 0.2 M – 10 min shaking	Crystalline Fe bound	a
8	HNO_3 – H_2O_2 (microwave digestion)	Residual	

a: Zeien and Brümmer, 1989; b: mod. Saeki and Matsumoto, 1994; c: Chang and Jackson, 1957.

3.3. MICROPROBE ANALYSIS

An ARL SEMQ Electron Microprobe/Scanning Electron Microscope equipment with 6 wavelength dispersive X-ray spectrophotometers (WDS) and a modified Kevex/Oxford/ANS Quantum energy dispersive X-ray spectrophotometer system (EDS) was utilized for imaging and elementeal detection of the soil samples. The SEM/microprobe operating conditions were 25 kV accelerating voltage and 50 nA beam current. More detailed analyses were done by EDS and WDS detectors that were set to detect K-α and L-α X-rays of: As, Fe, Zn, Cu, Mg, and S. EDS spectra were analyzed with software from ANS Quantum (America Nuclear Systems, Knoxville, TN).

3.4. STATISTICAL ANALYSIS

Basic statistical parameters and multivariate methods (i.e factor analysis) were utilised to interpret the data from the sequential extraction procedure using Statistica® version 4.2 for Windows®. Factor analysis was performed to reduce the number of variables and to detect structure in relationships between variables. This method enables to display most of the original variability in a smaller number of dimensions.

TABLE III

Total carbon an arsenic in the soil-size fractions

Sample		Fraction (g kg^{-1} of fine earth)	Inorg. C (g kg^{-1})	Org. C (g kg^{-1})	Org. C (% of total in fine earth)	As (mg kg^{-1})	As (% of total in fine earth)
951002	sand	698.5	0.0	5.90	40.6	559	37.5
	silt	285.9	0.0	17.9	50.4	2002	55.0
	clay	15.6	0.0	58.5	9.0	4935	7.5
951003	sand	371.3	0.0	4.60	14.3	317	16.2
	silt	563.2	0.0	14.2	67.0	800	61.9
	clay	65.5	0.0	34.1	18.7	2431	21.9
960057	sand	5228.3	0.0	8.00	17.0	70	14.4
	silt	352.9	0.0	218	31.3	170	23.4
	clay	125.8	0.0	102	51.7	1288	62.5
960065	sand	179.5	0.0	46.7	35.3	814	23.2
	silt	760.6	0.0	16.0	51.3	495	59.9
	clay	59.9	0.0	56.4	13.4	1774	16.9
960144	sand	678.2	0.0	6.50	33.5	250	48.3
	silt	305.8	0.0	25.3	58.8	529	46.3
	clay	16.0	0.0	63.2	7.7	1196	5.4
960149	sand	449.5	43.9	12.2	23.7	818	19.2
	silt	430.9	6.9	31.4	58.6	2367	53.3
	clay	119.6	2.1	34.2	17.7	4400	27.5

4. Results and Discussion

4.1. PARTICLE-SIZE SEPARATION

Bulk soil samples contain considerable amounts of sand and silt (Table III). Particle size analysis using the Sedigraph indicated that the silt fraction still contained 3–5% clay-sized particles, probably largely released upon treatment of the samples with Calgon solution (0.05%) and ultrasonic vibration prior to analysis. Using a similar technique of separation, Stemmer *et al.* (1998) have found similar amounts of clay-sized particles in the silt fractions.

4.2. Mineralogical and chemical composition

Quartz and micaceous layer silicates dominate the mineralogy in the majority of the soil. The amount of quartz decreases from the sand to the silt fraction, whereas the content of layer soilicates increases. Two soil samples are quite distinct from the others: sample 960065 contains > 70% feldspar and the sand fraction of sample 960149 presents considerable amounts of calcite (66%) and dolomite (12%). The most common clay mineral us illite, but vermiculite, kaolinite, and chlorite are present in some samples. The presence of illite and vermiculite, likely derived from mica, is in accord with the large content of this mineral in several soils.

Carbon is present only in organic form except sample 960149 that contains considerable amount of carbonates (Table III); this is consistent with expactation based on pH data (Table I).

The amounts of OC and total arsenic (Table III) increase considerably in the order sand < silt < clay, except sample 960065, in which the smallest amount of OC is present in the silt fraction. The high amounts of clay minerals and oxides in the clay fraction may explain the accumulation of As and OC in the clay fraction. In fact, oxide surface and the edges of clay minerals are positively charged at pH below, 7 thus attracting anions such as arsenate and arsenite (Sadiq, 1997) and interacting with organic matter (Harter and Naidu, 1995).

4.3. Sequential fractionation of arsenic

The amounts of arsenic extracted during the various steps of the sequential fractionation are shown in Table IV. Ammonium nitrate (step 1) and sulfate (step 2) extracted the least As. These extractants are expected to remove oxyanions from weak adsorption sites (Saeki and Mazumoto, 1994); these fractions are important since they are considered to be the most available to biota and most easily leached to groundwater (Brandstetter et $al.$, 1999). The sand and silt fractions released typically equal or larger amounts of arsenic than the clay-sized fraction in the first two steps of extraction, but the clay released more As from all the remaining steps (Table IV). This is consistent with the first two steps being less effective to extract As from oxides, which, based on the NH_4-oxalate extractions, were found to be present in larger amounts in the clay-size fraction (Table V). The high capacity of clay-sized particles for As may explain the positive correlation between clay and As content (Yang, 1983; Shen et $al.$, 1983) and adsorption (Livesey and Huang, 1981) as found in other studies.

Ammonium phosphate (step 3) extracted considerably more As than in steps 1 to 2. Phosphate competes with As for specific adsorption sites and is more effective than nitrate and sulfate to extract arsenate from soils (Galba and Polacek, 1973).

Step 4 (NH_4F) extracted less As than released in step 3, but more than the first two steps. The considerable release of Al and Si but slight dissolution of Fe and Mn (Table V), together suggest an association of NH_4F-extractable As with poorly-ordered aluminosilicate gels and allophane (Becket, 1989). The small amount of

TABLE IV

Arsenic extracted with the sequential extraction in a given size fraction (data in μg As g^{-1} soil)

Sample/extractant		NH$_4$NO$_3$[a]	(NH$_4$)$_2$SO$_4$[a]	NH$_4$H$_2$PO$_4$	NH$_4$F	NH$_2$OH-HCl + NH$_4$OAc	NH$_4$-oxalate	NH$_4$-oxalate + ascorbic acid	Residual
951002	Sand	0.84	7.29	69.6	15.1	12.8	484	128	3.34
	Silt	1.37	6.47	152	38.7	26.9	1370	396	7.00
	Clay	1.60	5.33	439	86.3	82.8	3410	969	135
951003	Sand	4.55	2.77	51.5	14.8	4.92	146	120	2.47
	Silt	1.27	3.58	152	35.3	9.31	420	289	8.87
	Clay	1.12	2.72	472	67.8	27.6	1020	773	61.8
950057	Sand	<d.l.	0.26	5.72	2.75	1.46	65.0	16.8	0.56
	Silt	<d.l.	<d.l.	10.2	10.4	3.79	122	46.7	1.88
	Clay	<d.l.	<d.l.	98.8	73.8	14.8	807	491	287
960144	Sand	<d.l.	0.13	6.30	1.24	0.99	68.4	282	3.28
	Silt	<d.l.	<d.l.	14.8	3.51	2.47	151	417	6.30
	Clay	0.13	0.13	35.3	12.8	5.85	337	681	35.3
960149	Sand	4.39	3.90	51.8	11.7	4.70	399	392	19.7
	Silt	4.88	7.00	202	73.4	33.8	1030	1370	136
	Clay	3.26	7.81	430	112	47	1540	1830	239
960065	Sand	1.60	4.79	233	96.1	30.4	368	133	7.25
	Silt	2.08	3.72	107	29.3	13.1	195	97.5	9.45
	Clay	1.39	1.40	471	175	50.8	1120	701	21.31

[a] <d.l. = < detection limit of 0.5 μg As L^{-1}.

TABLE V

Other elements extracted by the sequential extraction for each size fractions of soil 960144 (data in μg g^{-1} of soil)

Step	Sample	Al	Ca	Fe	Mn	Si
1. NH$_4$NO$_3$	Sand	35.2	268	0.6	17.3	0.7
	Silt	86.0	905	0.5	81.2	4.0
	Clay	102	2161	1.2	243	21.7
2. (NH$_4$)$_2$SO$_4$	Sand	0.8	17.3	0.6	1.9	n.d.
	Silt	2.0	33.7	1.0	5.7	n.d.
	Clay	8.8	125.7	3.7	24.3	10.0
3. (NH$_4$)H$_2$PO$_4$	Sand	20.2	15.7	13.9	3.3	6.5
	Silt	22.7	26.7	12.5	4.4	10.4
	Clay	149	28.6	112	12.2	108
4. NH$_4$F	Sand	266	0.5	32.3	0.5	86.4
	Silt	1078	1.8	50.3	1.1	112
	Clay	4568	2.5	164	5.5	269
5. NH$_2$)OH-HCl + NH$_2$OAc	Sand	57.8	21.3	30.0	1.55	n.d.
	Silt	228	73.2	46.5	510	n.d.
	Clay	925	144	51.3	1431	8.7
6. NH$_4$-oxalate	Sand	230	34.9	1345	50.8	n.d.
	Silt	852	53.2	5039	222	64.6
	Clay	2817	57.3	15444	973	570
7. Ascorbic ac. + NH$_4$-oxalate	Sand	2029	38.2	10934	26.1	682
	Silt	5787	56.5	23332	58.5	1704
	Clay	10228	53.2	34145	101	1815
8. HNO$_3$–H$_2$O$_2$	Sand	23751	904	21973	153	88.3
	Silt	52420	880	28271	163	174.5
	Clay	50559	98.9	14897	61.1	85.5

As in this fraction may explain the findings that soils enriched in Si and Al are typically low in As (Koyama, 1975; Shen *et al.*, 1983).

Step 5 (NH$_2$OH-HCl) extracted As in similar amount as step 4. NH$_2$OH-HCl is considered to be quite selective for easily reducible Mn oxides in soil (Chao, 1972; Karczewska *et al.*, 1994). This is supported by the fact that most Mn was

TABLE VI

Correlation coefficients between soil arsenic extracted with the sequential extraction and total arsenic (level of significance in parenthesis)

	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8
Total As	0.26	0.4	0.80	0.61	0.89	0.92	0.84	0.64
	(0.909)	(0.063)	(<0.01)	(0.012)	(<0.001)	(<0.001)	(<0.001)	(0.003)

typically released in this step (Table V), and by a mean molar Al:Mn ratio 42:1 in step 5 compared to 336.1 in step 4. Even though only small amounts of As are extracted by NH_2OH-HCl suggesting that Mn oxides are not a major sink of As in these soils, Mn oxides may catalyse redox transformations of As in soils, e.g. the oxidation of As(III) to As(V) (Oscarson *et al.*, 1983).

Most arsenic was extracted in steps 6 and 7, employed to dissolve amorphous and crystalline Fe-oxides, respectively. NH_4-oxalate used in steps 6 and 7 is effective in extracting Fe (Table V). The primary sources of Fe extracted by NH_4-oxalate are considered to derive from Fe oxides (Schwertmann, 1964). A strong association of arsenic with Fe oxides is also suggested by correlations found between NH_4-exalate-extractable Fe and the sorption parameters of Freundlich isotherms for As in 11 soils from the U.S.A. (Selim *et al.*, 1990); similarly, Langmuir adsorption maxima of As in several Canadian soils were correlated to NH_4-extractable Fe and Al (Livesey and Huang, 1991).

The distribution of DOC among the fractions of the SEP shows that $(NH_4)H_2PO_4$ and, especially, NH_4F extract considerable amounts of DOC. Smaller amounts of DOC extracted in steps 1, 2, and 5 suggest that only a minor fraction of As may be bound to soil organic matter. In spite of the study by Thanabalasingam and Pickering (1986) showing humic acids binding relatively large amounts of As (V) and As (III), there is no evidence in the literature that soil organic matter (SOM) may be a significant sink for As. This may be due to the strong competition of Fe oxides for As in soils; moreover, unlike metal cations, arsenate and arsenate anions can hardly accumulate at the predominantly negatively-charged surfaces of SOM.

Arsenic extracted in steps 1 and 2 is not correlated to total As in any of the size fractions, but is significantly correlated with steps 3–8 (Table VI).

Fractional analysis performed using the sequential fraction data of arsenic reveal that 2 principal factors explain 74% of the total variance (Table VII). In Factor 1, the variables with major loading (correlation between the original variable and the Factor) are steps 3 to 7 of the sequential extraction, whereas steps 1 and 2 have the major loading in Factor 2. Factor 1 could be related to strong extractans, and Factor 2 to weak extractants. Plotting the factor scores (values of individual observations for the Factor) against the different soil-size fractions, indicates op-

TABLE VII

Eigenvalues and factor loading from the factor analysis of arsenic data from the sequential
extraction

Eigenvalues – Extraction: Principal components

Value	Eigenvalue	% Total variance	Cumul. eigenvalue	Cumulative %
1	4.674751	58.43439	4.674751	58.43439
2	1.267205	15.84006	5.941956	74.27445

Factor loadings (Varimax normalized) – Extraction: Principal components

Variable	Factor 1	Factor 2
Step 1	0.037798	0.918258[a]
Step 2	0.326035	0.805224[a]
Step 3	0.901131[a]	0.144135
Step 4	0.855244[a]	0.073979
Step 5	0.922405[a]	0.197970
Step 6	0.854195[a]	0.182810
Step 7	0.727629[a]	0.404022
Step 8	0.638916	0.137731
Expl. variance	4.169311	1.772646
Prp. total	0.521164	0.221580

[a] Marked correlations are bigger than 0.7.

posite trends (Figure 1). This agrees with the finding that extractant 1 and 2 are
more effective on sand and silt whereas. As in the other extractants is primarily
associated with silt and clay.

4.4. MICROPROBE ANALYSIS

Microprobe analysis performed on the soil-size fractions were consistent with the
results obtained with the SEP: Fe oxides represent the major sink for As in all soil
fractions investigated. There was no evidence for As being associated with primary
minerals with the exception of arsenosiderite being found in one sample (960149)
from Carinthia; this area of Austria is well-known for its arsenosiderite deposits
(Dana, 1951).

SEM micrographs show marked differences between silt and clay-size fractions
(Figure 2). In silt the only detectable As was associated with Fe, apperently in
secondary minerals including oxide deposits and weathering rinds. This supports
the interpretation that As extractable by NH_4-oxlate is mainly associated with Fe
oxides.

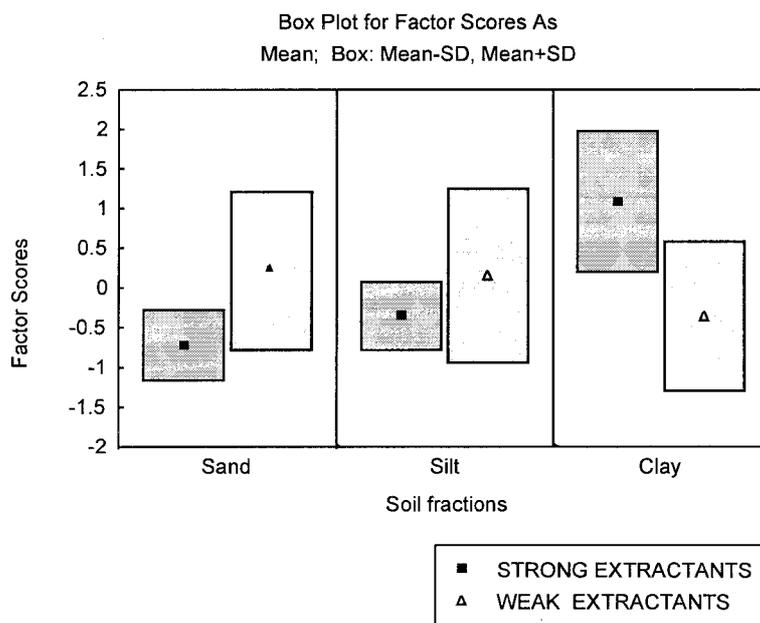Box Plot for Factor Scores As
Mean; Box: Mean-SD, Mean+SD

Figure 1. Plots of factor scores versus soil fractions from factorial analysis of SEP data.

SEM micrographs of the clay-size fraction indicate that this fraction is very homogeneous (Figure 2). This fraction, as noted above, contained the greatest amount of As and this was apparent in the EDS analyses that showed As diffusely disseminated throughout the clay-size material.

5. Conclusion

The distribution of total arsenic among various particle size fractions of the soil was: clay » silt > sand. This pattern of distribution is consistent with a higher sorption capacity of fine-textured fractions due to greater surface area and larger content of Fe oxides.

Arsenic is most abundant in the two acid NH_4-oxalate steps (step 6 and 7) of the SEP employed to estimate arsenic fractions of varying extractability. This finding, along with evidence from SEM/EDS analysis, indicates that most of the arsenic is associated with iron oxides in all the soils including the calcareous one.

Arsenic is typically less extractable by ammonium salts of nitrate, sulfate, phosphate and fluoride, and hydroxylaminechloride employed before the ammonium oxalate steps. These fractions may represent ecologically important forms of arsenic that can be mobilized more easily than arsenic associated with iron oxides (Brandstetter *et al.*, 1999). Ammonium nitrate and sulfate are more effective at extracting arsenic from sand and silt than from clay-sized fraction. According to
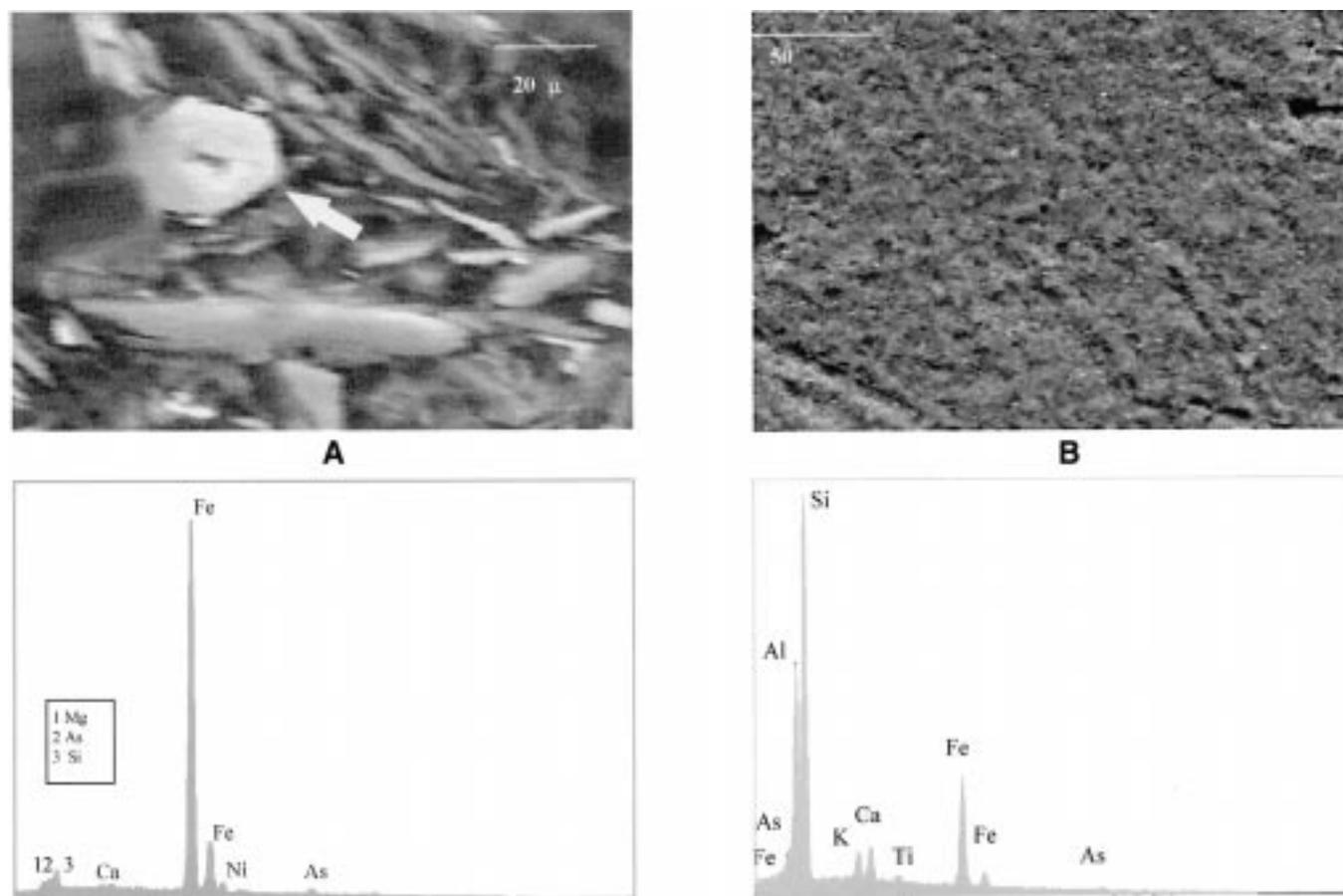
Figure 2. SEM micrographs and microprobe analyses (performed using energy dispersive X-ray spectrophotometer) of an iron oxide in sample 951003 silt (A) and clay fraction of sample 960149 (B).

the factorial analysis these fractions represents the most labile pools of soil arsenic. Unlike these labile pools, As that is bound more strongly (SEP steps 3–8) is significantly correlated with total As contents. These SEP steps are more effective for clay fraction, and share high loading in the same Factor of the factorial analysis.

Our results indicate that soil textural characteristics may be useful indicators of arsenic availability and mobility in soil. In agreement with other (Koyama, 197; Shen *et al.*, 1983; Yang, 1983) our results indicate that coarse textured soils low in Fe oxides are likely to yield the higher amounts of readily As. In fine-textured soils As is typically immobilised by Fe oxides that are homogeneously disseminated in the clay fraction; in silt, less homogeneous distribution of Fe oxide coatings on other soil minerals can locally cause extremely high concentrations of As associated with Fe oxides, indicating their enormous capacity to bind As.

These findings may explain the lower toxicity of As found in fine-textured soils (compare Jacobs and Keeney, 1970; Woolson *et al.*, 1973).

Acknowledgements

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