



ELSEVIER

The Science of the Total Environment 291 (2002) 123–134

**the Science of the
Total Environment**

An International Journal for Scientific Research
into the Environment and its Relationship with Man

www.elsevier.com/locate/scitotenv

Assessment of arsenic mobility in the soils of some golf courses in South Florida

Yong Cai^{a,b,*}, Julio C. Cabrera^a, Myron Georgiadis^a, Krish Jayachandran^{b,c}

^aDepartment of Chemistry, Florida International University, University Park, Miami, FL 33199, USA

^bSoutheast Environmental Research Center, Florida International University, University Park, Miami, FL 33199, USA

^cDepartment of Environmental Studies, Florida International University, University Park, Miami, FL 33199, USA

Received 12 June 2001; accepted 5 October 2001

Abstract

High concentrations of arsenic have been detected in soils and underlying groundwater of some South Florida golf courses, indicating the possible impact of the application of arsenic-containing herbicides. The mobility of arsenic in the soils from selected golf courses was studied using a simple two-step sequential extraction procedure. Sodium nitrate (0.1 M), potassium dihydrogen phosphate (0.1 M) and concentrated nitric acid were used to obtain mobile, mobilizable, and pseudo total arsenic fractions. Soils were separated into fine (<0.25 mm) and large (0.25–0.75 mm) particle size fractions. Arsenic contents were correlated with the distribution of iron ($R^2=0.4827$), manganese ($R^2=0.7674$) and aluminum ($R^2=0.5459$) in the particle size fractions, while such correlation was not observed for soil organic matter, indicating that the oxides/hydroxides of iron, manganese and aluminum control the distribution of arsenic in these soils. Sodium nitrate and potassium dihydrogen phosphate extractants used in this study extracted large portions of arsenic from most soil samples studied. This is especially true for the fine fraction where the extractable arsenic ranged from 9.2 to 51.3% with an average of $28.7 \pm 13.3\%$, whereas in the large fraction, arsenic ranged from 7.2 to 24.7% with an average of $15.4 \pm 6.4\%$. These extractants, however, release only small amounts of iron, manganese, and aluminum. It seems likely that arsenic can be released by sodium nitrate and potassium dihydrogen phosphate without significant dissolution of the oxides/hydroxides of iron, manganese, and aluminum in these soil samples. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Arsenic mobility; Sequential extraction; Golf courses; Soil

1. Introduction

Arsenic is an element of great concern in the terrestrial as well as aquatic environments because of the high toxicity of certain species. Recent research suggests that arsenic in drinking water

may be more dangerous than previously believed (Kim and Nriagu, 2000). The US Environmental Protection Agency (USEPA) and other agencies are currently reevaluating the current maximum contamination level (MCL) ($50 \mu\text{g}/\text{l}$) based on the health risk associated with arsenic in drinking water. The increased concern about arsenic risk to human health is the driving force behind the study of arsenic biogeochemical cycling in the environ-

*Corresponding author. Tel.: +1-305-348-6210; fax: +1-305-348-3772.

E-mail address: cai@fiu.edu (Y. Cai).

ment (Frey and Edwards, 1997; Kim and Nriagu, 2000).

The natural occurrence of arsenic in the aquatic environment is usually associated with sedimentary rocks of marine origin, weathered volcanic rocks, geothermal areas, and fossil fuels. Most of the arsenic derived from anthropogenic sources is released as a by-product of mining, metal refining processes, the burning of fossil fuels, and agricultural use (Cullen and Reimer, 1989; Nriagu, 1994). Industrial, commercial, and agricultural activities involving use of arsenic compounds have produced numerous sites in Florida with elevated arsenic concentration in soils (Tonner-Navarro et al., 1998). The impact of arsenic-containing herbicides, used for turf maintenance, on soil and groundwater beneath golf courses has become a topic of interest in Florida (Wiegand, 1999). Currently, twenty-five brands of herbicides containing the active ingredient monosodium methanearsonate (MSMA) are marketed for weed control on golf courses in Florida. Although actual application rates are not known, the labeled rate for liquid MSMA is approximately 1.2–2.3 l/ha. Following application, much of the MSMA not intercepted by foliage are deposited directly in the soil where a variety of chemical processes occurring in the heterogeneous environment produce several arsenic species (e.g. methylated to trimethylarsine, decomposed to inorganic arsenic compounds) (Tonner-Navarro et al., 1998; Tu et al., 2001). Recently, the Dade County Department of Environmental Resources Management (DERM) and the Florida Department of Agriculture and Consumer Services (FDACS) conducted a collaborative study of the ground and surface water quality at five Miami-Dade County municipal golf courses (Wiegand, 1999). The results of this study revealed that arsenic is present in groundwater samples at concentrations of potential concern. Groundwater contamination by arsenic is widespread under the five golf courses studied and appears to be related to arsenic detected in the unsaturated soils near the wells. The residential and industrial soil cleanup goals (SCG) set by the Florida Department of Environmental Protection are 0.8 and 3.7 $\mu\text{g/g}$, respectively. The highest

concentration of arsenic found in groundwater was 815 $\mu\text{g/l}$. The concentration of 120.7 $\mu\text{g/g}$ of arsenic was found in the surrounding surface soil, and exceeds both the MCL and SCGs, respectively. Groundwater is a vital resource that is used for drinking water, irrigation, and livestock production; thus the mobility, fate, transport, and the environmental factors that govern this transport are all issues that deserve close examination.

In most countries, the current standards for metal pollution evaluation in soils are based on the total metal concentrations obtained using strong acid digestion such as nitric acid or aqua regia (Gupta et al., 1996). It has been observed, however, that the mobility of a metal in soils and its toxicity to the biosphere are related to its association with various soil constituents rather than to its total concentration. Risk assessments based on the measurements of pseudo total metal content fail to take into consideration the mobility and bioavailability of metals in different forms. One of the approaches to the study of the solid-phase association of elements that has been extensively applied to metals is the sequential partial dissolution technique proposed by Tessier et al. (1979). This analytical procedure involves sequential chemical extractions separating trace metals into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. Although this technique provides some detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization and transport of trace metals in the environment, some criticisms have been expressed about the lack of selectivity of the extractants and trace element redistributions among phases during extraction (Chao and Sanzalone, 1989; Nirel and Morel, 1990; Shan and Chen, 1993). Considering the complexity of real environmental samples and the complicated multi-extraction steps employed, diverse results and interpretations regarding the usefulness of sequential extraction are not unreasonable. In order to simplify the sequential extraction method and make it easy to use for practical application, various sequential extraction procedures have been developed (Chao and Sanzalone, 1989; Aten and

Gupta, 1996; Gupta et al., 1996; Pansar-Kallio and Manninen, 1997; Gomez Ariza et al., 2000). Among those techniques reported, the three-level evaluation system, which separates metals into mobile, mobilizable, and pseudo total metal fractions, seems to be attractive because of its simplicity and potential application in risk assessment and risk management (Gupta et al., 1996). Neutral unbuffered salt solutions, such as NaNO_3 , CaCl_2 and NH_4NO_3 has been proposed as the extracting media for the mobile fraction, whereas complexing agent solution or buffered and unbuffered complexing and chelating reagents like EDTA, DTPA + CaCl_2 , and acetic acid have been recommended for the mobilizable fraction. Commonly used extracting media for the pseudo-total fraction were reported to be strong acid solutions, such as aqua regia, concentrated HNO_3 or HCl . The evaluation of actual risk could mainly be carried out through mobile and mobilizable metal fractions, whereas the pseudo total metal content plays an important role in evaluating potential risk (Gupta et al., 1996). In this study, an attempt has been made to develop a simple extraction scheme that can be used for risk assessment and management of arsenic-contaminated soils. Golf courses in South Florida were chosen as the model environment since arsenic application is controlled and therefore can be closely monitored. Only total arsenic was measured, the amounts of different arsenic species that may present in the soils were not taken into account. The aim of this study was not to identify specific compounds or particles to which arsenic binds, or in which form it exists in the soil, but rather to provide an extraction scheme for monitoring the 'operationally defined' association of arsenic in golf course soils. The results of this study will help understand and predict the extent of mobility and immobilization of arsenic in response to dynamic changes in the environment, which in turn will provide useful information for an appropriate arsenic risk management program. Since the grain size of the soil has been reported to be one of the most important factors in controlling the distribution and transport of metals, its effects on the arsenic mobility assessment process proposed was also evaluated.

2. Materials and methods

2.1. Soil physico-chemical properties and elemental analysis

Fourteen surface soil samples were obtained from DERM, Miami, FL. These samples were collected from five golf courses in Miami-Dade County and analyzed for physico-chemical properties and arsenic content. The samples were freeze-dried and separated into two size fractions. The fraction between 20 and 60 mesh (0.25–0.71 mm) containing coarse and medium sand, and the fraction that passed through 60 mesh (<0.25 mm) containing fine sand, coarse silt and clay.

Soil physical and chemical properties were measured using standard operating procedures. Soil pH was measured in 1:2 soil to deionized water ratio (McLean, 1982). Particle size distribution was determined by Hydrometer method (Thien and Graveel, 1997). Soil total carbon and total nitrogen were estimated by using Carlo-Erba CN analyzer and the total phosphorus was determined by dry ashing followed by ascorbic acid method (Olson and Sommers, 1982).

For pseudo total metal content analysis, soil samples (0.2 g dry wt. basis) were placed in microwave digestion vessels. After adding 10 ml concentrated HNO_3 , the vessels were sealed and the samples were digested for 15 min following a standard operating procedure (SOP, 2000), which was developed based on the EPA method 3051. After digestion, the samples were quantitatively transferred to 100-ml volumetric flasks and diluted to the mark with DDI water. After the particulates settled, 5 ml of the clear solution was placed in a 10-ml plastic test tube and diluted to 10 ml with water. Fifty microliters of internal standards (Y, Sc, and In, 10 ppm) were added, thoroughly mixed, and the samples were ready for ICP/MS analysis.

2.2. Sequential extraction

The mobile and mobilizable fractions were estimated by using 0.1 M NaNO_3 and 0.1 M KH_2PO_4 , respectively. The detailed procedures for

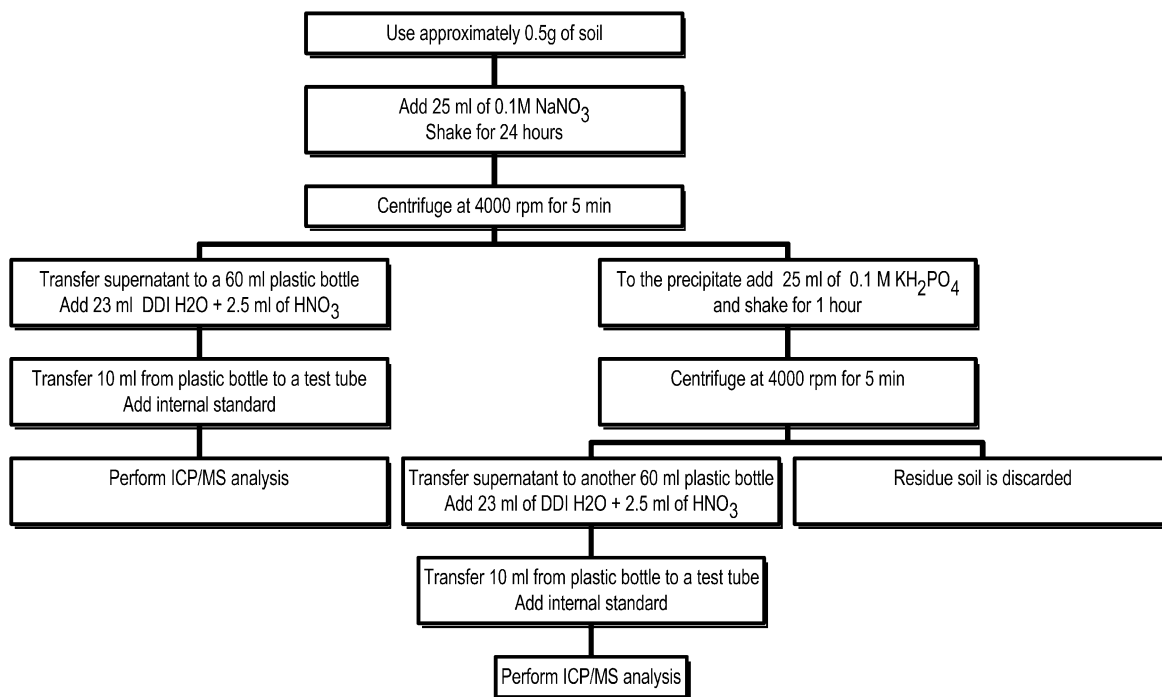


Fig. 1. Sequential extraction procedure with 0.1 M NaNO_3 and 0.1 M KH_2PO_4 for arsenic separation from soil samples.

the sequential extraction are illustrated in Fig. 1. Pseudo total arsenic concentration was obtained using concentrated nitric acid digestion.

2.3. Chemicals and apparatus

Arsenic, iron, manganese, aluminum standards, individual stock solutions of internal standards (ICP grade, 1000 ppm) were purchased from GFS Chemicals, Inc. Powell, OH, USA. Fresh calibration standards were prepared every week, or as needed, by diluting these analytical standards in 5% nitric acid. Trace metal grade hydrochloric acid and nitric acid were obtained from Fisher Scientific, Pittsburgh, PA, USA. All other chemicals used were of analytical grade or better. Standard reference material (SRM) 2704 (soil) was obtained from National Institute of Standard & Technology (NIST), Gaithersburg, MD, USA. The certified arsenic concentration in this SRM is 23.4 $\mu\text{g/g}$ dry wt. basis.

The ICP-MS instrument used for arsenic and other metal analysis was Model HP 4500 *plus* (Hewlett-Packard Co., Wilmington, DE, USA) equipped with a Babington-type nebulizer and an ASX-500 autosampler (Cetac Technologies Inc., Omaha, NE, USA). Instrument configuration and general experimental conditions were reported previously (Cai et al., 2000). Determination of iron was carried out using Perkin-Elmer 5100PC atomic absorption spectrophotometer. Acid digestion of the soils for pseudo total metal content was performed with a CEM Mars 5 microwave digestion system.

3. Results and discussion

3.1. Selection of the extractants

The metal concentration in neutral unbuffered salt extracts is a fair approximation of the concentration in the mobile fraction, which represents

Table 1
Soil characteristics

Sample I.D.	% Sand		% Silt		% Clay		pH		TN ^a (%)		TC ^a (%)		TP ^a (μg/g)		Ash/sed ratio ^d	
	Fine ^b	Large ^b	Fine	Large	Fine	Large	Fine	Large	Fine	Large	Fine	Large	Fine	Large	Fine	Large
A	74	83	17	8	9	10	7.25	7.21	0.37	0.54	8.56	11.56	428	783	0.87	0.89
B	53	89	45	9	3	2	7.37	7.27	0.80	– ^c	11.08	1.96	2721	530	0.77	0.94
C	65	97	34	1	2	1	7.23	7.71	0.41	–	6.55	3.35	2597	383	0.83	0.92
D	75	99	24	0	2	1	7.67	7.15	0.05	–	3.55	2.83	857	148	0.89	0.94
E	5	55	86	42	9	3	7.56	7.55	0.61	0.49	13.36	12.02	1803	1714	0.75	0.73
F	13	15	78	79	9	6	7.60	7.55	0.17	0.17	13.14	13.06	592	535	0.76	0.67
G	90	99	9	0	1	1	7.26	7.44	–	–	1.33	0.17	266	96	0.99	0.99
H	70	98	29	1	1	1	7.88	8.24	–	–	1.95	0.76	550	106	0.88	0.97
I	58	90	41	7	2	3	7.84	7.80	0.28	–	5.31	3.79	3878	1037	0.88	0.88
J	62	94	36	4	1	1	7.45	7.90	0.04	–	5.39	2.00	2516	760	0.90	0.95
K	63	68	27	23	10	9	7.83	7.83	0.47	0.44	12.64	11.87	644	646	0.64	0.70
L	55	61	41	36	4	3	7.40	7.35	0.60	0.49	14.45	13.39	2633	2990	0.73	0.75
M	69	95	26	5	5	0	7.80	8.15	–	–	2.13	0.66	648	117	0.97	0.99
N	30	50	67	47	3	3	7.63	8.86	0.57	0.62	15.60	16.40	837	838	0.73	0.67

^a Abbreviations: TN: total nitrogen; TC: total carbon; TP: total phosphorus.

^b Fine particle: <0.25 mm; large particle: 0.25–0.71 mm.

^c No data available.

^d The higher the ratio, the lower the content of organic matter.

equilibrium soil solution and mobile fraction of arsenic in soil systems (Gupta et al., 1996). Both nitrate and chloride salts have been proposed as the extractants for this purpose (Chao and Sanzalone, 1989; Gupta et al., 1996). Sodium nitrate solution (0.1 M NaNO₃) was chosen for this study since chloride interferes with the determination of arsenic using ICP/MS (Cai et al., 2000). NaNO₃ extracts bring water-soluble arsenic into solution. Non-specifically adsorbed soil arsenic can be replaced by the nitrate ion through anion exchange and mass action. Potassium dihydrogen phosphate (0.1 M KH₂PO₄) was selected as the extractant for mobilizable fraction. Because arsenate and phosphate are chemically similar, KH₂PO₄ should be an effective extractant to replace arsenate specifically adsorbed on the soils.

3.2. Soil characteristics and total element contents

Soil samples were first sieved through a 0.71-mm sieve (sieve No. 25). The sieved samples were further divided into two fractions, which, for the purpose of discussion, are defined here as fine

particle (<0.25 mm) and large particle (0.25–0.71 mm). The fine particle fraction is composed of clay, silt, and fine sand, whereas the large particle fraction contains mainly the medium sand (Gee and Bauder, 1986). These size fractions allow us to evaluate the role played by different sized particles on the mobility of arsenic in soils.

The results for soil physico-chemical characteristics are summarized in Table 1. The soil samples were about neutral pH, except for a few fractions that are alkaline in nature. Sand is the major soil component in both fine and large particle fractions (except for the samples E, F, and M which contained a large amount of silt). This is especially true for the large particle fraction. The clay content represents <10% of the bulk sample weight, indicating the soils were sandy loam in texture. Organic matter content was estimated by the ash/sediment ratio, where the higher ratio means lower organic matter content. Considerable amounts of organic matter were present in both fractions (ranged from 1 to 36%). Percentage of the organic matter content varied significantly between soils, however, fine and large fractions within each soil

Table 2
Concentrations of As, Fe, Mn, and Al ($\mu\text{g/g}$) in two soil fractions using HNO extraction

Sample I.D.	As		Fe		Mn		Al	
	Fine ^a	Large ^a	Fine	Large	Fine	Large	Fine	Large
A	3.88	11.04	3573	6229	22.53	81.12	5054.4	15692.3
B	10.65	6.30	3838	1221	52.66	29.59	1385.8	1089.8
C	9.00	11.37	4168	3272	92.57	175.58	591.1	481.1
D	9.63	6.57	2412	2053	81.39	25.25	323.6	217.3
E	20.88	52.19	3210	4328	61.59	149.21	2018.7	5589.0
F	6.53	15.99	4083	4285	38.61	88.52	1601.9	5233.9
G	1.96	0	2534	688	197.54	64.57	419.9	427.5
H	6.50	6.41	2134	988	43.91	95.96	558.9	817.3
I	17.90	19.52	4511	2043	140.50	125.91	1078.3	1661.8
J	19.82	17.69	4151	1506	122.20	155.01	1326.0	1322.4
K	9.67	8.62	3912	4155	18.38	14.67	3050.2	2737.0
L	39.38	33.95	7662	3009	180.41	136.60	1778.0	1391.5
M	19.54	2.98	3001	1626	550.36	91.57	1996.6	592.3
N	16.93	17.11	3838	3660	32.85	25.26	2915.8	3201.3

^a Fine particle: <0.25 mm; large particle: 0.25–0.71 mm.

sample showed similar content. The concentrations of total phosphorus varied clearly between samples, indicating possible effects from the application of phosphorus-containing fertilizers. In addition to the fertilizer application to the golf courses, it is clear that the soils are heterogeneous in nature and spatial variability is common.

Concentrations of As, Fe, Mn, and Al in both fine and large particle fractions are presented in Table 2. Arsenic concentrations ranged from 1.96 to 39.4 $\mu\text{g/g}$ for fine fraction and from below detection limit to 52.2 $\mu\text{g/g}$ for large fraction. A large difference in concentrations of arsenic in these fourteen soil samples was expected because the samples were collected from varied types of locations. Some of the samples may be heavily affected by the application of arsenic-containing herbicides (i.e. Mix/load areas), whereas others may not (Wiegand, 1999). Therefore, direct correlation of arsenic concentration and the content of other elements in these samples is not appropriate. However, the effect of mineral elements (Fe, Mn, and Al) on the distribution of arsenic can be reasonably evaluated by plotting the ratio of arsenic present in the fine fraction vs. the ratio of Fe, Mn, and Al in the same fraction (Figs. 2–4). It is clear that the percent of arsenic present in

the fine fraction is well correlated with that of Fe ($R^2=0.483$), Mn ($R^2=0.767$), and Al ($R^2=0.546$). It has been frequently reported that arsenic is strongly adsorbed by soil clay (Huang, 1994; Bhumbra and Keefer, 1994). Clay minerals and their composition are among the most fundamental factors affecting the mobility and bioavailability of arsenic in soils. Hydrous manganese and iron and aluminum oxides have been considered to be the principal solid phase components controlling the adsorption of arsenic in soils. It seems likely that the presence of the oxides of Fe, Mn, and Al in these soils will govern the mobility of arsenic in these soils. The lack of a good correlation between organic matter and arsenic distribution suggests that soil organic matter may not be playing a significant role in controlling arsenic mobility. Unlike metal cations, arsenate and arsenite existing as anions or neutral species under environmental conditions can hardly accumulate at the predominately negatively-charged surface of soils organic matter (Lombi et al., 2000). The chemical composition differs between different grain size groups of soil; thereby the complexing capability of metals may rely on the grain size. In many cases, fractionation of the particles accounts for increasing metal with decreasing grain size,

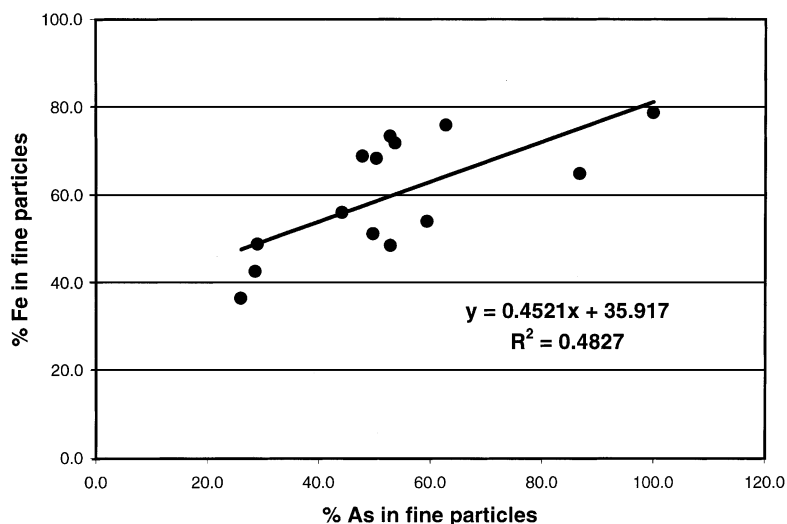


Fig. 2. Plot of percent concentration of arsenic in fine particles vs. the percent concentration of Fe in the same fraction.

because their strong association with fine grained clay minerals. Such relationship, however, was not observed in this study. This could be attributed to the fact that the soil samples collected for this study were mainly composed of sand, with very small percentage of clay in both fine and large fractions (Table 1).

3.3. Sequential extraction

Time required to reach the extraction equilibrium was first tested for both mobile (0.1 M NaNO_3) and mobilizable (0.1 M KH_2PO_4) fractions (Fig. 5). For 0.1 M NaNO_3 extraction, arsenic concentration in solution increased rapidly

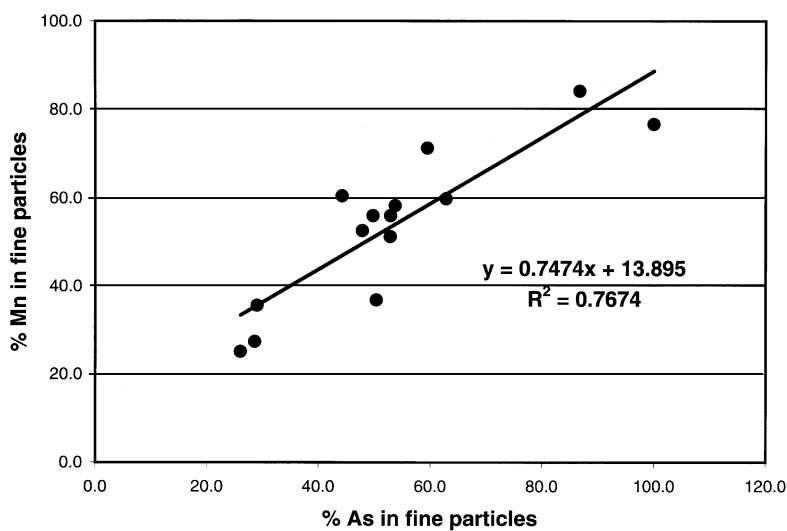


Fig. 3. Plot of percent concentration of arsenic in fine particles vs. the percent concentration of Mn in the same fraction.

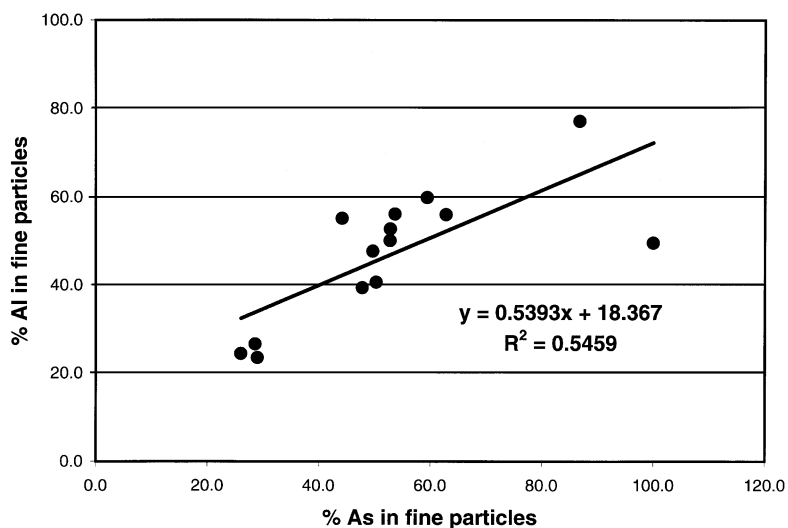


Fig. 4. Plot of percent concentration of arsenic in fine particles vs. the percent concentration of Al in the same fraction.

in the first 8 h, and slowed down after that. Extraction equilibrium can be reached much faster with 0.1 M KH_2PO_4 . No significant difference in the As concentration was observed during 24 h extraction. The extraction times selected for nitrate and phosphate fractions were 24 and 1 h, respectively.

The percent As, Fe, Mn, and Al extracted during the various steps of the sequential fractionation are shown in Table 3. Considerable amounts of arsenic can be extracted by 0.1 M NaNO_3 from both fine and large particles. This is especially true for the fine fraction where the extractable As ranged from 9.2 to 51.3% with an average of $28.7 \pm 13.3\%$,

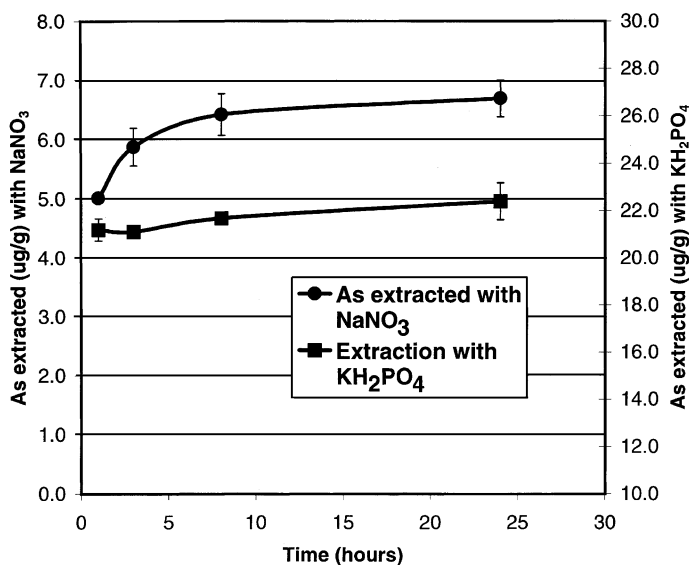


Fig. 5. Effects of extraction time on the amount of arsenic released from the soils with 0.1 M NaNO_3 and 0.1 M KH_2PO_4 .

Table 3
Percent (%) of As, Fe, Mn and Al extracted with 0.1 M NaNO₃ and 0.1 M KH₂PO₄ from both fine particle and large particles

Sample I.D.	As				Fe				Mn				Al			
	Fine ^a		Large ^a		Fine		Large		Fine		Large		Fine		Large	
	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄	NaNO ₃	KH ₂ PO ₄
A	42.90	40.15	14.48	16.83	1.64	0.24	1.94	2.72	– ^b	27.12	2.60	9.64	0.80	0.38	0.55	0.48
B	22.71	22.91	16.67	14.12	0.89	1.28	3.61	4.08	4.27	14.91	6.03	17.40	0.81	0.86	2.14	1.49
C	28.69	39.29	9.63	10.39	0.88	0.60	1.41	2.48	2.65	7.09	2.30	4.82	3.11	2.92	3.84	3.36
D	30.14	41.72	16.93	11.58	2.50	6.11	1.93	1.43	5.76	24.34	14.38	14.34	11.67	7.36	6.98	2.77
E	26.62	29.47	8.78	10.17	0.35	0.08	0.36	0.09	1.21	9.59	0.60	3.80	0.64	0.60	0.48	0.09
F	51.30	31.72	21.22	11.38	0.07	0.24	0.28	0.07	0.98	19.15	0.58	8.93	1.35	0.44	0.42	0.08
G	21.78	36.43	–	–	4.41	7.56	4.25	2.82	11.45	38.90	22.53	7.94	18.40	13.88	3.46	2.82
H	51.28	38.74	24.66	16.61	4.70	3.29	3.59	4.41	24.49	19.53	4.87	4.19	16.20	8.81	4.23	1.79
I	36.67	43.03	15.18	15.35	2.96	1.50	4.42	4.43	9.75	16.65	5.27	8.57	5.58	3.53	3.27	1.83
J	32.71	34.19	14.24	12.32	2.90	2.98	5.16	3.14	6.52	12.28	2.76	2.91	4.23	2.48	5.03	2.59
K	12.41	20.47	13.18	22.24	0.37	0.43	1.19	3.75	0.24	5.61	1.25	5.80	0.80	0.47	0.60	0.39
L	9.19	9.39	7.20	8.54	0.18	0.11	0.71	0.28	0.77	5.11	0.85	6.76	0.34	0.31	0.61	0.36
M	15.27	23.76	20.72	23.08	6.31	7.92	3.54	3.18	9.95	24.95	9.07	12.73	2.56	2.53	3.74	1.92
N	20.27	7.93	17.64	9.59	0.09	0.20	0.34	0.38	0.42	8.41	1.45	11.05	0.23	0.15	0.22	0.19

^a Fine particle: <0.25 mm; large particle: 0.25–0.71 mm.

^b No data available.

whereas in the large fraction ranged from 7.2 to 24.7% with an average of $15.4 \pm 6.4\%$. The 0.1 M NaNO_3 extracted fraction is important since it is considered to be the most available to biota and most easily leached to groundwater. The higher percentage of arsenic released in fine fraction compared with that of large fraction by the same extractant suggests that there is a possible difference in the interactions of arsenic with the particles of different sizes. The factors controlling the interactions in these size fractions are not clear at this moment. The mobilizable arsenic, defined as the fraction released by 0.1 M KH_2PO_4 , showed a similar pattern as that of the mobile fraction. The percentage of arsenic extracted ranged from 7.9 to 43.0% with an average of $29.9 \pm 11.5\%$ for the fine particles and from 8.5 to 22.2% with an average of $14.0 \pm 5.8\%$ for the large particles, respectively. It can be seen that the majority of arsenic present in the fine particles are either mobile or mobilizable, with a small percentage remaining as residual for most samples collected. However, small releases of arsenic by these two extractants were also observed for a few of the samples, such as sample L. No efforts were made to find the factors causing this difference.

Compared to arsenic, much smaller amounts of Fe and Al were generally extracted by both 0.1 M NaNO_3 and 0.1 M KH_2PO_4 , indicating that nitrate and phosphate are not efficient in releasing Fe and Al from these soils. Higher concentrations of Mn, however, were observed in 0.1 M KH_2PO_4 fraction with $16.7 \pm 9.7\%$ for fine particles and $8.5 \pm 4.3\%$ for the large particles, respectively. This result seems in accordance with the finding that arsenic distribution in the soils has a stronger correlation with Mn ($R^2=0.767$) compared with that of Fe ($R^2=0.483$) and Al ($R^2=0.546$).

The chemistry of arsenic precipitation–dissolution and adsorption–desorption is complex and depends on the charge of the absorbing species and the soil surface characterization. The results for arsenic fractions should reflect the geochemical behavior of arsenic in the surficial environment. In a recent study on sequential extraction of arsenic from contaminated soils, Lombi et al. (2000) found that only a very small proportion of arsenic

was extracted by NH_4NO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$, and relatively low concentrations of Fe, Mn, and Al were also observed in these two fractions. The greatest amounts of arsenic were extracted in steps of NH_4 -oxalate and NH_4 -oxalate + ascorbic acid, which targeted amorphous and crystalline oxide fractions, respectively. The results of current study are in agreement with the fact that nitrate and phosphate are not efficient in the extraction of Mn, Fe, and Al (especially the latter two elements). However, high concentrations of arsenic found in these two fractions indicate arsenic present in these soils are easily released by nitrate and phosphate. On the one hand, arsenic is strongly correlated with the distribution of Fe, Mn, and Al, while on the other hand, it is not in accordance with the dissolution of these mineral elements. In view of these facts, we hypothesize that arsenic present in the soil system studied interacts with the Fe, Mn, and Al-containing mineral particles via surface adsorption and/or complexation, rather than embedding inside of the mineral particles. These surface interactions cause arsenic to be easily released by ion exchange and specific replacement by phosphate without total dissolution of the mineral particles.

4. Conclusions

A simple two-level sequential extraction procedure was developed to evaluate the mobility of arsenic in South Florida golf course soils. Soils were separated into fine (<0.25 mm) and large (0.25–0.71 mm) particle fractions. The results indicate that arsenic is closely related to the distributions of Fe, Mn, and Al in these soils. No such correlation, however, exists for soil organic matter. Large amounts of arsenic can be released by 0.1 M NaNO_3 and 0.1 M KH_2PO_4 for most samples studied, suggesting that arsenic present in these soils is relatively mobile and mobilizable. This may potentially contaminate the underlying groundwater. It seems likely that the release of arsenic from the soils does not require the dissolution of Fe, Mn, and Al-containing mineral particles. Our study on South Florida golf course soils strongly agrees with the previous reports on

groundwater arsenic contamination. This is, to our knowledge, is the first study in exploring arsenic mobility in golf courses in South Florida region, where arsenic herbicides are heavily used. This study suggests that the use of arsenic-containing herbicides must be used with caution to protect groundwater contamination, and further research is needed in order to predict the mobility of arsenic in specific areas. Since fate and transport of arsenic in the environment are heavily dependent on the chemical forms (e.g. arsenate, arsenite, MMA, DMA) of arsenic present in the soil, speciation information should be included in the future studies.

Acknowledgments

This research was partially supported by the Foundation/Provost's Office Research Award at Florida International University (FIU). Soil samples were provided by the Dade County Environmental Resources Management (DERM). We would like to thank the Advanced Mass Spectrometry Facility (AMSF) at FIU for providing the access to the ICP/MS. We also thank Anita Holloway for her assistance for the preparation of this manuscript. This is contribution # 161 of the Southeast Environmental Research Center at FIU.

References

- Aten CF, Gupta SK. On heavy metals in soil: rationalization of extractions by dilute salt solutions, comparison of the extracted concentrations with uptake by ryegrass and lettuce, and the possible influence of pyrophosphate on plant uptake. *Sci Total Environ* 1996;178:45–53.
- Bhumbla DK, Keefer RF. Arsenic mobilization and bioavailability in soils. In: Nriagu JO, editor. *Arsenic in the environment, part I: cycling and characterization*. New York: John Wiley & Sons, Inc, 1994:51–82.
- Cai Y, Georgiadis M, Fourqurean JW. Determination of arsenic in seagrass using inductively coupled plasma mass spectrometry. *Spectrochim Acta Part B* 2000;B55:1411–1422.
- Chao TT, Sanzolone RF. Fractionation of soil selenium by sequential partial dissolution. *Soil Sci Soc Am J* 1989;53:385–392.
- Cullen WR, Reimer KJ. Arsenic speciation in the environment. *Chem Rev* 1989;89:13–764.
- Frey MM, Edwards MA. Surveying arsenic occurrence. *J Am Water Works Assoc* 1997;89:105–117.
- Gee GW, Bauder JW. Particle-size analysis. In: Klute A, editor. *Methods of soil analysis, part 1, physical and mineralogical methods*, 2nd ed.. Madison, WI: ASA and SSSA, 1986. p. 383–411.
- Gomez Ariza JL, Giraldez I, Sanchez-Rodas D, Morales E. Metal sequential extraction optimized for heavily polluted and iron oxide rich sediments. *Anal Chim Acta* 2000;414:151–164.
- Gupta SK, Vollmer MK, Krebs R. The importance of mobile, mobilizable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Sci Total Environ* 1996;178:11–20.
- Huang YC. Arsenic distribution in soils. In: Nriagu JO, editor. *Arsenic in the environment, part I: cycling and characterization*. New York: John Wiley & Sons, Inc, 1994:17–49.
- Kim MJ, Nriagu J. Oxidation of arsenic in groundwater using ozone and oxygen. *Sci Total Environ* 2000;247:71–79.
- Lombi E, Sletten RS, Wenzel WW. Sequential extraction of arsenic from different size fractions of contaminated soils. *Water, Air Soil Pollut* 2000;124:319–332.
- McLean EO. Soil pH and lime requirement. In: Page AL, Miller RH, Keeney DR, editors. *Methods of soil analysis, part 2*. Madison, WI: Soil Science Society of America and American Society of Agronomy, 1982:199–224.
- Nirel PMV, Morel FMM. Pitfalls of sequential extraction. *Wat Res* 1990;24:1055–1056.
- Nriagu JO. *Arsenic in the environment, part I: cycling and characterization*. John Wiley & Sons, Inc, 1994.
- Olson SR, Sommers LE. Phosphorus. In: Page AL, Miller RH, Keeney DR, editors. *Methods of soil analysis, Part 2*. Madison, WI: Soil Science Society of America and American Society of Agronomy, 1982:403–427.
- Pantsar-Kallio M, Manninen PKG. Speciation of mobile arsenic in soil samples as a function of pH. *Sci Total Environ* 1997;204:193–200.
- Shan XQ, Chen B. Evaluation of sequential extraction for separation of trace metals in model soil containing natural minerals and humic acid. *Anal. Chem.* 1993;65:82–807.
- Standard Operation Procedures (SOP), No. SOP-2000-I-001.1, Florida International University, Southeast Environmental Research Center, Environmental Analysis Research Laboratory, Miami, USA.
- Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* 1979;51:844–850.
- Thien SJ, Graveel JG. Particle size distribution. *Laboratory manual for soil science, agricultural and environmental principles*. The McGraw-Hill Companies, Inc, 1997:403–427.

Tonner-Navarro LE, Halmes NC, Roberts SM. Risk assessment of organic versus inorganic arsenic. Technical Report prepared for the Division of Waste Management, Florida Department of Environmental Protection, CEHT/TR-98-01, 1998, Center for Environmental and human Toxicology (CEHT), University of Florida.

Tu C, Ma LQ, Zhang W, Cai Y, Harris WG. Arsenic hyper-accumulation by Brake fern: chemical speciation and elemental association. *Plant and Soil*, 2001, submitted.

Wiegand GE. Preliminary report: environmental quality monitoring for pesticides and arsenic at five municipal golf courses in Miami-Dade County, Florida, 1999.