5 Arsenic Concentration and Bioavailability in Soils as a Function of Soil Properties: a Florida Case Study

Dibyendu Sarkar and Rupali Datta

CONTENTS

ABSTRACT

Background arsenic (As) concentrations are important measures of defining the level of contamination in soils and for setting up soil cleanup goals. Twelve surface soil samples from each of three ecological zones of Florida, namely, salt marsh, freshwater marsh, and pine flatwoods, were characterized to determine which soil properties most influence As retention and availability. Soils were analyzed for total As, phytoavailable As, and bioavailable As concentrations. The most important soil properties that control As biogeochemistry in soils were Fe, Al, Ca, and P contents; cation exchange capacity; and soil organic matter. Arsenic concentration was significantly higher in the salt marsh soils compared to the freshwater marsh and pine flatwoods soils; the latter two were not significantly different from one another. Phytoavailable As contributed towards 2 to 16% of total soil As. The amount of As bioavailable to the human gastrointestinal system was generally higher than As available to plants. Although total As concentration was greatest in salt marsh soils, percent bioavailability was the lowest. In contrast, pine flatwoods' soils had the highest percentage of bioavailable As in spite of having the lowest total As concentrations. Results demonstrate that total As content is not a good indicator of soil contamination level as far as risk to human health is concerned.

5.1 INTRODUCTION

Ecologists have classified natural vegetation in Florida into 26 ecological zones such as North and South Florida coastal strands; sand pine scrub; North and South Florida flatwoods; oak hammock; scrub cypress; salt marsh; mangrove swamp; sawgrass marsh; freshwater marsh; etc [1]. The type of vegetative community in an ecological zone is likely to depend on the type of soil that supports it. Three ecological zones were chosen to study background As concentrations and to identify the soil properties that influence soil As concentration — namely, salt marsh, freshwater marsh, and pine flatwoods.

Salt marshes of Florida are coastal ecosystems with communities of nonwoody, salt-tolerant plants occupying intertidal zones that exhibit characteristics of terrestrial and marine ecosystems [2]. The salt marsh community is located on the Atlantic coast, extending southwest towards the Gulf of Mexico and inland along tidal rivers (Figure 5.1a). This community appears as an open expanse of grasses, sedges, and rushes. Vegetation occurs in distinct zones as a result of the fluctuating water levels and salinity concentrations due to tidal action. Major plant species include black needlerush and seashore saltgrass [2]. Low, regularly flooded marshes are dominated by smooth cordgrass; high marsh supports salt myrtle, marshhay cordgrass, marshelder, saltwort, and sea oxeye. Soils are generally poorly drained, sandy clay loams underlain by loam sands or organic soils underlain by loam sands. Salt marshes are considered nutrient sinks where plants accumulate nutrients rapidly during the growing season [2].

Freshwater marshes are not uniformly distributed throughout the state. The greatest expanse is the Everglades in South Florida (Figure 5.1b). Several other marshes are associated with river floodplains and occur throughout Florida, appearing as an open expanse of grasses, sedges, and rushes, as well as other herbaceous plants in areas where soils are usually saturated or covered with surface water for 2 or more months during the year [3]. Plants that characterize this community include grasses (beakrushes, blue maidencane, bulrushes, common reed, etc.); herbaceous plants (arrow head, blue flag, cattail, fire flag, etc.); and shrubs (St. Johns wort, primrose willow, elderberry, etc.). Soils are generally dominated by peat, marl, and sand with high organic matter and nitrogen, but low phosphorus and potassium levels [3].

Pine flatwoods comprise the most widespread biological community in Florida, constituting about 30 to 50% of Florida's uplands ranging from northern to southern Florida (Figure 5.1c). It is easily identified by its flat topography and its typically scattered pine trees with an understory of saw palmetto and grasses [4]. The dominant trees characteristic of flatwoods are longleaf pine, slash pine, South Florida slash pine, and pond pine. The understory shrub layer includes, in addition

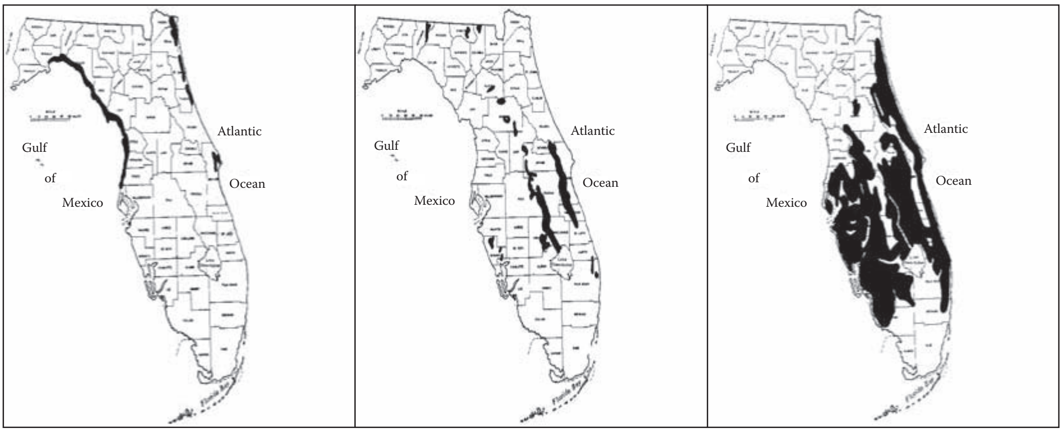

FIGURE 5.1 Ecological zones of Florida: (a) salt marsh; (b) freshwater marsh; and (c) pine flatwoods. (From Myers, R. and J. Ewel (Eds.), 1990, *Ecosystems of Florida*. University of Central Florida Press, Orlando, FL.)

to saw palmetto, gallberry, fetterbush, staggerbush, wax myrtle, etc. Soils that characterize pine flatwoods are poorly drained acidic fine sands with low amounts of nutrients and low organic matter content [4].

The U.S. Environmental Protection Agency (USEPA) has classified inorganic As as a Group A human carcinogen [5]. Arsenic is typically found in soils at background concentrations ranging from 0.1 to 40 mg/kg [6]. The main source of As in uncontaminated soils is the parent material from which the soils are derived [7]. Other sources of As in soils include atmospheric deposition [8] and bioconcentration by plants, aquatic organisms, and lower invertebrates [9–11]. An elevated health risk is associated with long-term human exposure to As in soils. Several studies have been conducted to establish background As concentrations in uncontaminated soils of Florida, with widely varying results. A level of 8 mg/kg was reported in agricultural soils [8,12] and a geometric mean (exponentiated mean of a log-transformed distribution) was reported of 1.1 mg/kg in surface soil based on a study of 40 mineral soils of Florida. Scarlatos and Scarlatos [13] reported As concentrations ranging from 1.1 to 54.3 mg/kg in 115 surface soil samples collected from Florida.

The residential soil cleanup goal set by the Florida Department of Environmental Protection (FDEP) is 0.80 mg/kg [14]. The maximum allowable level of As for oral intake is 0.3 μg/kg/d [15]. The importance of considering dietary intake of As through the food chain via uptake from contaminated soils [16], as well as soil ingestion from incidental hand-to-mouth activity by children playing in backyards, has been repeatedly emphasized in recent studies assessing public health risks associated with long-term exposure to low-level As-contaminated systems [17,18]. Adriano [19] summarized several soil properties that are most likely to influence soil availability of As: pH, texture (clay content); amorphous Fe–Al oxides; organic matter content; sulfur content; phosphate concentration; and soil redox conditions.

The most important parameter for accurate assessment of the risk posed by As to human health is its bioavailability. Bioavailability refers to the extent of absorption of a chemical into the bloodstream from the gastrointestinal tract, lungs, or skin [20]. It is also essential to consider phytoavailability (potential availability for plant uptake) because dietary intake of As can occur through the food chain via plant uptake from contaminated soils. Bioavailability and phytoavailability depend on soil characteristics; thus, the current study was geared towards examining As phytoavailability and bioavailability using 12 surface soil samples from each of the three aforementioned ecological zones of Florida. The main objectives of this study were:

- To identify and characterize the soil properties most likely to influence As concentration in surface soils collected from three ecological zones of Florida
- To measure total As concentration as well as the phytoavailable and bioavailable fractions of As in those soils
- To investigate whether the soils from the three ecological zones are significantly different in terms of total, phytoavailable, and bioavailable As

5.2 MATERIALS AND METHODS

5.2.1 Soil Sampling, Preparation, and Characterization

Surface soil samples from three ecological zones in Florida — namely, salt marsh, freshwater marsh and pine flatwoods — were used for this study. Twelve soil samples from each zone were obtained. A detailed description of the soil samples including their soil order, series, horizon, and type is listed in Table 5.1. Soil samples were air-dried and passed through a 2-mm sieve. Soils were characterized for pH, electrical conductivity, and water content using standard protocols; organic matter content was determined using the loss-on-ignition method [21]. Total C and N were determined using an

TABLE 5.1
Description of Soil Samples

Ecological zone	Sample ID	Soil order	Soil series	Horizon	Soil type
Salt marsh	SM-1	Entisol	Turnbull	0A	Muck
	SM-2	Entisol	McKee	A	Variant silt
	SM-3	Inceptisol	Hansboro	0E	Variant muck
	SM-4	Entisol	Hallandale	A	Fine sand
	SM-5	Entisol	Kesson	A	Fine sand
	SM-6	Entisol	Peckish	A1	Muck fine sand
	SM-7	Spodosol	Estero	0A	Muck
	SM-8	Inceptisol	Weckiwachee	0A1	Muck
	SM-9	Inceptisol	Durbin	0A1	Muck
	SM-10	Inceptisol	Durbin	0A1	Muck
	SM-11	Inceptisol	Tisonia	0A1	Variant muck
	SM-12	Spodosol	Lynn Haven	0A1	Fine sand
Freshwater marsh	FW-1	Inceptisol	Samsula	0A1	Loamy sand
	FW-2	Inceptisol	Brighton	0A	Muck
	FW-3	Entisol	Placid	A1	Fine sand
	FW-4	Alfisol	Pineda	A1	Fine sand
	FW-5	Alfisol	Winder	A	Sand
	FW-6	Inceptisol	Samsula	0A1	Muck
	FW-7	Entisol	Sellers	A1	Loamy sand
	FW-8	Inceptisol	Shenks	0A1	Muck
	FW-9	Alfisol	Winder	A	Sand
	FW-10	Inceptisol	Terra Ceia	0A1	Muck
	FW-11	Mollisol	Hendry	A	Sandy loam
	FW-12	Inceptisol	Kaliga	0A1	Muck
Pine flatwoods	PF-1	Entisol	Osceolla	A	Sand
	PF-2	Spodosol	Myakka	A	Fine sand
	PF-3	Spodosol	Eaugallie	A1	Fine sand
	PF-4	Spodosol	Smyrna	A	Fine sand
	PF-5	Spodosol	Smyrna	A	Fine sand
	PF-6	Spodosol	Immokalee	A	Fine sand
	PF-7	Spodosol	Immokalee	A	Sand
	PF-8	Spodosol	Eaugallie	A	Sand
	PF-9	Spodosol	Eaugallie	A	Fine sand
	PF-10	Spodosol	Immokalee	AP	Sand
	PF-11	Spodosol	Mandarin	A	Fine sand
	PF-12	Spodosol	Leon	A	Fine sand

elemental analyzer (Perkin Elmer 2400 Series II). Total Ca, Mg, Fe, Al, P, and As were extracted following USEPA method 3050B [22]. Phytoavailable As was obtained by shaking 1 g of soil with 50 ml of 1 *M* NH_4Cl solution for 30 min. Particle size and cation exchange capacity were not measured; values were obtained from the soil characterization database of Florida Cooperative Soil Survey (1967–1989).

Phosphorus was measured colorimetrically using the molybdate-ascorbic acid method [23] using Varian Cary 50 Spectrophotometer. Iron was also determined colorimetrically according to Olson and Ellis [24] as a complex with 1,10-phenanthroline reagent. Ca, Mg, and Al were analyzed using flame atomic absorption spectrometry and As was determined using graphite furnace atomic absorption spectrometry (GFAAS).

5.2.2 DETERMINATION OF BIOAVAILABLE ARSENIC

Bioavailable As was estimated according to the *in vitro* gastrointestinal method of Sarkar and Datta [25]. The reactions were carried out in 250-ml beakers in a 37°C water bath to simulate body temperature. Anaerobic conditions were maintained by passing argon gas through the solutions. Constant mixing of the solution was maintained using a stirrer to simulate gastric mixing. The extractant used consisted of 0.15 *M* NaCl and 1% porcine pepsin. One gram of soil sample was added to 150 ml of gastric solution, and the pH of the solution was adjusted to 1.8 using 1 *N* HCl. The solution was incubated for 1 h.

The solution was then modified for the intestinal phase by adjusting the pH to 7.0 using a saturated solution of $NaHCO_3$, followed by the addition of 525 mg of porcine bile extract and 52.5 mg of porcine pancreatin (Sigma Chemical Co., St. Louis, MO). In order to simulate absorption through the intestinal lining, a 40-cm^2 filter paper strip coated with Fe oxide was used. The Fe oxide strip was placed in a square bag (sides 6.5 cm) made of nylon membrane filter of 8-µm pore size. The bag was tied with a string and suspended in the reaction vessel. The solution was incubated for 1 h, at the end of which 10 ml of solution was collected, centrifuged at 5000 rpm for 30 min, and analyzed by GFAAS. Arsenic adsorbed by the Fe oxide strip was desorbed by shaking it vigorously in 80 ml 1 *N* HNO_3 for 1 h.

5.3 RESULTS AND DISCUSSION

5.3.1 CHARACTERIZATION OF SOILS

Soil physicochemical properties that are most likely to influence As concentrations in the soil samples collected from salt marsh, freshwater marsh, and pine flatwoods are presented in Table 5.2. The properties are described in terms of range, arithmetic mean (AM), geometric mean (GM), and their respective standard deviations (ASD and GSD). The majority of the procedures available in the literature on environmental statistics for computing AM assume that contaminant concentrations are approximately normally distributed [26]. The upper confidence level of the mean moves closer to the true mean as sample size increases; the 95th percentile of the distribution remains at the upper end of the distribution [27].

However, the distributions of elemental concentration in most soils are positively skewed and usually follow a log-normal distribution [16]. When dealing with a skewed distribution, the GM is a better maximum likelihood estimator of the central tendency than AM [16] is. The calculated baseline concentrations, assuming log-normality of the elemental distribution, better represent the natural level of chemicals in soils because the distorting effects of a few high values are minimized [16]. Table 5.2 shows that the surface soils studied represented a wide range of properties that could potentially affect arsenic retention and, thus, its availability to plants and humans.

5.3.2 TOTAL ARSENIC CONCENTRATIONS IN SOILS

Total As concentrations in the soil samples studied are given in Table 5.3. The salt marsh soils had the highest concentration of total As (GM 12.22 mg/kg), with one sample as high as 89.84 mg/kg. The pine flatwoods samples exhibited the lowest concentration of total As (GM 0.38 mg/kg), and the freshwater marsh samples were intermediate between the other two ecological zones (GM 2.41 mg/kg). A comparison of means using the least square difference (LSD) method revealed that mean total As concentration in the salt marsh was significantly higher than in the other two ecological zones at the 99% confidence interval ($\alpha < 0.01$). The mean total As concentrations in the freshwater marsh and the pine flatwoods were not significantly different from each other. All 12 of the salt marsh soils, 10 out of 12 freshwater marsh soils, and 1 out of 12 pine flatwoods soils exceeded the residential soil cleanup goal of 0.80 mg/kg set by the FDEP [14].

TABLE 5.2
Soil Characterization

			Soil properties											
Zone	No. of samples	Data	pH	Clay (%)	EC (µS/cm)	Fe (mg/kg)	Al (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	S (mg/kg)	C (%)	SOM (%)	CEC (cmol/kg)	P (mg/kg)
Salt marsh	12	Hi	8.09	3.3	68000	78.66	10.07	14643	57.04	6400	27.69	58.13	466.4	591.4
		Lo	4.41	0.0	925	ND	1.38	2012	29.80	100	0.10	0.69	12.79	120.7
		AM	5.33	0.72	24084	20.56	6.75	8335	44.71	3280	13.75	24.30	178.1	321.5
		ASD	1.16	1.26	23230	25.55	3.54	4594	7.38	2622	9.91	18.99	132.9	140.5
		GM	5.22	NC	13058	8.36	5.52	7024	44.10	1385	5.53	12.72	118.1	289.8
		GSD	1.10	NC	1.78	2.00	1.38	1.34	1.08	2.24	2.55	2.02	1.64	1.25
FW marsh	12	Hi	6.61	3.9	1110	54.40	8.06	13414	41.72	6300	44.76	52.31	218.1	506.1
		Lo	3.95	0.0	99	ND	ND	1365	16.49	ND	0.48	0.41	1.39	120.4
		AM	5.03	0.82	513.1	10.70	4.44	31.88	27.81	2770	17.06	10.94	76.76	220.5
		ASD	0.87	1.29	291.3	17.98	2.78	3503	7.61	2482	18.66	18.35	71.27	117.8
		GM	4.96	NC	435.9	4.43	3.33	2376	26.85	1596	8.08	4.61	37.13	198.4
		GSD	1.08	NC	1.32	1.82	1.49	1.34	1.13	1.77	1.88	1.86	1.95	1.22
Pine FW	12	Hi	7.48	3.6	235	0.49	5.03	1794	203.9	1400	8.14	8.26	18.34	182.0
		Lo	3.99	0.4	73	ND	ND	240.9	12.86	ND	0.80	0.27	3.23	110.1
		AM	4.62	1.30	177.6	0.25	1.81	1215	41.64	466.7	2.70	2.91	10.83	140.5
		ASD	0.94	0.96	56.7	0.34	1.55	390	51.56	457.9	2.82	2.33	6.26	23.77
		GM	4.55	1.03	168.1	0.07	1.28	1116	30.83	324.3	1.80	2.10	8.94	138.8
		GSD	1.08	1.36	1.17	3.31	1.51	1.25	1.33	1.46	1.48	1.49	1.35	1.07
Total	36													
Hi			8.09	3.9	68000	78.66	10.07	14643	57.04	6400	44.76	58.13	466.4	591.4
Lo			3.95	0.0	73	ND	ND	240.9	12.86	ND	0.10	0.27	1.39	110.1

TABLE 5.3
Arsenic Concentrations in Soils of Florida Ecological Zones

Arsenic pools	Ecological zone	No. of samples	Range (mg/kg)	AM ± ASD (mg/kg)[a]	GM ± GSD (mg/kg)[b]
Total	Salt marsh	12	1.10–89.8	21.8 ± 24.8 *a*	12.2 ± 1.73
	Freshwater marsh	12	0.1–9.38	3.98 ± 3.15 *b*	2.41 ± 1.76
	Pine flatwoods	12	0.20–1.21	0.42 ± 0.26 *b*	0.38 ± 1.21
Bioavailable	Salt marsh	12	ND–16.4	3.91 ± 5.78 *a*	1.40 ± 2.06
	Freshwater marsh	12	ND–1.29	0.36 ± 0.45 *b*	0.15 ± 1.87
	Pine flatwoods	12	ND–0.10	0.05 ± 0.03 *b*	0.04 ± 1.33
Phytoavailable	Salt marsh	12	ND–1.92	0.67 ± 0.72 *a*	0.26 ± 2.16
	Freshwater marsh	12	ND–0.19	0.06 ± 0.07 *b*	0.04 ± 1.68
	Pine flatwoods	12	ND–0.08	0.05 ± 0.02 *b*	0.04 ±1.19

[a] AM ± ASD = arithmetic mean ± standard deviation.

[b] GM ± GSD = geometric mean ± standard deviation.

Note: Different letters in the same column (specific to arsenic pool) indicate significantly different at α 0.1 using the LSD test.

Out of the 12 soil samples evaluated for the salt marsh ecological zone, 5 belonged to the Entisol soil order, 5 to the Inceptisol soil order, and 2 to the Spodosol soil order (Table 5.1). However, despite being officially classified as Inceptisols, all the five soil samples in that order had typical variant muck texture characteristic of Histosols. Histosols are often referred to as peat or muck. They contain at least 20 to 30% organic matter by weight and are more than 40 cm thick. Histosols typically form in areas of poor drainage, where soils are frequently wet. Such conditions retard the decomposition of plant and animal remains, which accumulate over time [28].

Entisols are soils that were formed relatively recently and are thus poorly developed, with only A horizon. Inceptisols are soils that exhibit minimal horizon development. They are more developed than Entisols, but still lack the features characteristic of other soil orders. Inceptisols are widely distributed and occur under a wide range of environmental settings. They are often found on fairly steep slopes, young geomorphic surfaces, and resistant parent materials [28]. Spodosols are acid soils characterized by an accumulation of aluminum and iron oxides beneath the surface. They typically have a light-colored E horizon (layer) overlying a reddish-brown spodic horizon. Spodosols often occur under coniferous forests in moist climates.

A qualitative evaluation of soil order impact on As concentrations revealed that total As varied as Inceptisol (Histosol) > Entisol > Spodosol. Inceptisols had the highest values of soil organic matter, CEC, total Fe, total Ca, and total P; Spodosols had the lowest. Similar findings were reported by Chen et al. [7], who observed that the highest mean As concentrations were associated with Histosols.

Out of the 12 samples evaluated for the freshwater marsh ecological zone, 6 were Inceptisols, 2 were Entisols, 3 were Alfisols, and 1 was a Mollisol (Table 5.1). Alfisols are forest soils that have relatively high native fertility. These soils are well developed and contain a subsurface horizon in which clays have accumulated. Alfisols are mostly found in temperate humid and subhumid regions of the world. Formed in grasslands, Mollisols occur primarily in middle latitudes. They are famous for their thick, dark surface horizon, which results from the addition of organic materials derived from plant roots [28]. The Mollisol sample was discounted even in a qualitative analysis because one sample cannot be considered to be representative of an entire soil order.

Total As varied with soil order as follows: Inceptisol > Alfisol > Entisols. Eleven out of twelve pine flatwood samples were Spodosols and one was an Entisol. Apparently, the Spodosols had the lowest As concentration corresponding to the lowest CEC, total Fe, Ca, P, and soil organic matter among the soil orders discussed.

5.3.3 INFLUENCE OF SOIL PROPERTIES ON ARSENIC CONCENTRATIONS

Soil pH generally has an impact on soil concentration of As, but such impacts depend on the nature of the variable charge mineral surfaces common in the soils [19]. Generally, sorption of As decreases with increasing pH [19]. This can be attributed to the negative surface charge on the adsorptive surface at higher pH, as well as the negative charge of As oxyanions [29]. Although the range of pH of the soils in the current study was quite large (3.95 to 8.09), the majority of the samples clustered in a small group ranging between 4.55 and 5.22 (Table 5.2). Not much difference is anticipated in the expected behavior of As oxyanions in small pH range, so soil pH was not expected to play a major role in explaining the variability in total As concentrations in the soils studied. A correlation coefficient of 0.001 (not significant at α 0.1) was obtained when total soil As data were regressed against the soil pH values (Figure 5.2a).

Sorption of As varies among soils and appears to be related to the oxide content of the soil [8,30,31]. Like phosphate, As is strongly adsorbed by amorphous iron and aluminum oxides [19]. Thus, presence of amorphous Fe and Al-oxides in soils is likely to enhance As retention. In the current suite of samples, total Fe concentrations varied between undetectable and 78.7 mg/kg (Table 5.2). The total Al content varied between below detection level and 10.1 mg/kg. Fe and Al were in much higher concentration in the salt marsh soils (GM 8.36 and 5.52, respectively) compared to the pine flatwoods soils (GM 0.07 and 1.28, respectively). Apparently, the salt marsh soils have greater As retention capacity than the pine flatwoods soils.

Total As concentration correlated significantly (at α 0.1) with total Fe + Al, and yielded a correlation coefficient of 0.57 (Figure 5.2b), indicating the role of Fe and Al oxides in retaining As in the surface soils. Calcium and magnesium in oxidized soils systems have the potential to precipitate As as Ca or Mg arsenate. Therefore, high Ca and/or Mg concentrations might imply greater retention of arsenic; as Figure 5.2c demonstrates, total soil As correlated significantly with total Ca + Mg concentrations. Table 5.2 demonstrates that Ca concentrations varied greatly among the soil samples studied (241 mg/kg to 14,643 mg/kg) with the highest concentration in salt marsh soils (7024 mg/kg). Magnesium contents were negligible compared to Ca and varied between 12.9 mg/kg and 57.1 mg/kg.

In general, As mobility and bioavailability are greater in sandy soils than in clayey soils. Woolson [32] reported that As phytotoxicity to horticultural crops was highest on a loamy sand soil and lowest on a silty clay loam. Others have also noted this inverse relationship between clay content and trend in bioaccumulation [33–35]. The main reason for this phenomenon is that hydrous Fe, Mn, and Al oxides vary directly with the clay content of the soil [19] because they primarily occur as coatings on the clay minerals or in the clay size fractions of the soils. Thus, the water-soluble fraction of As is generally higher in soils with low clay content than in those with high clay content [19].

However, certain clay minerals have permanent negative charge due to isomorphic substitution of a lower valence cation for a higher valence cation in the tetrahedral or octahedral layer [36]. Given that inorganic As predominantly occurs as oxyanions (arsenate or arsenite) in soil solutions, it is possible that negatively charged As ions are repelled by the negatively charged surface sites and thereby become more available for uptake by plants. Percent clay in the studied suite of soil samples under consideration varied between 0 and 3.9 (Table 5.2), representing a very small cluster. Therefore, As concentration in these soils was not expected to be influenced by clay contents, as demonstrated by their poor correlation with total soil As concentrations (Figure 5.2d).

Soil organic matter (SOM) is primarily composed of humic and fulvic acids [37]. Because of their acid-base, sorptive, and complexing properties, humic substances have a strong effect on the properties of water [38] and play an important role in the mobility of As in environmental waters. The adsorption of As by humic acids is high — in the pH range of 5 to 7 and when the humic acids have high ash and calcium content [39]. Humic acids can contribute more to the retention of

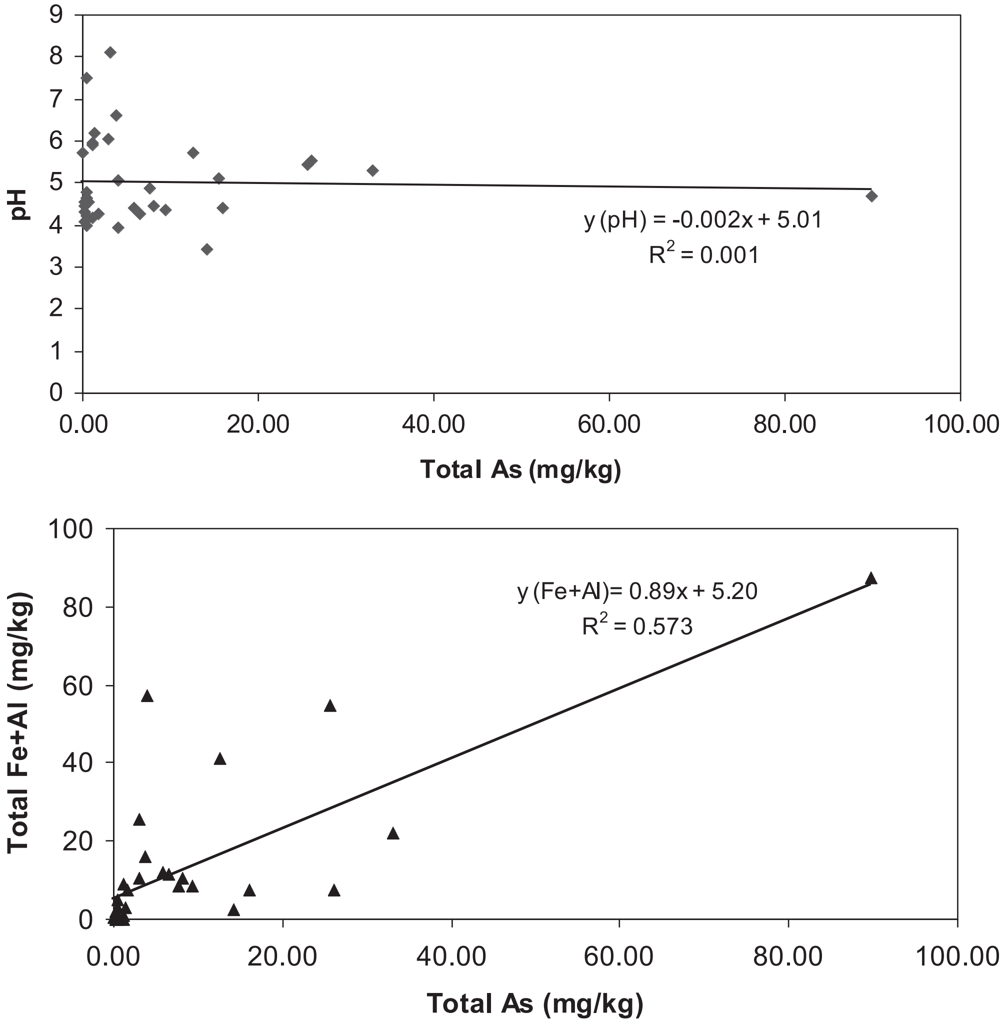

FIGURE 5.2 (A) Arsenic concentration in Florida soils as a function of soil pH ($n = 36$). (B) Arsenic concentration in Florida soils as a function of iron and aluminum concentrations ($n = 36$). (C) Arsenic concentration in Florida soils as a function of calcium and magnesium concentrations ($n = 36$). (D) Arsenic concentration in Florida soils as a function of clay content ($n = 36$). (E) Arsenic concentration in Florida soils as a function of soil organic matter content ($n = 36$). (F) Arsenic concentration in Florida soils as a function of cation exchange capacity ($n = 36$). (G) Arsenic concentration in Florida soils as a function of soil salinity measured as electrical conductivity ($n = 36$). (H) Arsenic concentration in Florida soils as a function of sulfur concentration ($n = 36$). (I) Arsenic concentration in Florida soils as a function of phosphorus concentrations ($n = 36$).

As in acidic environments than do clays and some metal oxides. The major retention sites on the humic acids at low pH systems are the amine groups [40].

Given the ideal pH conditions and a relatively high concentration of SOM (12.7%; Table 5.2), the soils from the salt marsh are likely to retain higher amounts of As than do freshwater marsh (4.61%) and pine flatwoods (2.1%). However, it should also be remembered that, although humic acids have strong metal retention capabilities, fulvic acids form soluble complexes of metals in waters; they probably keep some of these metal ions in solution and are particularly involved in iron solubilization and transport [38]. Therefore, the presence of fulvic acids can increase the mobility and the potential for leaching of As. This is because fulvic acids can be adsorbed onto

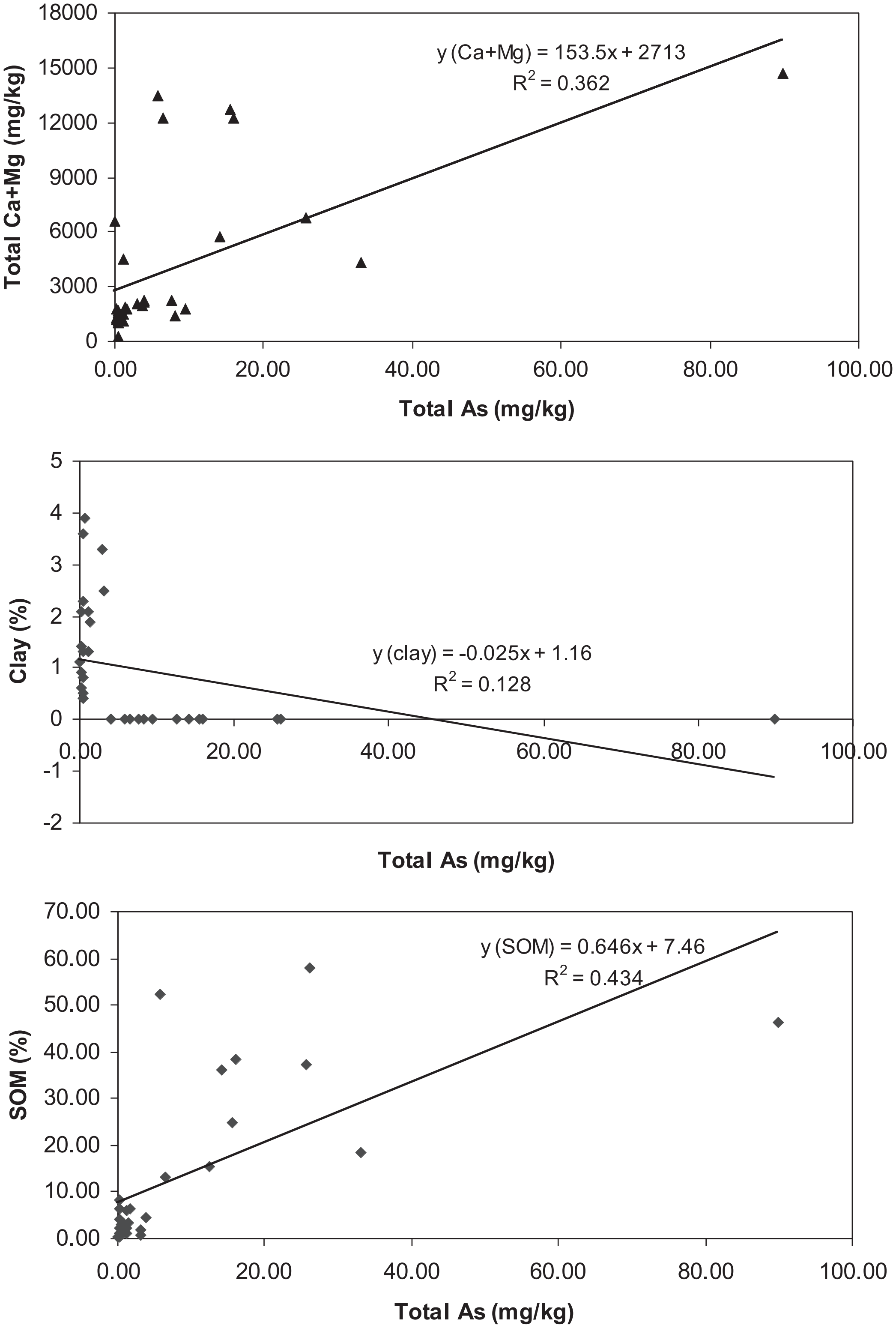

FIGURE 5.2 (continued)

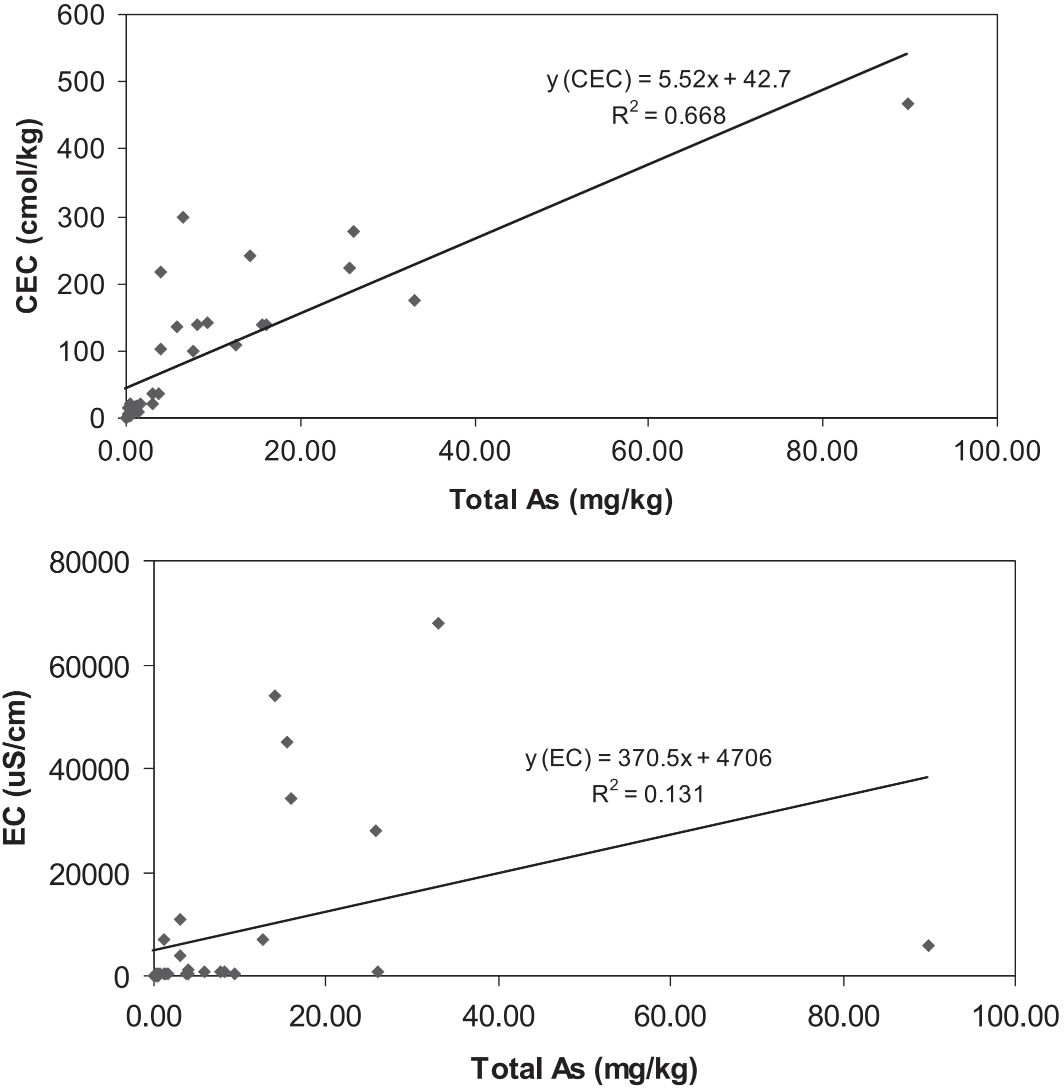

FIGURE 5.2 (continued)

the hydrous oxides of sediments by coulombic attraction, which leads to the formation of predominantly negatively charged surfaces due to the deprotonation of the functional groups [39].

In addition, fulvic acids can directly react with As, resulting in a decrease in adsorption of the corresponding As complex [41]. In this study, total soil As concentrations (pooled across the ecological zones) demonstrated a strong positive correlation with the SOM content with an R^2 value of 0.43, significant at α 0.1 (Figure 5.2e). Given the fact that the salt marsh samples contained significantly more As than freshwater marsh and pine flatwoods did (which clustered in the lower left hand corner of Figure 5.2e), it is logical to attribute this strong correlation to the As-binding capacity of SOM in salt marsh.

The quantity of reversibly adsorbed cations per unit weight of adsorbent (e.g., cmol(+)/kg) is called the cation exchange capacity or CEC [19]. The higher the CEC is, the greater is the amount of positive charge on the surface and the higher is the potential of the As oxyanions to form electrostatic bonds with the positively charged surface sites. Chen et al [7] showed a high degree of correlation between CEC and As in surface soils (r = 0.97) based on soil order. This is possibly

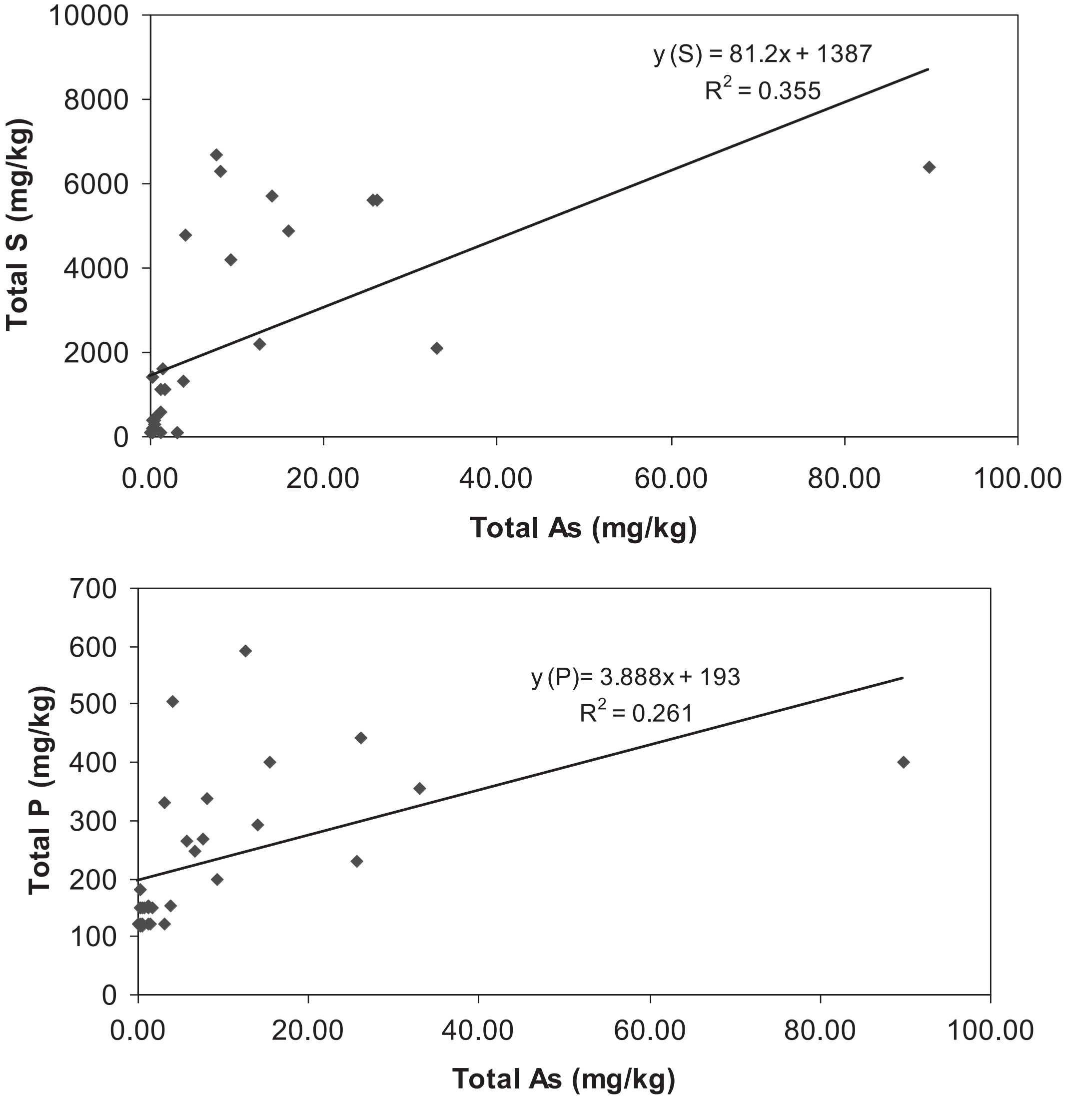

FIGURE 5.2 (continued)

because CEC was affected by the contents of clays, organic carbon, total Fe, Al, and probably P in soils. In the current study, the CEC of soils varied between 1.39 cmol/kg and 466 cmol/kg. The largest mean CEC was recorded in the salt marsh samples (118 cmol/kg), followed by freshwater marsh (37.1 cmol/kg) and pine flatwoods (8.94 cmol/kg), implying that As retention is likely to be greater in the salt marsh soils. A strong relationship between total soil As concentration and CEC was observed (R^2 value of 0.43, significant at α 0.1), as evident from Figure 5.2f.

Electrical conductivity is an expression of ionic strength of soil solution. Ions that undergo specific, inner-sphere complexation with surface functional groups are generally not affected by changes in solution ionic strength [42]. As has been reported to be predominantly adsorbed on metal hydroxides and other mineral surfaces via inner-sphere surface complexation mechanism via ligand exchange [43]; however, in certain cases, it may also undergo outer-sphere complexation if the bonding between As and the surface functional group is primarily electrostatic [44]. In such circumstances, soil EC is likely to have a major impact on As retention by soils.

Based on the strong correlation between soil As and CEC (which implied an electrostatic phenomenon), this possibility seemed plausible in the case of the soil samples studied. The EC of the soils exhibited an enormous range, varying between 73 and 68,000 μS/cm. The mean EC of the salt marsh samples (13,058 μS/cm) was significantly higher than that of freshwater marsh (435.9 μS/cm) and pine flatwoods (168.1 μS/cm). However, no apparent correlation was observed between total soil As and soil salinity; the R^2 value of 0.13 was not significant at α 0.1 (Figure 5.2g).

Sulfides also play an important role in retaining and remobilizing As from contaminated soils and sediments [39]. In a contaminated fluvial system, where surface sediments are oxidized while the lower buried layers are reduced, the concentration and partitioning of As are controlled by the redox interface. When reduction occurs, the adsorbed and coprecipitated As is released to the porewater [46]. Sulfides in the reduced environment will scavenge the As with the formation of arsenic sulfide precipitates [45,47]. Although a reducing environment is quite unlikely for the soil samples investigated in the current study, (which were collected primarily from the surface horizons), the marshlands of Florida were formed under reducing conditions [48]; thus, a significant portion of total As is likely to be associated with S in those soils.

As evidenced from the data presented in Table 5.2, freshwater and saltwater marsh samples had high mean S content (1596 mg/kg and 1385 mg/kg, respectively) compared to pine flatwoods samples, in which the S content varied between undetectable to 1400 mg/kg with a mean value of 324.3 mg/kg. Total soil As correlated positively with S content in the soil samples studied with a correlation coefficient of 0.36 significant at α 0.1 (Figure 5.2h), indicating the role of sulfides in retaining As in the surface soils, particularly those from the marsh ecosystems.

Phosphorus and arsenic exhibit very similar chemical properties. P and As are group VA elements and have very similar atomic radius (1.33 vs. 1.23); bonding radius (1.2 vs. 1.06); ionization potential (9.81 vs. 10.48 V); and electronegativity (–2.18 vs. –2.19). Both form oxyanions in +5 oxidation state; these are their most common environmental species. Phosphates are stable over a large range of pH and pE, and As can exist in the +3 oxidation state and easily forms links with sulfur and carbon [49]. Phosphates and arsenates undergo similar types of retention in soil minerals via (primarily) inner-sphere surface complexation. Thus, phosphates have demonstrated strong abilities to compete with As for sorption sites in environmentally important pH ranges [50].

Therefore, it is logical to assume that As, like P, will be similarly and significantly retained by positively charged, high specific surface soil components, such as amorphous Fe/Al oxides; presence of high concentration of P in soils could be indicative of As enrichment. Elevated As concentrations in sediments from the south Atlantic and along the Gulf Coast of Florida have been reported [51,52]; P deposits and soil pesticide residues were the hypothesized main sources of elevated As [52]. This is possible because phosphate rocks have a relatively high As concentration (6.6 to 121 mg/kg) compared with average (1.8 to 6.6 mg/kg) nonphosphorite rocks [53].

Chen et al. [7] identified soil P content as one of the most important soil properties that influence soil As concentration. In the studied soil samples, P concentration varied between 110.1 and 594.4 mg/kg, with the highest concentration in salt marsh soils (289.8 mg/kg), followed by freshwater marsh (198.4 mg/kg) and pine flatwoods (138.8 mg/kg) soils (Table 5.2). Total soil As correlated positively and significantly (at α 0.1) with total soil P, yielding a correlation coefficient of 0.26 (Figure 5.2i).

5.3.4 Arsenic Availability in Soils

Bioavailable and phytoavailable As fractions followed the same general trend as total soil As concentrations (Table 5.3). Phytoavailable As fraction, geared towards estimating the approximate amount of As in soils likely to be readily available for uptake by plants, represented only a small percentage of total As with the geometric mean concentration varying between 0.26 mg/kg in the salt marsh and 0.04 mg/kg in the freshwater marsh and the pine flatwoods.

The extractant used for estimating phytoavailable As was a neutral salt solution (ammonium chloride) designed to extract the soluble and exchangeable fractions of soil As. Apparently, only a small percentage of the total As in soils of all three ecological zones was soluble or exchangeable. This result is expected because the soil samples investigated in this study were almost exclusively collected from the surface horizons, and the soluble/exchangeable fractions were already exhausted as a result of plant uptake or they might have leached through the soil profile. This may be particularly true for the Spodosols, which are characterized by highly leachable soil types. O'Connor and Sarkar [54] studied leaching of phosphate in a typical Florida Spodosol and reported rapid vertical migration of P through the soil profile until it reached the characteristic hardpan, i.e., the spodic horizon, when the transport became lateral, controlled by subsurface topography.

The *in vitro* bioavailable fraction, geared towards estimating the approximate amount of As in soils likely to be available to human intestinal system in case of incidental hand-to-mouth exposure [55,56], also represented a small percentage of total As, although the concentrations were generally higher than the phytoavailable As fractions. Apparently, this fraction was extracting not only the soluble and exchangeable As, but also the reversibly adsorbed As fraction such as those possibly complexed by the SOM. Still, a significant amount of total soil As remained potentially unavailable to the human gastrointestinal system.

Figure 5.3 represents the bioavailable and phytoavailable As fractions as percentages of total soil As. The phytoavailable fraction varied between 1.8% in salt marsh soils and 13.5% in the pine flatwoods soils. Comparison of means using the LSD method revealed that, at the α 0.1 level, the mean percent total As phytoavailable in the pine flatwoods soils was significantly higher than that in the freshwater marsh and salt marsh soils. Although such a clear statistical differentiation among the ecological zones was not obtained, the mean percent of bioavailable As varied in the order: pine flatwoods (13.15%) > freshwater marsh (9.67%) > salt marsh (7.62%). Apparently, although

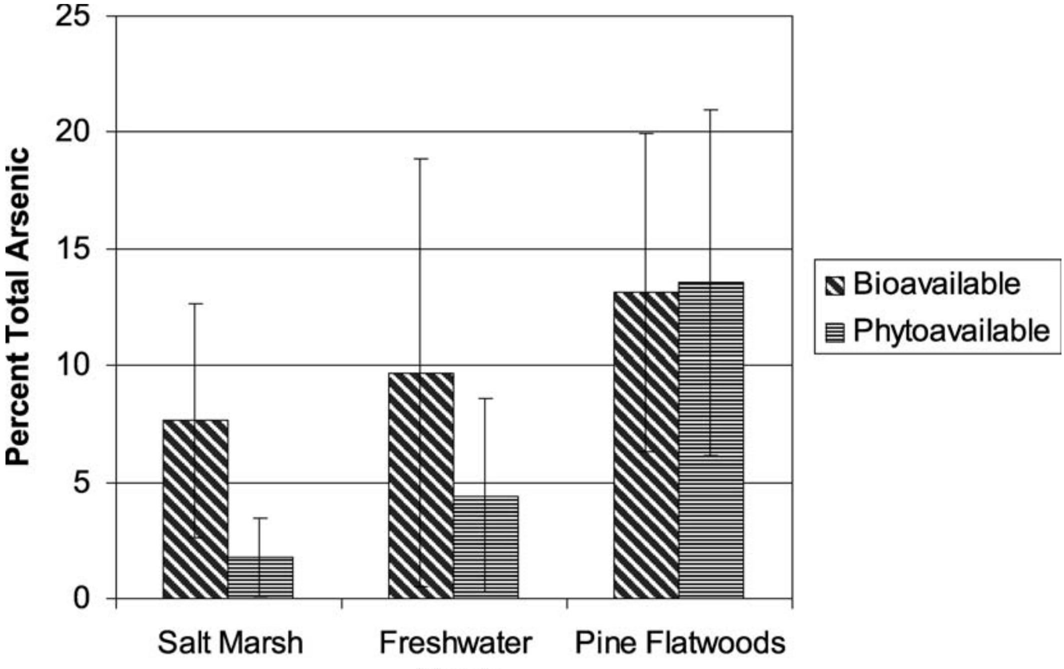

FIGURE 5.3 Percent of total arsenic that is bioavailable or phytoavailable. Data represent mean values and standard deviations.

the salt marsh soil samples had much higher concentrations of total As than the other ecological zones did, their availability to plants or the human intestinal system was the lowest.

On the other hand, although pine flatwoods had the lowest mean total As concentration, a relatively higher percentage was extracted by the solutions designed to extract the bioavailable and phytoavailable fractions. This is probably because As in the salt marsh soils is much more strongly retained by soil components by irreversible adsorption onto Fe/Al oxides and/or in the form of Ca/Mg-arsenical precipitates, as indicated by the data presented in Table 5.2. Thus, total As is not a good indicator of the level of contamination in soils from a human health risk assessment perspective.

5.4 CONCLUSIONS

- The soil properties most likely to influence As concentration in the Florida surface soils studied are the concentrations of Fe, Al, Ca, P, S, SOM, and CEC.
- Mean As concentration was significantly higher in the salt marsh soils compared to that in the freshwater marsh and pine flatwoods soils; the later two were not significantly different from each other.
- Only a small portion of the total As was phytoavailable.
- The bioavailable portion of As was generally higher than that of phytoavailable As in freshwater marsh and pine flatwoods soils.
- Although total As concentration was highest in salt marsh soils, percent bioavailability of As was the lowest. In contrast, pine flatwoods soil had the highest percentage of bioavailable As despite having the lowest total As concentration.
- Total As concentration is not a good indicator of soil contamination level as far as risk to human health is concerned.

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