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Chapter 16

A greenhouse study on soil-arsenic forms and their bioaccessibility in two chemically variant Florida soils amended with sodium arsenate pesticide: Preliminary results

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Abstract

Long-term application of arsenical pesticides in agricultural lands has resulted in high levels of arsenic (As) in certain soils. Conversion of former agricultural lands to residential areas has increased human contact with soil–As. Soil ingestion from incidental hand-to-mouth activity by children is now a very important issue in assessing human health risk associated with exposure to arsenical pesticide-applied former agricultural soils. Human health risk from exposure to soil–As is restricted only to those fractions of As in the soil that are available to the human gastrointestinal system. This study followed up on a static incubation experiment aimed at addressing the issue of soil variability on As bioaccessibility as a function of soil chemical properties, but in a greenhouse column system accounting for dynamic interactions between soils, water, plants, and pesticides. Two chemically variant soil types were chosen based on their potential differences with respect to As reactivity. The soils were amended with sodium arsenate pesticide at two high rates. Rice (*Oryza sativa*) was used as the test crop. A sequential extraction scheme was employed to identify the geochemical forms of As in soils (soluble, exchangeable, organic, Fe/Al-bound, Ca/Mg-bound, residual) immediately after spiking and after six months of equilibration. Concentrations of these As forms were correlated with the in-vitro fractions of As to identify those As species that are most likely to be bioaccessible in the human gastrointestinal system. Results from this study verified those obtained from the static incubation experiment, and demonstrated that As bioaccessibility is a function of soil speciation of As and that soil–As forms are a function of soil chemical properties.

16.1. Introduction

Arsenic is one of the most abundant elements on the earth (ranked as the 20th most abundant element) and occurs in many chemical forms. Varying amounts of As are naturally present in many soils, with concentrations ranging from 0.2 to 40 $\mu g\, g^{-1}$ (Walsh et al., 1977). However, elevated levels of As can be present in the environment as a result of mineral weathering and dissolution, geothermal activity, and numerous anthropogenic activities, including but not limited to mining and smelting activities, pesticide use, and coal combustion (Manning et al., 1998). As a result, it is the most common contaminant at hazardous waste sites in the United States and has been classified by the U.S. Environmental Protection Agency (EPA) as a group A human carcinogen (Southworth, 1995).

During the 1970s, agricultural products within the U.S. accounted for approximately 81% of the total As used (Adriano, 2001). By the 1980s, agricultural application accounted for only 46% of As use in the U.S. (Adriano, 2001). The average As contents in agricultural fields that received As-containing pesticides and defoliants range from 5 to 2553 $mg\, kg^{-1}$ (Walsh and Keeney, 1975). Although the use of arsenical pesticides has reduced, long-term application of such pesticides in agricultural lands has resulted in high levels of As residues in certain soils (Murphy and Aucott, 1998). Moreover, leaching of As from chromated copper arsenate (CCA)-treated wood may also elevate soil arsenic levels (Cao and Ma, 2004). Arsenic concentrations as high as 350 $mg\, kg^{-1}$ have been observed in soils near CCA-treated decks in Connecticut (Stillwell and Gorny, 1997). Murphy and Aucott (1998) reported As-contaminated soils in residential developments located on former apple orchards.

During the last two decades, rapid encroachment of suburban development on lands previously used for agriculture in fast metropolitan areas has tremendously increased the potential for human contact with soil–As (Datta and Sarkar, 2004). Moreover, since CCA-treated wood has been used extensively as fences and utility poles in urban neighborhood, As exposure via consumption of home-grown vegetables and fruits may constitute a potential health risk (Schoof et al., 1999). Soil ingestion from incidental hand-to-mouth activity by children is now a very important issue in assessing human health risk associated with exposure to arsenical pesticide-applied agricultural soils, which are now being used for residential purposes (Sarkar and Datta, 2004).

A critical parameter that allows for realistic health risk assessment in arsenic-contaminated soils is an estimate of "bioaccessible" As. Bioaccessibility refers to the extent of absorption of a chemical into the bloodstream from the gastrointestinal tract, lungs, or skin (Halmes and

Roberts, 1997). Studies investigating As ingested by humans suggest that close to 100% of soluble inorganic As is absorbed by the gastrointestinal tract (US EPA, 1992). In contrast to As in drinking water (soluble As), As in soils generally exists as mineral forms or as soil–As complexes that will be incompletely solubilized during transit through the gastrointestinal tract. Research indicates that As must be dissolved in order to be absorbed (Freeman et al., 1995); therefore, As in soil will be less well absorbed than As in drinking water (Ruby et al., 1996). This is because the majority of the soil forms of As are geochemically stable and/or insoluble in human gastric/intestinal juices and, hence, are not likely to be available for systemic absorption.

Adriano (2001) summarized several soil properties that are most likely to influence soil availability of As, namely, pH, texture (clay content), amorphous Fe–Al oxides, organic matter content, sulfur content, phosphorus concentration, and soil redox conditions. Incubation studies on As bioaccessibility and speciation have shown that As speciation is a direct function of soil properties and that these geochemical forms of As again affect the bioaccessibility (Sarkar and Datta, 2004). However, since incubation studies are static equilibrium experiments that fail to provide the more realistic viewpoint of a dynamic system, either a field study or a greenhouse study would generate data encompassing more realistic scales and growing condition. However, given the hazardous nature of As and its potential toxic effects on human health, a field scale study to investigate As bioaccessibility is an unrealistic proposition. Thus, the reported greenhouse study aimed at addressing the issue of soil variability on As speciation and bioaccessibility in a greenhouse column study. The primary objective of this study was to evaluate the relationship between geochemical speciation of As and bioaccessibility involving dynamic interactions between soil, water, and plants in a temperature and humidity controlled greenhouse setting. Preliminary results obtained after six months of soil–plant–pesticide equilibration have been presented in this report.

16.2. Materials and methods

16.2.1. Soil sampling, preparation and characterization

Two soils were used for the greenhouse study. Surface soil from the Immokalee series (the State soil of Florida) was collected from the Southwest Florida Research and Education Center, Immokalee, Florida, and the Millhopper series soil was collected from the University of

Florida campus at Gainesville, Florida. The soil samples were air-dried and passed through a 2-mm sieve and characterized for various soil properties. Soil pH, electrical conductivity, particle size, water content, and cation exchange capacity were measured using standard protocols (Sparks, 1996). Organic matter was measured using the loss-on-ignition method (Sparks, 1996). Plant-available Ca, Mg, and P were extracted by Mehlich III solution (Mehlich, 1984). Oxalate-extractable Fe and Al was obtained using Tamm's reagent (Sparks, 1996). Total P was extracted using the ignition method (Sparks, 1996). Total recoverable Ca, Mg, Fe, Al, P, and As was obtained by soil digestion according to USEPA method 3050B (USEPA, 1996). Phosphorus was measured colorimetrically by an UV/Visible light spectrophotometer using the molybdate–ascorbic acid method (Sparks, 1996). Ca, Mg, and Al were analyzed using the flame atomic absorption spectrometry (FAAS) and As was analyzed by graphite furnace atomic absorption spectrometry (GFAAS).

16.2.2. Greenhouse study

16.2.2.1. Soil amendments and plant growth

Both Immokalee and Millhopper soils were spiked with sodium arsenate at two rates 675 and 1500 mg As/kg soil. These two rates were selected to represent the higher and lower end of the superfund soil–As concentrations. PVC columns (13″ tall × 6″ id) were used in this greenhouse study. The bottom 7″ of the column was filled with white sand that had no arsenic retention capacity. Pesticide amended soil was packed in the top 6″ of the PVC column. Each column was provided with a reservoir compartment to hold the excess leachate and a hole was fitted with nalgene tubing to collect the leachate. The columns were arranged in a randomized block design and were rotated periodically to account for variances in temperature and sunlight within the greenhouse. Rice was used as the test crop because of their reported tolerance to As-enriched irrigation water in Bangladesh and India. The number of PVC columns with treatment were 12 (2 soils × 2 rates × 3 replicates) plus 6 controls (2 soils × 3 replicates). The first leaching was induced after two weeks of pesticide application. Rice was harvested in those columns where there was germination of rice seedlings. The second leaching took place after rice was harvested in late August. Leachate water was analyzed for soluble As using the GFAAS. Soils were collected from the surface layer immediately after spiking (0 time) and after six months of soil–pesticide equilibration and assessed for soil–As forms and in-vitro bioaccessible As.

16.2.3. Sequential extraction procedure

Sequential extraction scheme developed by Chungao and Zihui (1988) was employed to identify the various operationally defined forms of As, as follows:

1. *Water-soluble phase*. One gram of soil was extracted at room temperature for 30 min with 50 ml of deionized water under continuous shaking. The samples were centrifuged, filtered, and analyzed for soluble As.
2. *Exchangeable phase*. The residual soil from the water-soluble fraction step was shaken at room temperature for 30 min with 50 ml of 1 M NH_4Cl. The mixture was centrifuged, and the supernatant was analyzed for exchangeable As.
3. *Fe- and Al-bound phase*. The soil residue from step 2 was shaken at room temperature for 17 h with 50 ml of 0.1 M NaOH. The residue after centrifugation was washed twice using 25 ml of saturated NaCl solution. The supernatant from these washes were pooled and analyzed to determine the As fraction bound to Fe/Al oxides.
4. Ca- *and Mg-bound phase*. The residual soil was extracted using 50 ml of 0.25 M H_2SO_4 by shaking for 1 h at room temperature. The residue after centrifugation was washed twice using 25 ml of saturated NaCl solution. The supernatant from these washes were pooled and analyzed to determine the As fraction bound to Ca/Mg compounds.
5. *Organic matter and sulfide-bound phase*. The residual soil was digested using 3 ml of 30% H_2O_2 (adjusted to pH 2.0 using HNO_3) at 85°C for 3 h. To prevent adsorption of extracted As to the oxidized soil, the samples were cooled and 5 ml of 3.2 M NH_4OAc in diluted HNO_3 was added. The samples were diluted to 20 ml with deionized water, followed by shaking for 30 min at room temperature, and then analyzed to determine the soil organic matter and sulfide-bound As.
6. *Residual phase*. The remaining soil was extracted using 25 ml of concentrated HNO_3 at 105°C, until approximately 5 ml of solution remained. The samples were diluted to 25 ml with deionized water, centrifuged, and the supernatants were analyzed for As-bound to the silicate framework.

All the above separations were done by centrifugation at $3000 \times g$ for 30 min. The supernatants were filtered and analyzed for As using GFAAS.

16.2.4. In-vitro procedures

The fraction of bioaccessible As was estimated following the method of Rodriguez et al. (1999) with certain modifications made by Sarkar and Datta (2003). Reactions were carried out in 250 ml beakers in a 37°C water bath to stimulate body temperature. Anaerobic conditions were maintained by passing argon gas through the solutions. The pH of the solutions was continuously monitored. The in-vitro gastrointestinal method was conducted in two sequential phases, a low pH gastric phase, followed by a higher pH intestinal phase.

1. *Stomach phase*. The gastric-phase solution consisted of 0.15 M NaCl and 1% porcine pepsin (Sigma Chemical Co., St. Louis, Missouri). 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, at the end of which 10 ml of the solution was collected, centrifuged at 3000 × g for 30 min and analyzed by GFAAS.
2. *Absorbed-intestinal phase*. At the end of the stomach phase, 10 ml of the gastric solution was added to replace the solution removed for analysis The pH of the solution was adjusted 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, Missouri). To simulate absorption through the intestinal lining a 40-cm^2 filter paper strip coated with ferric oxide was used (Sarkar and O'Connor, 2001). The ferric 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 the solution was collected, centrifuged at 5000 rpm for 30 min and analyzed by GFAAS. As adsorbed by the ferric oxide strip was desorbed by shaking it vigorously in 80 ml of 1 N HNO_3 for 1 h.
3. *Preparation of ferric oxide strips*. Ferric oxide strips were prepared according to Sarkar and O'Connor (2001). In brief, Whatman no. 8 filter papers were immersed in a 10-g/100-ml ferric chloride solution for 1 h. The filter papers were air-dried, followed by immersion in a 2.7 M NH_4OH solution for 1 min for deposition of ferric oxide. The iron oxide-coated papers were air-dried and used to mimic As adsorption in the in-vitro absorbed-intestinal phase.

All analyses were carried out in triplicates and the results are shown as mean values. Replicates had to fall within 95–105% to be considered acceptable. Recoveries of 90–110% of spikes and external standards were considered acceptable.

16.3. Results and discussion

16.3.1. Soil properties

The soils for this greenhouse study were selected based on their potential differences with respect to As reactivity. It has been reported that soil properties, such as clay content, pH, CEC, total C, P, Ca and Mg contents, and oxalate-extractable Fe and Al contents influence soil speciation of As and hence, bioavailability (Adriano, 2001). Soil characterization data for Immokalee and Millhopper soils are shown in Table 16.1. The primary difference between these two soils was in their Fe/Al, Ca/Mg, and P contents. While the Immokalee soil is an acid sand with low Fe/Al, Ca/Mg, and P contents; Millhopper is an acid sandy loam with high extractable Fe/AL oxides, as well as high Ca/Mg and P content. Being sandy and lacking positively charged adsorptive surfaces (e.g. amorphous Fe/Al oxides), the Immokalee soil is likely to have minimal As retention capacity (Pierce and Moore, 1980; Oscarson et al., 1981) and hence, potential of increased As bioaccessibility. Millhopper soils, on the other hand, have high oxalate extractable Fe and Al (i.e., high amorphous Fe–Al oxide contents) and is likely to have higher As retention capacity, and hence, potential of decreased As bioaccessibility. Based on the incubation study results (Sarkar and Datta, 2004), Immokalee was used as a control soil to study the effect of soil properties such as Fe/Al, Ca/Mg, and P content in Millhopper in a dynamic greenhouse column setting. Both soils were slightly acidic with pH ranging from 6.0 to 6.4.

Table 16.1. Selective chemical properties of soils (Immokalee and Millhopper)

Properties		Immokalee	Millhopper
pH		6.0	6.4
EC ($\mu S\,cm^{-1}$)		59	145
CEC ($Cmol\,kg^{-1}$)		777	2356
Sand (%)		99.7	96.8
SOM (%)		0.84	4.38
As ($mg\,kg^{-1}$)		15.0	16.5
P ($mg\,kg^{-1}$)	Mehlich 3	4.0	134
	Total	208	4875
Ca + Mg ($mg\,kg^{-1}$)	Mehlich 3	266	886
	Total	1178	3155
Fe + Al ($mg\,kg^{-1}$)	Oxalate	66	704
	Total	212	4745

EC, Electrical conductivity; CEC, cation exchange capacity; SOM, soil organic matter.
Note: Data represent mean of three replicates.

Moreover, since Millhopper soils have high P content, retained As could potentially desorb from the pesticide-applied soil. Phosphorus has similar properties like As, and is likely to compete with As for sorption sites in soils, resulting in desorption and, hence, increased bioaccessibility (Woolson et al., 1973).

16.3.2. Total arsenic in soil, water, and plants after six months of soil equilibration

Figure 16.1 shows the distribution of As in soil and leachate water in the Immokalee and Millhopper soils amended with sodium arsenate at two rates 675 mg kg^{-1} and 1500 mg kg^{-1}. In case of Immokalee, for both pesticide application rates, the majority of As was present in the leachate. Very small amount of As was present in the surface soil. This is expected for Immokalee since it is a sandy soil with low extractable Fe/Al and, hence, very low As retention capacity. Therefore, the majority of As moved downwards to the bottom of the column, and became a part of the leachate water (Fig. 16.1). In soil, As is mainly associated with Fe oxides and hydroxides (Fassbender, 1974; Akins and Lewis, 1976; Hale et al., 1997). It has been found that the sorption of dissolved As on soil is controlled by Fe oxides (Fordham and Norrish, 1983; Elkhatib et al., 1984) and increases with Fe- and Al-oxide contents (Jacobs et al., 1970). Since Millhopper has high Fe/Al content, it has high As retention capacity compared to that of Immokalee. As a result, a significant amount of As was retained in the surface soil, to a similar degree in that of the leachate water (Fig. 16.1). Arsenic uptake by the rice plants was minimal in Immokalee soil (data off-scale in Fig. 16.1), and there was no growth of rice in the Millhopper soil. A review of phytotoxic levels of soil As found that inorganic As is five times more toxic in sands than in clay soils (Sheppard, 1992). This agrees with observations that plant uptake of As is usually relatively low on clays and slits and high on sands and sandy loams (Woolson, 1973; O'Neill, 1995). Because of the high concentration of As in the surface soil, the seedlings did not germinate in the Millhopper soil. However, in Immokalee, the majority of As leached downwards; hence, there was plant growth for both pesticide application rates. However, the amount of As taken up by the rice plants was negligible compared to the amount of As presents in the soil and the leachate.

16.3.3. Geochemical forms of arsenic in soils

Soil speciation is the process of identification and quantification of the various "operationally defined" species, forms or phases of metals and

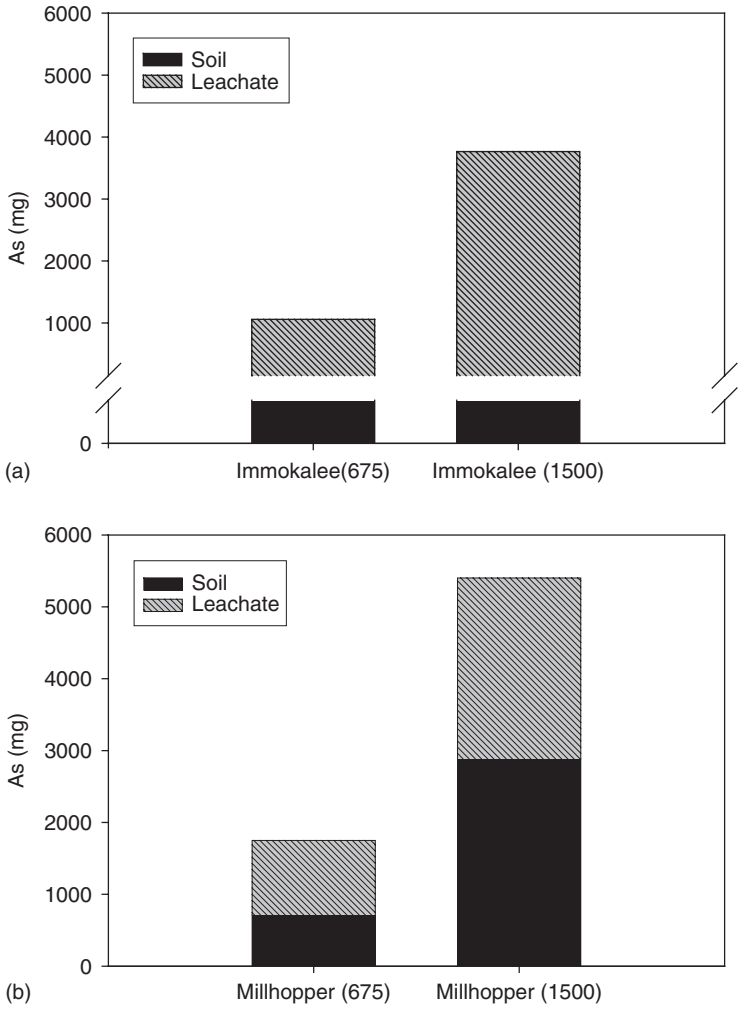

Figure 16.1. Mass balance for As in (a) Immokalee and (b) Millhopper soils. Plant As concentration in the Immokalee soil was minimal and there was no plant growth. So they are not shown here.

metalloids occurring in the soil (Pickering, 1981). Metals may occur in soils and sediments in various fractions, chemical species or forms: adsorptive-exchangeable, carbonate-bound, oxide-bound, organic matter-bound, and detrital or crystal lattice metals (Salomon and Forstner, 1980). These geochemical forms of heavy metals in soils affect their solubility, the risk of ground water pollution, and bioavailability (Harrison,

1981; Xian, 1989). It has been increasingly accepted that certain geochemical forms of arsenic are not bioavailable (Anawar et al., 2004).

Figure 16.2 shows the geochemical speciation of As for both soils amended with 675 mg kg^{-1} of As. In case of Immokalee soil, about 94%

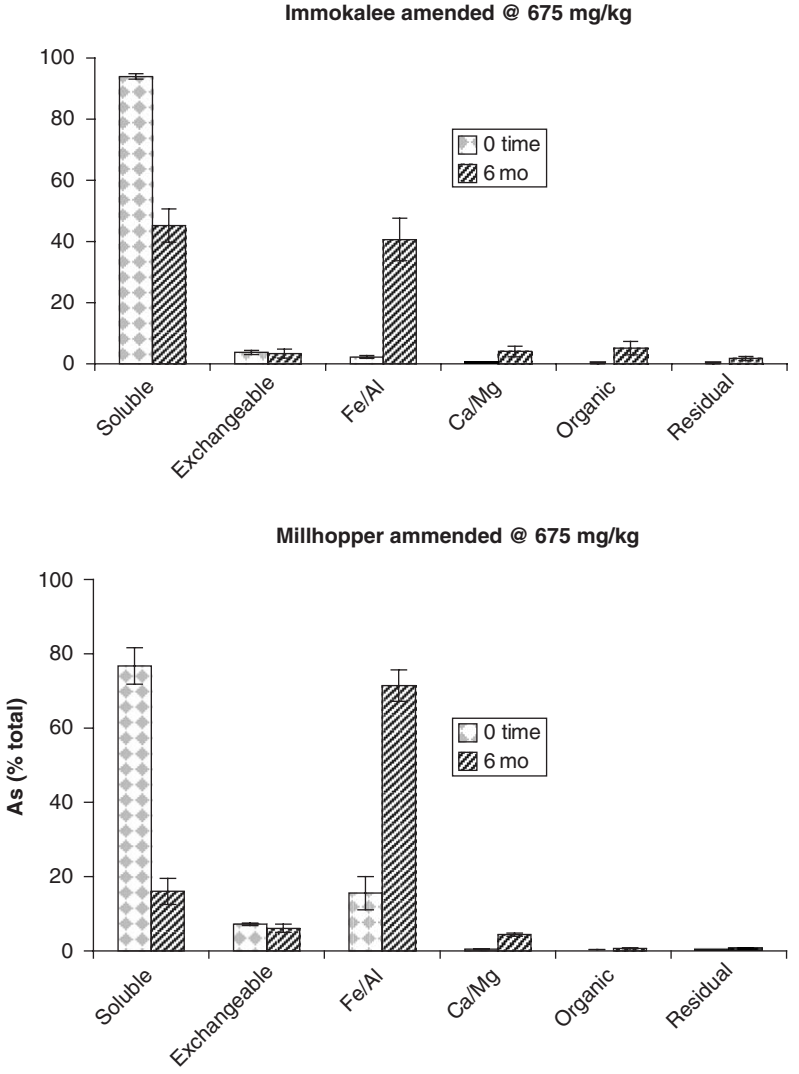

Figure 16.2. Geochemical speciation of As in pesticide-applied soil (675 mg kg^{-1} As) at time 0 and after 6 months of equilibration.

of the total applied As was extracted in the soluble fraction immediately after spiking the soil with pesticides (0 time). Since soluble fraction of As is considered both bioaccessible and phytoavailable (Sarkar and Datta, 2004), about 94% soluble fraction of the total As would have been available for plant uptake immediately after pesticide application. Owing to the phytotoxic effect of As seeds were not germinated. The phytotoxicity of As residues is influenced more by its chemical form than by amount. According to Woolson et al. (1971), soils with water-soluble As generally were more phytotoxic than those with no detectable water-soluble As. However, the soluble fraction of As decreased to 45% after six months of soil equilibration with pesticides. Moreover, after six months of soil equilibration, the Fe/Al-bound fraction increased from 2% to 41%. This indicated the strong tendency of the As oxyanions to be adsorbed by amorphous Fe/Al oxides, despite a low concentration of Fe/Al oxides in Immokalee soil natively. Very little As was extracted in the remaining fractions; cumulatively, the exchangeable, Ca/Mg-bound, organic bound, sulfide-bound, and residual As accounted for less than 10% of the total As in the surface soil at both times (Fig. 16.2). For the Millhopper soil, about 76% of the total applied As was extracted in the soluble form immediately after spiking; approximately 7% was extracted in the exchangeable fraction, and the Fe/Al-bound fraction contributed to about 16% (Fig. 16.2). After six months, the amount of As-bound to the soluble fraction decreased to 16%. However, at the same time, the amount of As retained by the Fe/Al fraction increased to 71%. Thus, after six months of soil–pesticide equilibration, the Fe/Al oxides proved to be the primary phase controlling As mobility in Millhopper soil, which had abundant oxalate-extractable Fe/Al natively. Similar results were obtained in both Immokalee and Millhopper contaminated with $1500\,mg\,kg^{-1}$ of As (data not shown).

16.3.4. Bioaccessible arsenic in soils

Human health risk from direct exposure to soil arsenic via hand-to-mouth action should ideally be restricted only to those fractions of As in the soil that are bioaccessible, i.e., available to the human gastrointestinal system (Datta and Sarkar, 2004). Arsenic exists in many geochemical and soil mineralogical forms, many of which are geochemically stable and/or insoluble in human gastric/intestinal juices and, hence, are not likely to be available for systemic absorption (Sarkar and Datta, 2004). According to Rodriguez (1998), As adsorbed hysterically to Fe/Al oxide is considered to be unavailable for plant uptake, and is also not likely to be bioavailable to human gastrointestinal system. Because calculated health risk is a direct

function of the input value for chemical dose (Ng, 1999), using total soil arsenic concentrations to quantify daily chemical intake for risk characterization typically results in carcinogenic risk results greater than the lowest possible amount (i.e., 10^{-6}) for soils in naturally occurring background settings (Rodriguez et al., 2003). Thus, bioaccessible As should be used instead of total soil As (as is the current practice) to determine the risk associated with exposure to contaminated soil (Sarkar et al., 2004).

Bioaccessibility experiments were conducted to estimate the amount of arsenic that would be available to the human stomach as well as to the intestine. In the stomach phase (for $675\,mg\,kg^{-1}$ As application rate), approximately 80% of the total applied As was bioaccessible at 0 time in the Immokalee soil, while in Millhopper 85% of As was bioaccessible. However, after six months of soil–pesticide equilibration, bioaccessibility decreased to 51% and 62% in Immokalee and Millhopper soils, respectively (Fig. 16.3). In case of Immokalee soil (having less Fe/Al content and thus less As retention capacity) most of As was leached out after the first leaching. So the bioaccessibility for Immokalee soil was less compared to Millhopper soils which had more As owing to its high Fe/Al content. However, there was wide variability in experimental data represented by the large error bars. In the absorbed intestinal phase, in both soils, more than 85% of the applied As was bioaccessible at time 0; this decreased to 53% in Immokalee and 37% in Millhopper after six months of equilibration (Fig. 16.3). Since Millhopper soil has higher Fe/Al content (i.e., higher As retention capacity), a significant portion of the applied As was expected to be unavailable to the human gastrointestinal system. However, the results indicated that the virtually irreversible Fe/Al-bound As re-solubilized in the strong chemical environment that exists in the human gastrointestinal system, and hence, became bioaccessible. Similar trends were observed in soils contaminated with $1500\,mg\,kg^{-1}$ of As (data not shown).

16.3.5. Correlation between geochemical speciation and bioaccessibility of soil arsenic

Figure 16.4a,b shows the correlation between bioaccessible As (stomach phase) and As extracted by the different steps of the sequential extraction method. In case of Immokalee (Fig. 16.4a,b), at 0 time, the correlation between the bioaccessible and the soluble fraction was 68% and with the Fe/Al-bound forms, it was 62%. However, with an increase in equilibration time (six months), the correlation between bioaccessible and Fe/Al-bound As forms increased to 91% and the correlation between the

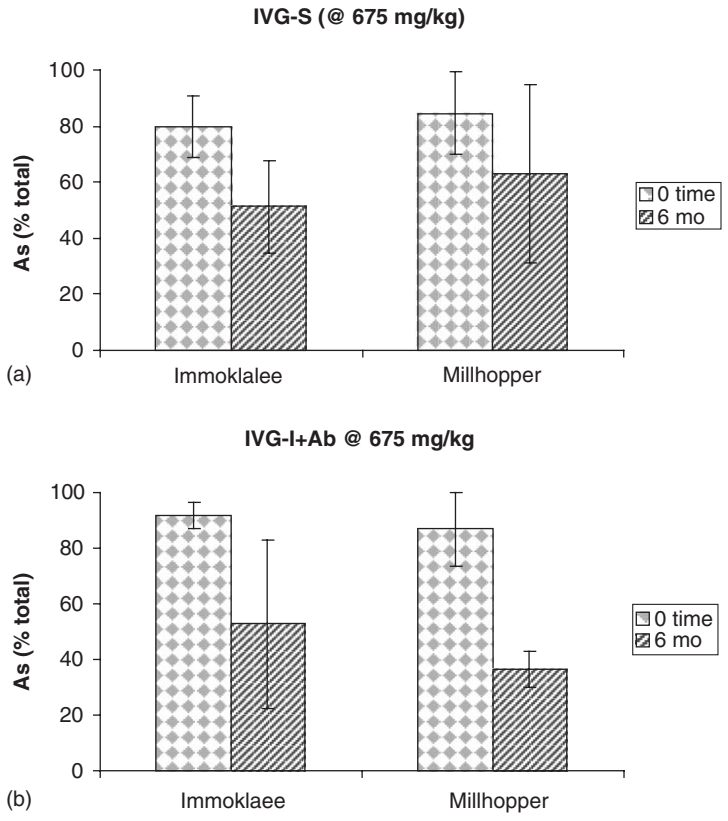

Figure 16.3. Arsenic bioavailability in pesticide-applied soils (675 mg kg^{-1}) using two in-vitro methods at time 0 and after 6 months equilibration.

bioaccessible and soluble As fraction decreased to 35%. Increase in correlation of bioaccessible As with the Fe/Al-bound As fraction was rather unexpected, because, as mentioned in the earlier paragraph, Fe/Al oxides are reported to adsorb As hysterically, thereby decreasing potentially bioaccessible As (Chen et al., 1999). Apparently, As-bound to Fe/Al oxides is not stable in the highly acidic (pH 1.8) environment of the stomach, resulting in re-dissolution of a fraction of adsorbed As, thereby accounting for the high correlation (91%) between bioaccessible As and that adsorbed by the Fe/Al phases in the soil. According to Rodriguez et al. (2003), the amount of arsenic dissolved in the stomach (i.e., potentially bioavailable) is comprised of As fractions between the surficially complexed (desorbable) As and As inside the mineral matrix associated with iron oxides.

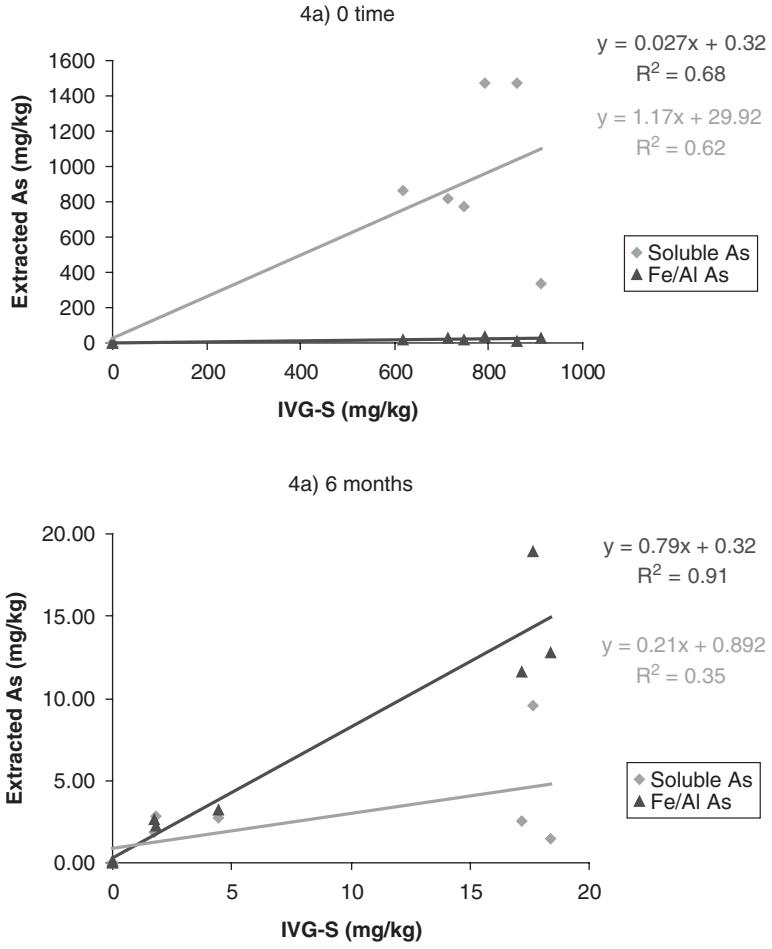

Figure 16.4. Relationship between bioavailable arsenic estimated using the in-vitro gastrointestinal stomach (IVG-S) method and As geochemical forms at time 0 and after 6 months equilibration in (a) Immokalee and (b) Millhopper.

For Millhopper soil (Fig. 16.4c,d) at 0 time, bioaccessible As strongly correlated with both soluble (86%) and Fe/Al (95%) bound As fractions. However, after six months of soil–pesticide equilibration the correlation between bioaccessible and Fe/Al-bound As decreased to 63%. This result is similar with an earlier incubation study on Millhopper soil contaminated with sodium arsenite pesticide (Datta and Sarkar, 2004). At 0 time when there is no soil–pesticide equilibration, the metastable As–Fe/Al phase that formed re-dissolved in the highly acidic environment of the

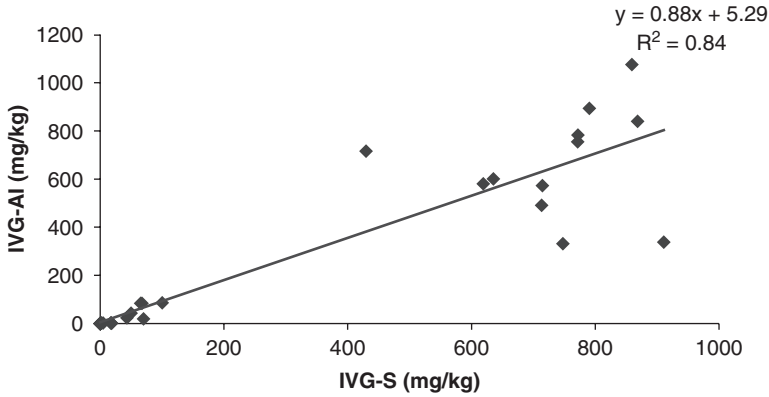

Figure 16.5. Correlation between As extracted by the two in-vitro methods. Data have been pooled for two soils contaminated with sodium arsenate at three rates for 0 and 6 months ($n = 36$). In-vitro gastrointestinal absorbed-intestinal (IVG-AI).

human stomach (pH 1.8). However, with time this phase stabilized and a fraction of As adsorbed onto Fe/Al oxides exhibited the classic hysteric character (Datta and Sarkar, 2004). Since hysterically adsorbed As is not bioaccessible, the correlation between the bioaccessible fraction and the Fe/Al-bound As decreased.

Similar results were obtained when As obtained from various steps of sequential extraction was correlated with bioaccessible As obtained by the IVG absorbed-intestinal method (data not shown). Figure 16.5 shows the correlation between As extracted by the two in-vitro bioaccessibility methods. A significant ($p \leqslant 0.01$) correlation coefficient (0.84) was obtained, indicating that both methods were extracting As from similar soil–As pools.

16.4. Conclusions

The reported greenhouse study demonstrated, similar to the earlier incubation experiment that soil properties have a marked impact on geochemical speciation of As, with the majority of As extracted in the soluble form at 0 time in both soils. Immokalee, being an acid sand with minimal oxalate-extractable Fe/Al had very low As retention capacity and thus, a very small amount of As was present in the surface soil after six months of soil–pesticide equilibration. The majority of the pesticide-applied As moved downwards to become a part of the leachate. As a result, some plant growth was observed in Immokalee soil. However, in case of

Millhopper, As was found in equivalent amounts in the surface soil and in the leachate. This resulted in no plant growth in Millhopper soil. After six months of soil–pesticide equilibration, the majority of As extracted in the Millhopper soil was in the Fe/Al-bound form. This indicated that As adsorbed onto the amorphous Fe/Al oxides, which resulted in decreased As bioaccessibility. However, the fact that not all As adsorbed onto the Fe/Al oxides were unavailable to the human gastrointestinal system indicated that part of the pre-adsorbed As re-dissolved in the harsh chemical environment of the simulated human stomach/intestinal juices. The reported study demonstrated that As bioaccessibility is a function of geochemical speciation of As, which is a function of soil chemical properties.

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