Distribution of Arsenic in Chemically Variant Dipping Vat Site Soils

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Arsenic is a naturally occurring element with soil background concentrations ranging between 0.1 to 40 mg kg^{-1} (Rodriguez, 1998). Anthropogenic activities such as mining, smelting of ore, and the widespread use of pesticides have resulted in higher than background concentrations of arsenic in the environment. The United States Environmental Protection Agency (USEPA) has classified arsenic as a Group A carcinogen. Chronic exposure to arsenic can result in impaired nerve functioning, various types of cancer, and impairment of kidney and liver functioning (Mandal et al., 2002). The primary pathways of human exposure to soil arsenic are *via* dermal contact, inhalation, and ingestion.

Historically arsenic has had many uses, such as medicine, pesticides, herbicides, and feed additives (Mandal et al., 2002). The global use of arsenic as a pesticide or herbicide has resulted in contamination of large areas previously used for agricultural purposes (Chappel, 1995). Mandal et al. (2002) reported that in 1955, worldwide production of white arsenic was 37,000 tons, out of which 10,800 tons were produced in the U.S. Once arsenical pesticides are applied to a soil, the toxic metalloid is likely to persist for several years even without further application (Walsh, 1975). The potential for migration of arsenic, as well as transformation from As(V) to the more toxic As(III) are also concerns for remediation of former agricultural sites, which are rapidly being developed for residential purposes.

Dipping vats (DV) filled with slurry of arsenical pesticides have been historically used to treat cattle and sheep for ticks (Ng, 1999). The dip structure is a concrete lined pool with a drop on one side and a ramp on the other. Animals were herded through and dropped into the vat at the drop side and allowed to swim to the ramp on the other side (McLaren et al., 1998). According to Ng (1999), each bath could contain about 2,800 gallons of dipping solution. However, not all dip structures were lined with concrete, allowing for the pesticides to leach through the soil and result in contamination of shallow groundwater underneath the vat. Moreover, the slurry was typically pumped out of the vat directly onto adjacent areas several times a year, resulting in further spreading of contamination.

DV sites are located throughout much of the Southern U.S. along the U.S.-Mexico border, where cattle imported from Mexico are dipped (Mulbry et al., 1996).

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Although arsenical pesticides are no longer used to prepare the dipping slurries, there are numerous DV sites in the U.S. that are contaminated with arsenic due to historical, indiscriminate usage of arsenical pesticides. Such contaminated DV sites are typically considered Superfund Sites in the U.S., but in other countries, such as Australia, old and unused dip sites are typically demolished, and the land is redeveloped for residential, recreational and horticultural use, some containing arsenic concentrations as high as 21,000 mg kg^{-1} (McLaren et al., 1998). However, majority of this soil arsenic may not be soluble, hence, not available for uptake by plants. Determination of plant uptake (i.e. phytoavailability) is critical when determining the potential exposure pathways for soil-borne contaminants (Juhasz et al., 2003).

A critical parameter that allows for realistic assessment of human health risk from exposure to arsenic-enriched soils is an estimate of bioavailability, i.e., the extent of absorption of a chemical into the bloodstream from the gastrointestinal tract, lungs, or skin (Halmes and Roberts, 1997). Hence, bioavailability is an inverse function of soil retention *via* processes such as adsorption, ion exchange, or precipitation. Factors that generally influence arsenic retention in soils include soil pH, amorphous iron and aluminum oxide contents, soil organic matter, concentrations of phosphorous, calcium, and magnesium, cation exchange capacity, and clay content (Adriano, 2001). Bioavailability of arsenic is currently determined using animal models, also known as *in-vivo* studies. *In-vivo* studies are time consuming, expensive, and require highly trained personnel, making such endeavors rather unappealing for regular, day-to-day practice. Several *in-vitro* methods ("beaker" models) for the estimation of bioavailable arsenic have been developed in recent years, which were able to simulate *in-vivo* data with varying degrees of success (Davis et al., 1992; Rodriguez et al., 1999). However, these studies did not take into account the issue of variability in soil properties and its effect on arsenic bioavailability.

The primary objective of the reported study was to assess the distribution of arsenic in five former DV site soils with variant physico-chemical characteristics. Arsenic speciation and bioavailability in pesticide-contaminated soils were also evaluated. A qualitative assessment of the impact of soil properties on arsenic fate in pesticide-applied soils was made. Correlations were drawn between human bioavailability and plant availability of arsenic with total soil arsenic.

MATERIALS AND METHODS

Soil samples were collected from five DV sites in the U.S. and Australia. The samples varied in soil chemical properties and background arsenic concentrations, representative of a wide range of pesticide contamination. The soils were dried at 105°C for at least 24 hours, ground lightly with a mortar and pestle and passed through the 2mm sieve (Chappell et al., 1995, McLaren et al., 1998). The soils were then characterized for pH, EC, clay content, soil organic matter, total carbon, phosphorus, calcium, magnesium and oxalate extractable iron and aluminum contents using standard methods described in Mylavarapu and Kennely (2002) and Sparks (1996).

Table 1. Soil properties

Site	Clay (%)	pH	CEC[¶] (Cmol kg⁻¹)	Ca+Mg (mg kg⁻¹)	Oxal Fe+Al (mg kg⁻¹)	Total C (%)	Total P (mg kg⁻¹)	Total As (mg kg⁻¹)
DV 1	2.5	6.7	817	1453	370	0.4	432	46.5
DV 2	7.2	5.3	1082	4014	942	1.4	354	220
DV 3	46.1	5.8	1163	1371	890	3.9	5243	1882
DV 4	30.5	5.7	1115	8599	430	5.8	814	1862
DV 5	38.5	6.7	1514	5150	870	1.4	988	1805

[¶]CEC = Cation Exchange Capacity; (n=15).

Sequential extraction was performed according to the procedure described by Chappel, et al. (1995) for the following operationally-defined soil-arsenic forms: 1) Water-soluble 2) Exchangeable 3) Fe- and Al-bound 4) Ca- and Mg-bound 5) Organic matter and Sulfide-bound and 6) Residual phase. Bioavailable arsenic was estimated following the *in-vitro* gastric method of Rodriguez et al. (1999) with certain modifications (Sarkar and Datta, 2003). Modified USEPA Method 3050B was used to analyze soils for total arsenic. Soluble and exchangeable arsenic obtained from the first two steps of the sequential extraction protocol were combined to obtain phytoavailable arsenic concentrations.

The extracts were filtered and analyzed for arsenic using a Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS). All analyses were carried out in triplicates and mean values were reported. Replicates had to fall within 95-105% to be considered acceptable. Recoveries of 90-110% of spikes and external standards were considered acceptable. Analyses that did not satisfy these QA/QC protocols were reanalyzed.

RESULTS AND DISCUSSION

The soils for this study were chosen based on the differences in their physical and chemical properties, such as clay content, pH, CEC, total C, P, Ca, and Mg contents, and oxalate-extractable Fe and Al contents, all of which are likely to influence soil speciation of arsenic, and hence arsenic bioavailability (Adriano, 2001). Soil characterization data are shown in Table 1. While arsenic concentrations in uncontaminated soils normally range between 0.1 to 40 mg kg⁻¹ (Rodriguez, 1998), total arsenic concentrations for DV soils in this study ranged between 46.5 and 1882 mg kg⁻¹ (Table 1).

Surface soils from DV 1 were found to be least contaminated with arsenic compared to soils from the other four sites. This sample represented a sandy soil with low clay content, and relatively low oxalate extractable Fe and Al concentrations (i.e., low amorphous Fe-Al oxide contents) and, hence, was least likely to retain arsenic in the upper six inches. There is a strong possibility that with time, the originally applied arsenic in DV 1 has migrated downwards to
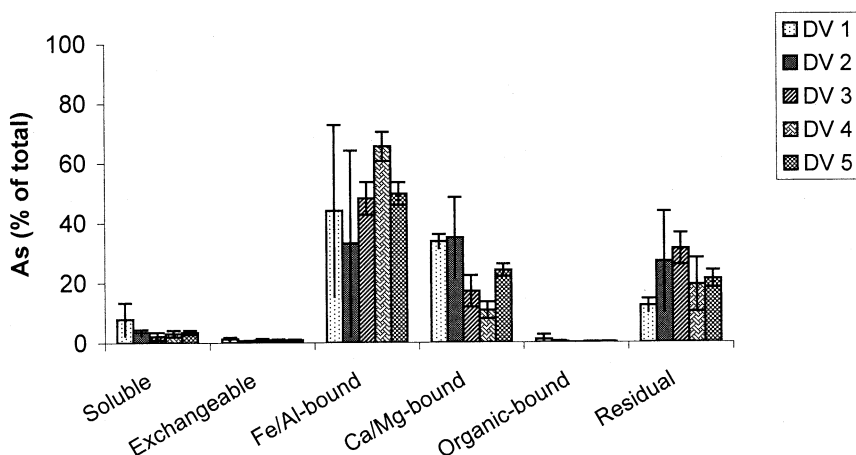
Figure 1. Geochemical speciation of arsenic in dipping vat site soils (n=15).

deeper soil horizons, resulting in a lower arsenic concentration in the surface soil. Out of the five soils studied, DV 3 had the highest total phosphorous concentration, much higher than soils from other DV sites selected for the reported study. Phosphorous is likely to compete with arsenic for sorption sites in soils, making arsenic more bioavailable, since phosphorous and arsenic are both Group V elements with similar chemical properties (Woolson et al., 1973). Also, phosphorous has a smaller ionic radius, enabling it to remove arsenic from sorption sites. Phosphorous concentration in the studied soils was higher than normal background level, possibly because of the application of organophosphate pesticides after the use of arsenical pesticides were banned (McLaren et al., 1998). Organophosphate pesticides are currently used in cattle dip vats along the Texas/Mexico border (Mulbry et al. 1996). McLaren et al. (1998) reported that phosphate concentrations were much higher in the DV soils they studied compared to normal agricultural soils. Woolson et al. (1973) reported that heavy additions of phosphorous to arsenic-enriched soils displaced 77% of total arsenic with the soluble fractions migrating to lower depths in the soil profile. Samples with higher clay contents (DV 3, 4, 5) had higher soil arsenic concentrations.

Figure 1 shows the percentage of total soil arsenic extracted at each step of the sequential extraction procedure. Majority of the arsenic extracted (33-66%) was bound to the Fe/Al fraction of the soils. Such high percentage of arsenic association with amorphous Fe/Al oxides was expected in soils from DV 2, 3, and 4, which had high concentrations of clay sized particles and oxalate-extractable Fe and Al. However, in soils from DV 1 and 2, where the clay content was much lower (amorphous Fe/Al oxide phases are typically smaller than 0.0039 mm in diameter), the Fe/Al fraction accounted for 33-45% of total soil arsenic. This demonstrates the very important role that sesquioxides of Fe and Al play as arsenic scavengers in soils. Soluble and exchangeable arsenic fractions (lablile forms) contributed to less than 10% of total arsenic, irrespective of the soil types. Majority of labile soil arsenic has either leached down the soil profile, or has been
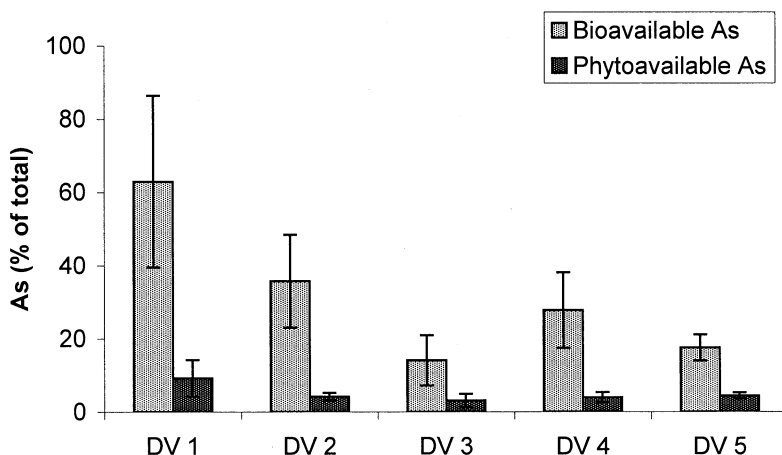
Figure 2. Bioavailable arsenic (extracted by the IVG-stomach method) and phytoavailable arsenic, both expressed as percentage of total As (n=15).

taken up by the plants, or has been converted to less mobile mineral forms, given the soil-pesticide equilibration time in the order of tens of years in the DV sites. A considerable percentage of total soil arsenic was associated with Ca/Mg phases (11-35%; Figure 1). This was not surprising given the relatively high Ca/Mg concentrations in all the soils studied (1371-8599 mgkg^{-1}; Table 1). At such high concentrations, arsenic generally forms precipitates with Ca or Mg, depending upon redox conditions (Datta and Sarkar, 2004). Residual arsenic accounted for a relatively large percentage of the total arsenic extracted from the soils (20-40%; Figure 1). Residual arsenic is very tightly bound to the mineral framework of the soil that is very difficult to extract under normal environmental conditions (Ng, 1999). The large residual arsenic fraction is a clear evidence of the impact of soil ageing on arsenic speciation. None of the soil samples had a high concentration of soil organic matter, as evidenced indirectly by the relatively low total carbon contents (0.4-5.8%; Table 1). Organic-bound arsenic fraction was found to be negligible in the sequential extraction scheme, generally accounting for less than 1% of the total soil arsenic (Figure 1).

Human health risk from direct exposure to soil arsenic via hand-to-mouth action should ideally be restricted only to those fractions of arsenic in the soil that are available to the human gastrointestinal system (Datta and Sarkar, 2004). Bioavailable arsenic can be used instead of total soil arsenic to determine the risk associated with exposure to contaminated soil. In the reported study, *in-vitro* bioavailability experiments were performed in order to obtain an estimate of the amount of arsenic that would be available to the human stomach. Rodriguez et al. (1999) used this approach to determine bioavailable arsenic in soils and obtained excellent correlations between *in-vitro* and *in-vivo* data generated using immature
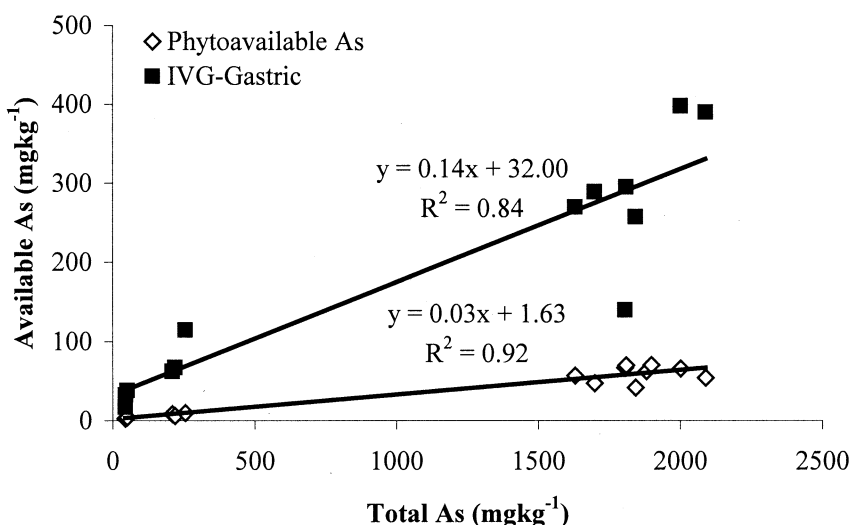
Figure 3. Correlation between total, bioavailable, and phytoavailable arsenic in soils from the DV sites (n=15)

swine, the only animal method currently approved by the USEPA. Results of the bioavailability study are shown in Figure 2. While DV 1 had the lowest amount of total soil arsenic (46.5 mg kg^{-1}) among the five study sites, bioavailable arsenic were significantly higher in DV 1 (63%) compared to the other soil samples examined in the reported study. This can be attributed to the sandy texture of the soil, which was characterized by it's very low clay content (2.5%) and the low amount of oxalate-extractable Fe/Al, contributing to lesser retention, and hence, greater arsenic bioavailability. This soil had the largest concentration of soluble arsenic, resulting in a relatively high phytoavailable arsenic pool (9%). The remaining soil samples had higher clay content, ranging between 7 and 57%, and higher oxalate-extractable Fe+Al (Table 1). Soil from DV 3 had the lowest percentage of phytoavailable and bioavailable arsenic (1.2 and 14%, respectively; Figure 2). Interestingly, DV 3 also had the highest concentration of total soil phosphorous (Table 1). Apparently, this relatively high concentration of phosphorus in soil was not able to out-compete arsenic from the surface sorption sites, which was expected based on reported literature (Woolsen et al., 1973; De Brouwere et al., 2004). High levels of amorphous Fe/Al oxides (i.e., high positive charge; large specific surface) in DV 3 soil (Table 1) provided sufficient binding sites for both arsenic and phosphorus oxianions. Arsenic adsorbed hysteritically to amorphous Fe/Al oxides is generally considered unavailable for plant and human uptake (Rodriguez, 1998). Soil from DV 4 had the largest concentration of Ca/Mg compounds (Table 1), and had ~30% bioavailable arsenic, although phytoavailable arsenic concentration was quite low (Figure 2). Apparently, arsenic associated with Ca/Mg phases is not available for plant uptake; however, the alkaline Ca/Mg phases could possibly re-dissolve in the acidic environment of the human gastric system, thereby increasing arsenic bioavailability.

Correlations were drawn between total, bioavailable, and phytoavailable arsenic in soils from the five DV sites (Figure 3). Total soil arsenic correlated highly with bioavailable and phytoavailable arsenic fractions (R^2 values of 0.84 and 0.96, respectively). Bioavailable arsenic also correlated highly with phytoavailable arsenic, with a correlation coefficient of 0.81 (data not shown), indicating that both availability methods were extracting arsenic from similar soil arsenic pools. The correlation coefficients were significant at $\alpha \leq 0.05$.

This study demonstrated that soil properties have a marked impact on geochemical speciation of arsenic. Because phytoavailability and human bioavailability of arsenic is a direct function of its geochemical speciation, consideration of soil properties is necessary when assessing human health risk from exposure to arsenic-enriched soils.

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