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Human health risk from arsenical pesticide contaminated soils: A long-term greenhouse study

Shahida Quazi[a,1], Dibyendu Sarkar[b], Rupali Datta[c,*]

[a] Environmental Geochemistry Laboratory, University of Texas at San Antonio, San Antonio, TX, USA
[b] Department of Earth and Environmental Studies, Montclair State University, Montclair, NJ, USA
[c] Department of Biological Sciences, Michigan Technological University, Houghton, MI, USA

HIGHLIGHTS

- Soil arsenic bioaccessibility is dependent on soil aging.
- Soil aging led to a decrease in cancer risk for arsenical pesticide amended soils.
- Organic arsenical changed to inorganic as a function of equilibration time.
- Excess cancer risk for 3 of the 4 soils was above USEPA's acceptable range.

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ABSTRACT

Arsenic (As) bioaccessibility is an important factor in estimating human health risk. Bioaccessibility of As in soils is primarily dependent on As adsorption, which varies with residence time. This study evaluated the effect of soil aging on potential lifetime cancer risk associated with chronic exposure to As contaminated soils. Four soils, chosen based on their differences in As reactivity, were amended with two arsenical pesticides – sodium arsenate, and dimethylarsinic acid (DMA) at two rates (675 and 1500 mg kg^{-1}). Rice was used as the test crop. Soil was sampled immediately after spiking, after 6 months, 1 year, and 3 years. Bioaccessible and total soil As concentrations were used to calculate lifetime excess cancer risk (ECR), which decreased significantly with soil–pesticide equilibration time. Immokalee soil, with the least As adsorption capacity, showed the highest decrease in ECR after 6 months resulting in values lower than the USEPA's cancer risk range of 1×10^{-4} to 1×10^{-6}. For all other soils, the ECR was much higher than the target range even after 3 years. In the absence of significant changes in As bioaccessibility with time, the total soil As concentration more directly influenced the changes in ECR values with soil aging.

1. Introduction

Arsenic contamination in soil has been the focus of regulatory actions at hazardous waste sites, to guide decisions on soil cleanup goals [1]. Health risk assessment plays an important role in these decisions. Incidental soil ingestion is one of the chief contributors to human health risk assessment, especially in children [2] due to their hand to mouth activity [3,4]. Conservative risk assessments that assume bioaccessibility to be 100% often do not accurately predict soil As toxicity [5]. Risk assessment using bioaccessible As concentrations is more realistic and would provide improved cost-benefit analysis of site remediation options [6]. Arsenic may be present in different geochemical forms, which vary in their bioaccessibility [5,7]. A site specific estimation of bioaccessible As helps in the accurate measurement of the risk at contaminated sites [8].

Elevated As concentrations in soil can result from both natural and anthropogenic sources [9]. In the 1940s inorganic pesticides were used extensively in the USA due to their low cost and effectiveness [10,11]. Although the USEPA banned the use of inorganic pesticides in the late 1980s and early 1990s, large agricultural tracts were already contaminated [12–14]. The use of less toxic organoarsenicals can also be a problem due to the conversion of organic species to inorganic As species by biotic and abiotic processes [15]. Lately, these methylated arsenical compounds except for monosodium methyl arsenate (MSMA) have also been phased out from the U.S. market, following their ineligibility for re-registration [16]. However, sites contaminated with years of organoarsenical pesticide application still exist [17]. The transformation of organic As pesticides to inorganic species affects the

* Corresponding author. Tel.: +1 906 487 1783; fax: +1 906 487 3167.
E-mail addresses: shahida.quazi@gmail.com (S. Quazi), sarkard@mail.montclair.edu (D. Sarkar), rupdatta@mtu.edu (R. Datta).
[1] Present address: Department of Physical and Environmental Sciences, University of Toronto, Toronto, Ontario, Canada.

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toxicity and bioavailability of arsenical pesticides [18,15]. Several studies have reported that organoarsenicals (DMA/MMA) convert to inorganic forms such as As(V) in soils. Studies by Woolson et al. [19] and Akkari et al. [20] have reported As(V) to be the predominant form in soils contaminated with DMA. The degradation of DMA to As(V) in cacodylic acid (DMA) contaminated soils have also been reported previously [18,21,22]. A previous greenhouse study in our lab with DMA contaminated soil also reported the presence of As(V) after 3 years of pesticide equilibration in gastric solution [23]. The inorganic forms present in the gastric solution in our study were a result of the dissolution of the As species that were already present in the surface of the solid phases in soil [23]. This was demonstrated in previous in vitro experiments using standard solutions of As(III), As(V), MMA, and DMA, in which no changes in oxidation state of As occurred [24]. A recent micro-X-ray absorption near edge structure (XANES) study by Shimizu et al. [25] confirmed the demethylation of dimethylarsenate to As(V) over a 1 year period under aerobic conditions. Woolson et al. [19] reported that 80% of the applied cacodylic acid (DMA) degraded predominantly to As(V) with small amounts of MMA within 60 days, where MMA was the intermediate byproduct of degradation of DMA to As(V). Similar results were also reported by Gao and Burau [21] and Sierra-Alvarez et al. [22]. Gao and Burau [21] also reported that 73% of initial DMA was demethylated to As(V) within 70 days. The conversion of organic arsenicals to inorganic forms is of serious concern due to increasing encroachment of suburban housing developments on agricultural land, escalating the risk of human exposure to As [4].

Potential lifetime ECR for soil contaminated with As is associated with the bioaccessible fraction of As [26]. Arsenic may be present as discrete mineral phases, co-precipitated with soil minerals or organic matter, or complexed by a variety of organic and inorganic ligands. Dissolution of As, and thereby As bioaccessibility is dependent on the distribution of As among these phases as well as the physical relation between the phases and soil [27,28]. Surface-bound As or a fraction present in the exterior portion of individual As-bearing grains is responsible for the bioaccessible fraction [28]. Since bioaccessibility is dependent on the As release from the solid phases, retention of As within the soil is an important factor in the evaluation of risk to contaminated soils [27]. Moreover, soil incubation time affects the contaminant retention. Studies have shown that contaminant availability decreases with soil incubation time [27]. Thus soil aging is an important factor in health risk. Earlier studies in our laboratory on soils spiked with sodium arsenate [29] and DMA [23] have shown that As bioaccessibility decreased with time. Studies have also reported that As bioaccessibility is a function of soil properties, which affects the cancer risk [4,30]. This study aimed to identify the effect of soil–pesticide equilibration time on As bioavailability and potential lifetime cancer risk due to chronic As exposure in a greenhouse setting. Arsenic bioaccessibility and total As concentrations at different time periods were used to calculate ECR as a function of soil aging.

2. Experimental

2.1. Soil sampling, preparation and characterization

Surface soils (0–15 cm) of the Immokalee, Millhopper, Pahokee Muck, and Orelia series were used for the current greenhouse study. Details of the soils are presented in Quazi et al. [29]. Soil pH, electrical conductivity, particle size, water content, and cation-exchange capacity were measured using standard protocols [31]. Mehlich III and Tamm's reagent were used to extract plant-available P and oxalate-extractable Fe/Al, respectively [31,32]. Total recoverable Ca, Mg, Fe, Al, P, and As values were obtained by soil digestion according to USEPA method 3050B [33]. Phosphorus was measured colorimetrically by an UV/Visible light spectrophotometer using the molybdate-ascorbic acid method [34]. Calcium, Mg, and Al were analyzed using flame atomic absorption spectrometry (FAAS), and As was analyzed via graphite furnace atomic absorption spectrometry (GFAAS). The analyses were carried out in triplicates and the results presented as mean values. Results were accepted only when the replicates were within the 95–105% of the mean value. Recoveries of 90–110% of spikes and external standards were considered acceptable.

2.2. Greenhouse study

2.2.1. Soil amendments and plant growth

Soils were amended with sodium arsenate and DMA at two rates (675 and 1500 mg As kg^{-1} soil), representing the higher and lower end of typical Superfund soil–As concentrations. Persistent use of arsenical pesticides in agricultural fields during multiple crop cycles also results in high arsenical concentrations that are similar to superfund As concentration. The PVC columns used in this study had the following dimensions: 33 cm tall × 15 cm internal diameter. The bottom 18 cm of the column was filled with white sand and the top 6 in. was filled with pesticide-spiked soils. The total number of columns used in this study were 48 (4 soils × 2 pesticides × 2 rates × 3 replicates) plus 12 controls (4 soils × 3 replicates). The columns were arranged in a randomized block design to account for variances in temperature and sunlight within the greenhouse. Each column was fitted with a nozzle at the bottom connected with Nalgene tubing to collect the excess leachate into a Nalgene bottle. Approximately 1 L of deionized water was added to each of the columns to induce leaching. After collection, the leachates were brought immediately to the laboratory and stored at −4 °C for analysis. The total As concentration of the leachate water was analyzed using the GFAAS. Rice was planted in the columns as a cover crop. Rice is often cultivated in agricultural lands that have accumulated arsenical pesticides at levels much higher than the baseline concentration [35]. In Bangladesh, paddy soils have been found to contain high As concentration due to the use of As laced water for irrigation [36,37]. Hence, rice was chosen to understand its tolerance to As. In this particular study, the results of the plant data have not been discussed, because uptake by rice plants was not significant, and had no influence on the risk.

Seeds were first surface-sterilized in 3% H_2O_2, rinsed with distilled water and then sowed directly to the soil [23]. Harvesting was done after six months of soil pesticide equilibration. The rice plants were watered regularly and Miracle-Gro® All purpose Plant Food was used as fertilizer. The soils were maintained at 70% water holding capacity. The first sampling of the soil was done immediately after spiking the soils with the two pesticides (time 0). Approximately 5 g of surface soils were collected at different time periods: time 0, after 6 months, 1 year, and 3 years and were used to assess the in vitro bioaccessible forms, geochemical forms and total As concentrations.

2.3. In vitro procedures

Arsenic bioaccessibility was estimated following the method described by Rodriguez et al. [2] with certain modifications made by Sarkar and Datta [38]. In brief, the experiments were carried in 250 mL beakers in a 37 °C water bath to simulate body temperature in two phases: a gastric phase (low pH) and an intestinal phase (high pH). For the gastric phase, 0.15 M NaCl and 1% porcine pepsin (Sigma Chemical Co., St. Louis, Missouri) and for the intestinal phase 525 mg of porcine bile extract and 52.5 mg of porcine pancreatin (Sigma Chemical Co., St. Louis, Missouri) were used. After the addition of soil to the gastric solution and adjusting the pH to 1.8, the solution was incubated for 1 h. In the case of the intestinal phase,