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Arsenic biogeochemistry and human health risk assessment in organo-arsenical pesticide-applied acidic and alkaline soils: An incubation study

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Abstract

Organo-arsenical compounds are considered non-carcinogenic, and hence, are still allowed by the regulatory agencies for use in agriculture as pesticides. Due to rapid encroachment of suburban areas into former agricultural lands, the potential for human exposure to soil-arsenic has increased tremendously in recent years. However, insufficient data is available on the stability of organo-arsenicals in soils; as to whether they remain in an organic form, or are converted over time to potentially carcinogenic inorganic forms. A static incubation study was conducted to estimate soil speciation and in-vitro bioavailability (i.e., bio-accessibility) of arsenic as a function of soil properties. Two chemically variant soil types were chosen, based on their potential differences with respect to arsenic reactivity: an acid sand with minimal arsenic retention capacity and an alkaline clay loam with relatively high concentrations of Fe/Al and Ca/Mg. The soils were amended with dimethylarsenic acid (DMA) at three rates, 45, 225 and 450 mg/kg, and incubated for 1 year. A sequential extraction scheme was employed to identify the geochemical forms of arsenic in soils, which were correlated with the in-vitro bioavailable fractions of arsenic. Human health risk calculated in terms of excess cancer risk (ECR) showed that risk assessment based on bioaccessible arsenic concentrations instead of the traditional total soil arsenic is a more realistic approach. Results showed that soil properties (such as pH, Fe/Al content and soil texture) of the two soils dictated the geochemical speciation, and hence, bioaccessibility of arsenic from DMA, indicating that the use of organic arsenicals as pesticides in mineral soils may not be a safe practice from a human health risk perspective.

Keywords: Dimethylarsenic acid; Geochemical speciation; In-vitro bioaccessibility; In-vivo bioavailability; Soil properties; Excess cancer risk

1. Introduction

Biogeochemical cycling of arsenic has been under intensive investigation due to the health risk associated with this group A human carcinogen (Frey and Edwards, 1997; Kim and Nriagu, 2000). Anthropogenic activities are considered to be the major contributor of arsenic found in contaminated sites (Cullen and Reimer, 1989; Nriagu, 1994; Davis et al., 2001). Several authors have addressed the problem of soil and groundwater contamination due to the use of arsenical pesticides (Carolyn et al., 2002; Chun, 2002; Brouwere et al., 2004). In the late eighties and early nineties, the USEPA banned usage of many inorganic arsenic-based pesticides (USEPA, 1992; Southworth, 1995). However, organic forms of

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arsenic are considered non-carcinogenic and are still being used on agricultural lands.

Organo-arsenical pesticides, such as monomethylarsenic acid (MMA) and dimethylarsenic acid (DMA), are used mainly as herbicides (Pongratz, 1998). Documented data indicate that transformation of organic and inorganic forms occur in soil systems, mainly through redox reactions and bio-transformation processes (Cullen et al., 1979; Henry et al., 1979), indicating that the transformation of non-carcinogenic organic arsenicals to carcinogenic inorganic species is possible in soil systems (Rodriguez, 1998), which might pose a significant health risk. However, the issue of the influence of soil properties on the transformation of organo-arsenical pesticides to inorganic forms has not been adequately addressed in a comprehensive study involving a variety of pesticide-contaminated soil types.

A critical parameter for realistic health risk assessment in arsenic-enriched soils is an estimate of "bioavailable" arsenic, which is the extent of absorption of a chemical into the bloodstream from the gastrointestinal tract, lungs or skin (Halmes and Roberts, 1997). Bioaccessibility of arsenic in soil types is dependent on several parameters that are controlled by the chemical composition of the soil. Evidence suggests that pH, redox potential, clay content, oxides/hydroxides, carbonates, organic matter and microbial community structure play a key role in speciation, retention and bioaccessibility of arsenic in soils (Woolson, 1977; Polemio et al., 1982; Sadiq, 1997; Adriano, 2001).

Due to rapid expansion of suburbia in the U.S., pesticide-applied former agricultural soils are now routinely being converted to residential developments. Ingestion of arsenic-contaminated soil due to incidental hand-to-mouth activity by children is now being increasingly taken into account in assessing human health risks associated with exposure to such soils. However, realistic methods to quantify the percentage of bioaccessible arsenic are rarely employed. The majority of the baseline risk assessment studies of Superfund sites have used the extremely conservative estimate that all (100%) arsenic present in soil is bioaccessible by equating arsenic solubility in water with that in soils. However, several in-vivo animal studies have shown that bioavailability of arsenic in soils may be significantly less than that in water. Ng et al. (1993) used rats to obtain a mean arsenic bioavailability value of 69%; Greon et al. (1994) used dogs to obtain an absolute arsenic bioavailability value of 8%; Rodriguez et al. (1999) used immature swine (the sole USEPA-approved model) and estimated relative bioavailable arsenic to vary between 2.7% and 42.8% depending on arsenic concentrations in soil ingestion dose. Because calculated health risk is a direct function of the input value for chemical dose, the assumption of using an input value of 100% bioaccessibility for exposure to arsenic-enriched soils potentially overestimates the actual risk, thereby elevating the expenses associated with site-cleanup. Moreover, arsenic exists in many geochemical/mineralogical forms in soils. Several of these arsenic species are geochemically stable and/or insoluble in human gastric/intestinal juices and, hence, are not likely to be available for systemic absorption. Therefore, an appropriate evaluation of pathway-specific arsenic bioaccessibility requires accurate, case-specific information on geochemical fate of arsenic.

Dimethylarsenic acid is considered to be a less toxic organic form of arsenic, and is commonly used as herbicide (Cai et al., 2002). While the toxicology of DMA has been extensively studied (Kenyon and Hughes, 2001), the environmental fate, stability, distribution and bioaccessibility of DMA and other organo-arsenicals in soils are still rather incompletely understood. Hence, a static incubation study was initiated as the first step toward understanding arsenic geochemistry in soils with varying chemical properties amended with DMA. The major objectives of this study reported here were: (i) to estimate bioaccessibility using an in-vitro technique, (ii) to decipher the relationship between soil-arsenic speciation and bioaccessibility, and (iii) to calculate the human health risk ensuing from exposure to DMA-contaminated soils. A follow-up column study allowing for dynamic interactions between soils, water, DMA and plants is currently in progress in a temperature and humidity controlled greenhouse setup.

2. Materials and methods

2.1. Soils sampling, characterization and laboratory incubation study design

The two types of soils used in this study, the Immokalee series Spodosol and the Tobosa series Vertisol, were collected from the surface horizons of Southwest Florida Research and Education Center, Immokalee, Florida and the Texas Agricultural Experiment Station, San Angelo, Texas, respectively. The soils were selected such that they vary widely in their pH, clay content, Fe/Al and Ca/Mg concentrations, to represent a range of properties that are important for arsenic retention and/or bioaccessibility. Air-dried and sieved (2 mm) soils were used for the determination of pH, electrical conductivity (EC), soil moisture and organic matter content using standard protocols (Sparks, 1996). Exchangeable cations were extracted by 1 M ammonium acetate (pH 7.0) and cation exchange