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Volatilization of Arsenic in Contaminated Cattle Dipping

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In Florida, as well as in many other southern states, one anthropogenic input of arsenic into soils can be attributed to the past extensive use of cattle dipping vats that were used to eradicate ticks. These vats were in operation from 1906 to 1962 (Graham 1977). Each vat could hold approximately fifteen hundred to two thousand gallons of arsenical solution (Dawson 1913). The amount of arsenic trioxide (white arsenic) added was enough to give a solution concentration typically about 1.92 mg/mL (Ellenberger 1919). These vats were generally emptied yearly onto adjacent soil, either untreated, as recommended by the U.S.D.A. (Ellenberger 1919) or treated, to form an insoluble compound as proposed by the Florida State Board of Health (Dawson 1913). There are approximately thirty-four hundred cattle dipping vat sites in Florida alone. With such an extensive introduction of arsenic into the soil, there is a need to understand the transport and redistribution mechanisms of arsenic in order to accurately assess the potential toxicity risk to humans and other life forms.

One redistribution mechanism is by volatilization. According to Sandberg and Allen (1975) as much as 35% of the arsenic species in soil may be eventually volatilized as arsine, dimethylarsine, and trimethylarsine. The production of volatile arsenic can be accomplished either aerobically or anaerobically. Anaerobically, bacteria such as *Methanobacterium, Pseudomonas,* and *Alcaligenes* have been cited as the causative agents (Cullen 1989). The volatilization of arsenic by bacteria under aerobic conditions has been demonstrated for *Staphylococcus aureus* and *E. coli* (Cullen 1989). Other microorganisms, besides bacteria, have been shown to convert arsenic to the volatile methylated species. Fungi, such as *Candida humicola, Gliocladium roseum* and *Penicillium* sp. have been shown to produce volatile trimethylarsine aerobically (Cullen 1989). Under aerobic conditions, soil treated with arsenate has been shown to evolve 1.5% of the arsenic as unidentified volatile species (Woolson 1977).

This study was conducted to establish the amount and location of volatile arsenic species at an arsenic contaminated cattle dipping vat site. Laboratory studies were undertaken to establish the relationship of oxic conditions in subsurface soils to the volatilization of arsenic. Other experiments were conducted to isolate and identify the causative agent.

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MATERIALS AND METHODS

The study site was adjacent to a cattle dipping vat in Paynes Prairie State Preserve outside Gainesville, Florida. The site was found to be contaminated with arsenic up to 110 mg As/g soil. The soil was identified as Millhopper sand, a loamy, siliceous, hyperthermic Grossarenic Paleudult. Soil samples for chemical and biological experimentation were taken by bucket auger at a depth of 132 centimeters and a distance of 12.2 meters from the vat, where arsenic contamination was the greatest. The samples were placed in plastic bags, transported to the laboratory and stored at 4°C until further use. No samples were stored for more than three months.

A surface soil gas flux trap was constructed using a plexiglass box, 15x30x30 cm, covered with aluminum foil resting on a 10-cm aluminum collar driven into the soil (Rolston 1986). Gas collection was facilitated by a 2.5 amp air pump attached to a rotameter set at 49.6 L/hr. Volatile arsenic gases were collected for six weeks into a Supelco ORBA-32 tube containing 0.65 g activated coconut charcoal. Subsurface soil gas samples were collected by passing 30 ml of gas through ORBA-32 tubes six times a month for one year using an apparatus made from 501 stainless steel 0.64 cm tubing with the sampling ports covered by "Gore-Tex" (expanded TFE on loosely woven polyester cloth from W.L. Gore, Inc.), (Magnussen 1989). Subsurface gas sampling probes were installed to a depth of 132 cm, with as little disturbance to the last 60 cm of soil as possible. An initial sampling was drawn off to evacuate the sampling tubes, following which the tubes were left undisturbed for two weeks. Control sampling tubes were installed at an equal depth and at an equal distance from the vat, but on the uphill side where no arsenic had been detected in the soil.

Manifold experiments were conducted by flushing 100 g arsenic contaminated soil samples in flasks with pre-moistened ambient air or industrial grade nitrogen. Samples of autoclaved soil, soil with 1 mL deionized sterile water, and soil with 1 mL sterile 20% aqueous glucose solution were examined in duplicate. The evolved volatile arsenic gas was collected on 0.65 g activated coconut charcoal (ORBA-32 tube by Supelco, Inc.).

A fungus was isolated from the arsenic contaminated soil by sequential 1:10 dilutions into a media of thiamine/succinic/glucose solution following Cox and Alexander (1973). The fungus was identified from the microchondrial structure as a *Fusarium* species. (Barr-on 1968). 100 mL media with 0.02 g $Na_2HAsO_4.7H_2O$ were inoculated with the *Fusarium* species. Volatile arsenic was swept from the flask by flushing with pre-moistened ambient air or industrial grade nitrogen. The arsenic fumes were collected on 0.65 g activated coconut charcoal.

All samples (0.65 g charcoal or 0.5 g soil) were digested by HNO_3 acid in Teflon bombs in accordance with E.P.A. method #3051 (U.S.E.P.A. 1992). All digests were diluted to 100 mL prior to analysis. Analysis of arsenic was accomplished using a Perkin-Elmer Atomic Absorption Spectrophotometer model 2380 equipped with

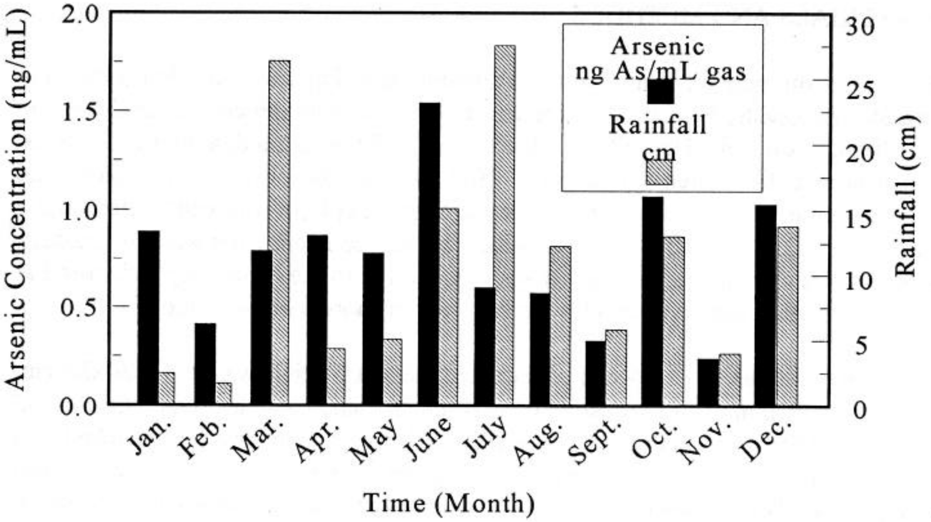

Figure 1. Sub-surface volatile arsenic gas flux and rainfall for 1996 at a contaminated cattle dipping vat site.

a graphite furnace model HGA-400 and an autosampler model AS-40. Deuterium lamp background correction was employed. Due to unknown interferences, all charcoal samples had to be analyzed by method of standard additions. Results were confirmed by Perkin-Elmer Hydride System model MHS-10.

RESULTS AND DISCUSSION

Volatile arsenic gas flux from off the surface soil at the selected cattle dipping vat site was not detected. Collection of gaseous arsenical species was attempted by continuously purging the air in a sample collection box situated over the area of greatest subsurface arsenic contamination (110 mg/g soil). At a gas flow rate of 49.6 L/hr, the 13.5 L collection box was fully purged every 11.2 minutes. These results conflicted with the findings reported by Braman (1975). The differences in results were attributed to the variation in arsenic's time of application and its placement. Braman (1975) applied sodium arsenite to the soil and grass surface, and immediately placed a bell jar over the applied area for sampling. In contrast, the soil at the cattle dipping vat site in this study was contaminated more than thirty years ago and the majority of the arsenic contamination at the sampling point was located at a depth of greater than 100 cm.

To ascertain that arsenic was being volatilized, subsurface probes were installed. The control samples did not show the presence of arsenic. Spearman rank non-parametric correlation test showed no relationship between arsenic volatilized and rainfall when all twelve datum pairs of arsenic concentration (ng/mL) and rainfall (cm) were used (Fig. 1). On the other hand, when the two months of excessive rainfall (> 25 cm) were

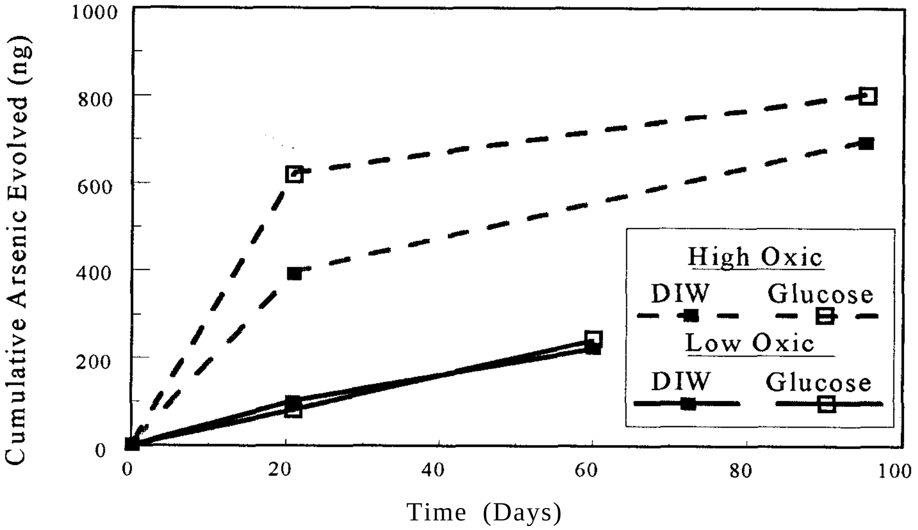

Figure 2. Cumulative volatile arsenic evolved from contaminated subsurface soil under various oxic conditions.

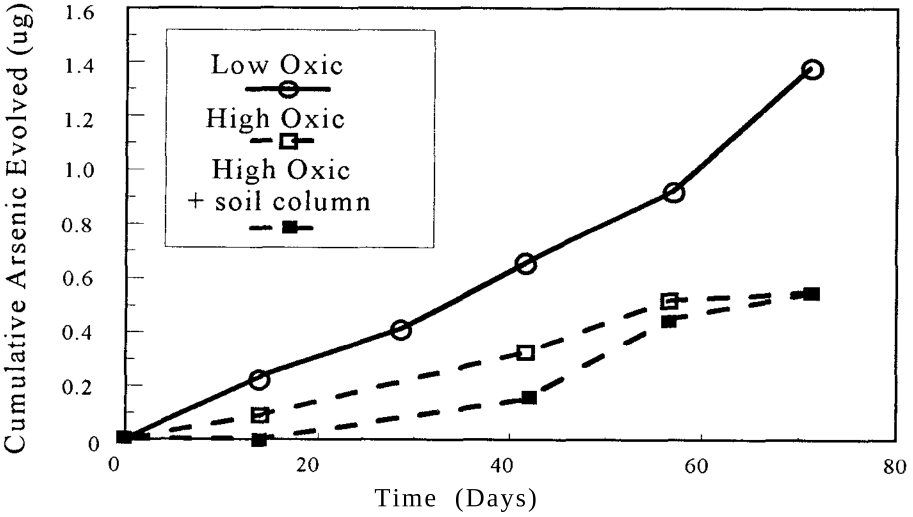

Figure 3. Volatilization of arsenic by *Fusarium* sp. under various oxic conditions with and without a soil column scrubber.

excluded, then a slight correlation was found. The rank correlation coefficient was 0.612 at a significance level of 0.06 (Eisensmith et al, 1992). Possible explanations are that the correlation under non-excessive rainfall was due to an influx of nutrients, while excessive rainfall may have limited volatile arsenic species by converting the gaseous arsenicals to another form or that the excessive rainfall caused oxygen depletion in the system which adversely affected the rate of volatile arsenic formation.

The data in Figure 1 showed that the arsenic was being volatilized in situ at the Payne's Prairie site. Less arsenic was volatilized under low oxic conditions (O_2 = 250 ppm) than high oxic conditions (ambient air) with and without glucose (Fig. 2). Glucose addition had no effect under low oxic conditions. In contrast, arsenic volatilization was stimulated by glucose addition under high oxic conditions. Hyphae were found to develop throughout the soil samples in the high oxic/glucose flasks.

A *Fusarium* species that was isolated from the soil was placed in arsenic media under high and low oxic conditions (Fig. 3). To test the hypothesis that the re-adsorption by overlying soil was inhibiting the release of volatile arsenic to the atmosphere, ten grams of 0-5 cm surface soil were packed into small columns and placed in line after the inoculated fungal media flask, but before the charcoal collection tube, for two of the high oxic samples. Initially, the soil appeared to reduce the amount of As reaching the carbon trap; however, the student's t-test revealed no statistical difference in the means with or without the soil columns. In comparing the effect of the oxygen level, it was found that low levels stimulated the release of volatile arsenic species. This was attributed to the formation of a fungal mat on top of the media for the low oxic levels; in contrast, under higher oxygen content, the fungus was distributed throughout the media. In the high oxic cases, arsenic species produced may not evolve from the aqueous solution before being converted to a nonvolatile species. Stability diagrams for arsenic in aqueous systems of pH=4-10 showed that, regardless of pE, arsenic acid was the only stable species (Cullen 1989). This suggests that conversion kinetics determined the amount of gaseous arsenic evolved.

We are currently investigating other sites to learn if arsenic is being volatilized and if so, we will attempt to identify the causative agents.

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