



Processes controlling arsenic solubility and mobility in soils
by Clain Alan Jones

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Crop and Soil Science
Montana State University
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Abstract:

The practice of liming to remediate contaminated soils and mine tailings has the potential to mobilize arsenic (As), due to the pH dependence of As sorption reactions on oxide minerals and layer silicate minerals. Two low pH samples (pond tailings and reprocessed tailings) collected near Anaconda, Montana were subjected to unsaturated column transport experiments before and after liming. Soluble As concentrations measured in column effluent increased by factors of 10 (reprocessed tailings) to 400 (pond tailings) following liming. Based on the experimental data collected, increased mobility of As with liming appears to be consistent with the pH dependence of sorption reactions of As on Fe oxide minerals rather than dissolution-precipitation reactions involving As.

Groundwater As concentrations in the northern portion of the Lower Madison River Valley, Montana, are above the state human health standard ($0.24 \mu\text{M}$) and correlate with high soluble As concentrations in overlying soils. Sixteen paired (irrigated and nonirrigated) sites were sampled in four major regions adjacent to the Madison and Upper Missouri Rivers to determine if the contamination was caused by irrigation. There were no significant differences ($\alpha=0.05$) in total or soluble As concentrations between irrigated and nonirrigated soils within any of the four regions. In addition, sorption coefficients (K_d values) in six paired soils selected for additional chemical characterization were not significantly different ($\alpha=0.05$) between irrigated and nonirrigated sites. Based on the suite of data, it was determined that irrigation history has not significantly affected As solubility or attenuation capacities in soils of the study area.

Reduction of arsenate [As(V)] to arsenite [As(III)] influences the mobility and toxicity of As, yet the mechanisms controlling the rate of reduction in soils and natural waters are poorly understood. Reduction experiments were conducted anaerobically in serum bottles with a range of glucose and As(V) concentrations. At As(V) concentrations ranging from 6 to $600 \mu\text{M}$, the rate of As(V) reduction was first-order with respect to initial As(V) and highly dependent on the number of As(V) reducers. In a parallel study, reduction rates of As(V) with the unenriched population were evaluated in the presence of goethite or ferrihydrite. The results indicate that rates of As mobilization during reduction are strongly controlled by oxide surface area and As surface coverage.

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ABSTRACT

The practice of liming to remediate contaminated soils and mine tailings has the potential to mobilize arsenic (As), due to the pH dependence of As sorption reactions on oxide minerals and layer silicate minerals. Two low pH samples (pond tailings and reprocessed tailings) collected near Anaconda, Montana were subjected to unsaturated column transport experiments before and after liming. Soluble As concentrations measured in column effluent increased by factors of 10 (reprocessed tailings) to 400 (pond tailings) following liming. Based on the experimental data collected, increased mobility of As with liming appears to be consistent with the pH dependence of sorption reactions of As on Fe oxide minerals rather than dissolution-precipitation reactions involving As.

Groundwater As concentrations in the northern portion of the Lower Madison River Valley, Montana, are above the state human health standard ($0.24 \mu\text{M}$) and correlate with high soluble As concentrations in overlying soils. Sixteen paired (irrigated and nonirrigated) sites were sampled in four major regions adjacent to the Madison and Upper Missouri Rivers to determine if the contamination was caused by irrigation. There were no significant differences ($\alpha=0.05$) in total or soluble As concentrations between irrigated and nonirrigated soils within any of the four regions. In addition, sorption coefficients (K_d values) in six paired soils selected for additional chemical characterization were not significantly different ($\alpha=0.05$) between irrigated and nonirrigated sites. Based on the suite of data, it was determined that irrigation history has not significantly affected As solubility or attenuation capacities in soils of the study area.

Reduction of arsenate [As(V)] to arsenite [As(III)] influences the mobility and toxicity of As, yet the mechanisms controlling the rate of reduction in soils and natural waters are poorly understood. Reduction experiments were conducted anaerobically in serum bottles with a range of glucose and As(V) concentrations. At As(V) concentrations ranging from 6 to $600 \mu\text{M}$, the rate of As(V) reduction was first-order with respect to initial As(V) and highly dependent on the number of As(V) reducers. In a parallel study, reduction rates of As(V) with the unenriched population were evaluated in the presence of goethite or ferrihydrite. The results indicate that rates of As mobilization during reduction are strongly controlled by oxide surface area and As surface coverage.

CHAPTER 1

INTRODUCTION

Arsenic (As) is the twentieth most common element found in the earth's crust (Cullen and Reimer, 1989). Concentrations of As in many soils and waters are elevated due to geothermal activity, pesticide applications, and mining operations (Stauffer and Thompson, 1984; Peryea, 1991; Neuman et al., 1993a). High concentrations of As have been found to cause toxicity in plants, animals, and microorganisms (Tamaki and Frankenberger, 1992; Pontius et al., 1994; Jiang and Singh, 1994). Therefore, understanding the processes controlling the toxicity, solubility, and mobility of As should prove useful in developing management strategies designed to minimize impacts of As on living organisms.

The oxidation state, or valence, of As affects both its toxicity and mobility. The primary oxidation states (and chemical forms) of As are: +5 (arsenate), +3 (arsenite), 0 (elemental arsenic), -3 (arsine). Arsenate, As(V), is thermodynamically stable in oxidized environments and arsenite, As(III), is thermodynamically stable in reduced environments. At neutral pH, As(V) species are negatively charged (e.g. H_2AsO_4^- , HAsO_4^{2-}), whereas As(III) is uncharged (H_3AsO_3^0). Methylation of As(III) leads to the formation of organic As acids (e.g. methylarsonic acid, dimethylarsinic acid). In highly

reduced environments, As solid phases (As^0 , As_2S_3 , AsS) and arsine gases (AsH_3 , $(\text{CH}_3)_3\text{As}$) are thermodynamically stable.

Crop yields have been found to be significantly decreased ($\alpha=0.05$) by As application rates of 25 mg kg^{-1} for rice (Onken and Hossner, 1995) and 50 mg kg^{-1} for ryegrass and barley (Jiang and Singh, 1994). As(III) had a significantly greater effect than As(V) on yield of ryegrass ($\alpha=0.001$) and barley ($\alpha=0.01$), yet no significant effect on rice yield ($\alpha=0.05$). Growth of microorganisms has been found to be inhibited at $13 \mu\text{M}$ As(III), whereas the same population tolerated 1,000 fold more As(V) (Tamaki and Frankenberger, 1994). Mammalian toxicity is also dependent on As species based on the LD_{50} (dose that is lethal for 50% of test animals). For example, the LD_{50} in rats for As(V) and As(III) are 20 and 14 mg kg^{-1} , respectively, whereas the LD_{50} for dimethylarsinic acid ranges from 700 to $2,600 \text{ mg kg}^{-1}$ (Tamaki and Frankenberger, 1992). The observed differences in toxicity between As species for plants, microorganisms, and animals are likely due to differences in mechanisms causing toxicity. Synthesis of adenosine triphosphate (ATP) is inhibited by As(V) due to its similarity to phosphate, whereas As(III) inactivates enzymes by reacting with protein sulfhydryl groups (Tamaki and Frankenberger, 1992).

Chronic toxic effects of As exposure in humans include cancers of the skin, lung, bladder, and liver (Pontius et al., 1994). Much of the existing epidemiological data regarding chronic toxicity in humans was gathered from 60 villages in Taiwan, where As concentrations in drinking water range up to $13 \mu\text{M}$ (Brown and Chen, 1995).

A risk assessment conducted with these data found that the current EPA drinking water standard of $0.67 \mu\text{M}$ ($50 \mu\text{g L}^{-1}$) results in a 0.9 – 1.7% risk of death from cancer assuming an intake of 1 L d^{-1} (Pontius et al., 1994). However, a second evaluation of the data found no increased risk of cancer from drinking water containing less than $1.34 \mu\text{M}$ As (Brown and Chen, 1995). Although uncertainties exist regarding relationships between As concentration in drinking water and cancer risks, the compiled toxicological data demonstrate that As may be harmful to living organisms at concentrations commonly observed at contaminated sites (Korte and Fernando, 1991; Moore, 1994; Nimick et al., 1998).

Equilibrium solution concentrations of As(V) in soils are generally controlled by sorption processes, rather than precipitation/dissolution reactions, due to the high solubility of metal arsenates (Robins, 1981; Sadiq et al., 1983; Dove and Rimstidt, 1985; Nishimura et al., 1987). Iron, manganese, and aluminum oxides have been found to sorb 10 to 1,000 fold more As than layer silicates (montmorillonite, kaolinite) or calcite (Hingston et al., 1971; Oscarsson et al., 1981; Goldberg and Glaubig, 1988). Sorption of As(V) to iron and aluminum oxides has been found to decrease at high pH (Goldberg, 1986; Darland and Inskeep, 1997a; Raven et al., 1998); thus, it was hypothesized that liming As-contaminated soils may increase As mobility. Liming is a common practice used to raise pH and promote plant reestablishment in acidic, contaminated mine tailings, yet the effects of liming on As transport are not well established. Therefore, a study was undertaken to assess the effects of liming on As

mobility in mine tailings (Chap. 2). Results from this study should prove useful to mine remediation specialists in designing mitigation strategies for contaminated sites.

Geothermal hot springs in Yellowstone National Park have resulted in elevated concentrations of As in the Madison and Missouri Rivers (Nimick, 1998). A previous study suggested that high concentrations of As in soil porewaters of the Lower Madison River Valley, Montana were caused by evapoconcentration of As-rich irrigation water withdrawn from the Madison River (Sonderegger and Ohguchi, 1988). Therefore, a study (Chapter 3) was conducted to i) determine the effects of long-term irrigation on As solubility and ii) evaluate processes affecting As sorption and solubility in soils of the Madison and Upper Missouri Rivers.

Although As(III) does not sorb as strongly as As(V) to Fe oxides at low As:Fe ratios (Pierce and Moore, 1982), recent work shows that As(III) sorbs more strongly than As(V) at high As:Fe ratios (Manning et al., 1998; Raven et al., 1998; Sun and Doner, 1998). In sulfidic sediments, As(III)-sulfide solid phases (e.g. As_2S_3 , AsS) may control the solubility of As (Moore et al., 1988). Thus, the oxidation-reduction (redox) status of soils and waters may strongly control the mobility of As. Although the effects of redox potential on the thermodynamic stability of As(V) and As(III) species have been well established (Ferguson and Gavis, 1972), less is known about the rates of As(V) reduction to As(III) in either soils or waters. Therefore, a third study (Chapter 4) was undertaken to i) evaluate processes controlling microbial reduction rates of soluble As(V) and ii) determine the effects of reduction on As solubility in the presence of Fe oxides.

CHAPTER 2
ARSENIC TRANSPORT IN CONTAMINATED MINE TAILINGS
FOLLOWING LIMING

Introduction

Liming is an established, effective method for immobilizing trace metals, elevating pH, and promoting plant reestablishment in low pH, contaminated mine tailings (Neuman et al., 1993b); however, increases in soil pH may result in arsenic (As) mobilization due to the pH dependence of sorption reactions. This raises the concern of contaminating drinking water supplies following liming in soils or tailings containing elevated levels of As that are hydraulically connected to groundwater or surface water. The U.S. EPA may reduce the maximum contaminant level for As in drinking water from $0.67 \mu\text{M}$ to between 0.0067 and $0.134 \mu\text{M}$, due to recent evidence that the current criteria may result in human cancer risks as high as 13 in 1000 (Pontius et al., 1994). Consequently, there is significant interest in processes controlling the transport of As into surface or ground waters.

Previous studies have investigated the pH effects of As sorption on soils or well-characterized solid phases (Hingston et al., 1971; Goldberg and Glaubig, 1988).

Goldberg and Glaubig (1988) found that the sorption of arsenate by montmorillonite and kaolinite was highest near pH 5 and dropped significantly between pH 7 and 9. Hingston et al. (1971) determined that arsenate sorption on both goethite and gibbsite decreased with increasing pH. Goldberg (1986) reported good correlations between experimental and modeled arsenate sorption on Fe and Al oxides using a constant capacitance model, which assumed a ligand exchange mechanism. Jacobs et al. (1970) showed that the elimination of amorphous Fe and Al by treatment with oxalate substantially reduced or eliminated arsenate sorption capacity in 24 Wisconsin soils, implying soil arsenate was primarily sorbed to oxides of Fe and Al. In contrast, arsenate solid phases are generally believed to be nonexistent in surface soils, due to their relatively high solubility, except at high arsenate levels (Robins, 1981; Sadiq et al., 1983; Dove and Rimstidt, 1985; Nishimura et al., 1987). For example, Dove and Rimstidt (1985) found that at an Fe activity of 1 mM, arsenate activities needed to be at least 0.01 M for scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) to be stable, which is much higher than typically found in soil porewater. Thus, the effects of pH on arsenate solubility in soils are due primarily to surface complexation reactions rather than precipitation-dissolution reactions.

One of the recommended liming strategies for maximum metal immobilization in mine tailings of the Clark Fork River Basin of Montana consists of raising the soil pH to near 10, using a mixture of $\text{Ca}(\text{OH})_2$ and CaCO_3 and allowing the soil to equilibrate for approximately one year prior to plant reestablishment. During

equilibration, the pH generally declines to values near 8 (Schafer et al., 1989). Field research at contaminated mining sites in the Clark Fork Basin has shown that this liming strategy results in metal immobilization, yet may lead to As mobilization (Neuman et al., 1993a).

The objectives of the present study were to (i) determine the extent of As mobilization in low pH mine tailings after liming and (ii) evaluate probable mechanisms for increased As transport after liming. To accomplish these objectives, several representative mine tailings and metal-contaminated soils were characterized and two of the tailings were subjected to transport experiments with and without liming.

Material and Methods

Sample Collection and Characterization

Six samples (0 to 0.30-m depth) were collected within two km of an abandoned copper smelter located in Anaconda, Montana, and included pond tailings (PT), smelter stack deposits (SSD), and reprocessed tailings (RT). All sampling locations were within a site that was placed on the National Priority List in 1983 due to metal contamination following 96 years of copper smelting (Neuman et al., 1993b). Samples were collected in triplicate at two locations. Concentrations of total As and total cations (Ca, Cu, Fe, Mn, Pb, and Zn) were determined using X-ray fluorescence (Jones, 1982) and particle size analysis was performed using the hydrometer method

(Gee and Bauder, 1986). Saturated pastes (Rhoades, 1982) were centrifuged at 10,000 *g* and filtered through 0.20- μm nylon filters to characterize soil solution chemical content. The resulting filtrates were analyzed for dissolved organic carbon (DOC) using a Dohrmann DC 190; cations, B, and S by inductively coupled plasma spectrometry (ICP); and Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-} by ion chromatography (IC). Total alkalinity was measured by HCl titration to an inflection point near pH 4.5. These titrated samples were then sparged with N_2 (g) for more than 15 min, titrated to the original pH with NaOH, and retitrated to the inflection pH with HCl in order to calculate carbonate and noncarbonate alkalinity. Continuous-flow hydride generation atomic absorption spectrophotometry (HGAAS) was utilized to analyze As. Samples were acidified to 3M HCl, prereduced with 1% KI, and treated with both 5M HCl and 0.6% sodium borohydride (NaBH_4) in 0.5% NaOH. Flow rates were approximately 7 and 1 mL min^{-1} for samples and reagents, respectively. Generated arsine was quantified at 193.7 nm in an air-acetylene flame (Perkin Elmer 3100). The As detection limit, estimated as three standard deviations of 50 absorbance blank readings, was 3.4 nM. Free ion activities were estimated using the aqueous chemical equilibrium model, GEOCHEM (Sposito and Mattigod, 1979) as modified by Parker et al. (1987). Stability constants for pertinent aqueous complexes were obtained from compiled thermodynamic equilibrium data (Sadiq and Lindsay, 1979; Sposito and Mattigod, 1979; Nordstrom and May, 1989).

Each sample was subjected to a sequential extraction for As (Johnston and Barnard, 1979; Ganje and Rains, 1982) based on developed procedures for extraction of phosphorus (Olsen and Sommers, 1982) and organically bound metals (Tessier et al., 1979). Although sequential extractions yield only qualitative information on As fractionation, this procedure was useful for assessing the relative lability of As among the different samples. The method consisted of sequential extractions in the following order: 1 M NH_4Cl , 0.1 M NaOH , 0.3 M citrate bicarbonate (CB), 0.3 M citrate dithionate bicarbonate (CDB), 1 M HCl and 30% H_2O_2 /0.8 M NH_4OAc . All samples were analyzed for As with HGAAS; the CDB and H_2O_2 extracts were also analyzed with ICP. The residual solids were digested using a four acid heat-treatment (Welsch et al., 1990) and As levels in the resulting digests were determined using HGAAS.

Selected grains of pond tailings (PT) and reprocessed tailings (RT) were affixed to Al stubs, coated with C and viewed with a scanning electron microscope (SEM). The grains were mapped for 15 elements using energy dispersive analysis of x-rays (EDAX) to identify particles enriched in As, Fe, or S. Particles that contained high levels of these elements were analyzed in further detail to determine semiquantitative atomic ratios using standardless analysis with PROZA correction (Goldstein et al., 1992).

Column Experiments

Unsaturated column experiments were conducted on limed and unlimed PT and RT. Liming treatments consisted of adding a mix of 60% CaCO_3 /40% $\text{Ca}(\text{OH})_2$ at

concentrations of 3.0 and 25.6 g kg⁻¹ of PT and RT, respectively. The CaCO₃/Ca(OH)₂ ratio and liming concentrations were determined from acid-base accounting as part of a remedial investigation study (Schafer et al., 1989). The PT (25% sand, 56% silt, 19% clay) was diluted 3:1 with 40-200 mesh SiO₂ (Fluka) to assure adequate flow, whereas the RT (95% sand, 3% silt, 2% clay) was left undiluted. Columns (5 cm diameter, 20 cm long PVC pipe) were sealed with rubber O-rings in polycarbonate end caps. A plastic porous plate (Soil Measurement Systems, Las Cruces, New Mexico) was inserted within each bottom end cap to control soil matric potential. Soil columns were packed by tapping lightly between successive soil additions and then were saturated from the bottom with 5 mM K₂SO₄. Upon complete wetting, a 20 kPa vacuum was applied to the bottom of the column, and 5 mM K₂SO₄ was delivered to the top of the column at 10 mL hr⁻¹ with a syringe pump. This flow rate equates to a pore water velocity of approximately 1.7 cm hr⁻¹. The vacuum was adjusted over the course of the experiments to maintain volumetric water contents (θ_v) between 30-36% and 23-28% for the PT and RT, respectively. These water contents were well below the saturated water contents in each respective column. Under these conditions the columns remained aerated and it was assumed that soluble As was present as arsenate (As(V)) rather than arsenite (As(III)). Unlimed control columns were sampled for approximately 23 and 100 pore volumes for the PT and RT, respectively, then treated with a high pH influent (0.1 M KHCO₃, adjusted to pH 10.1 with KOH, and bubbled with air to maintain the pH level). All effluent samples were analyzed for pH, EC, As,

