

Arsenate and Arsenite Retention and Release in Oxide and Sulfide Dominated Systems

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Chapter 1

Final Project Summary

Project Number: TEX05091

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Problem and Research:

Metal pollution of surface water resources in Texas is a significant problem, and is caused by the inflow of sediments from oil fields, old mines and industrial sites, and by the discharge of metal contaminated sewage and industrial effluents. In the preliminary phases of this project we were interested in a range of contaminant metals; however, following early experiments it was determined that emphasis would be given to arsenic due to the importance of several arsenic contaminated sites in east and central Texas. Three important general field and laboratory observations have been made concerning arsenic and have served as a basis for these studies: (1) correlations between metal concentrations of suspended solids or sediments (as measured by the recommended EPA and USGS methods) and metal levels in fish are often poor, (2) metal concentrations in pore waters of bottom sediments are often highly variable (with time and space) and often considerably higher (but sometimes lower) than in the overlying water column, (3) arsenic speciation and solubility are strongly influenced by redox potential. Existing EPA and USGS methods for quantifying the arsenic level of sediment or suspended solids primarily involve digestion by strong acids. While these methods do provide an indication of total concentration of metals, they often do not provide a reliable measure of bioavailability, either directly to aqueous animals or indirectly through the food chain.

Inorganic arsenic exists primarily in the +3 or +5 oxidation states (depending on redox potential), and its reactions in soils and sediments are influenced by pH, redox potential, dissolved organic or inorganic components, and sediment colloids (especially Fe sulfides and Fe, Mn, and Al oxides and hydroxides) and organic matter. Arsenic is often concentrated at the surfaces of suspended and

sediment colloids (as surface adsorbed and occluded species or possibly as poorly ordered solid solutions). Arsenic (+3 and +5) is bound, by ligand bonding mechanisms, at the surfaces of solid phase Fe, Al and Mn oxides, though there are major discrepancies in the literature concerning the relative bonding strengths of arsenate and arsenite. These reactions at colloidal surfaces strongly influence its availability within the biosphere in oxidized systems. Arsenic (+3) is readily precipitated as As_2S_3 or coprecipitated in the FeS_2 or FeS structure, and these compounds often control the solubility of arsenic in low redox environments. Because of these reactions, arsenic is likely strongly influenced by the presence of inorganic sulfur.

The objectives of the study were as follows:

- (1) To characterize the concentrations and chemical forms of arsenic and the factors which influence its retention and release
- (2) To evaluate the role of the periodic oxidation/reduction processes that may occur in sediments on retention and release of arsenic
- (3) To evaluate the probable role of biologically induced processes (e.g., oxidation/reduction, acidification, and ligand exchange) which may influence the mobilization of precipitated or adsorbed arsenic
- (4) To develop surface dissolution procedures to assess heavy metal mobilization potential in sediments in the aquatic environment, with emphasis on calcareous stream bed sediments,

The primary benefit of this study will be to improve procedures for assessing the bioavailability and potential biological hazard of metals in suspended solids and sediments. Accomplishment of these objectives has enabled us to recommend procedures for assessing biohazard potential and ultimately to better monitor aquatic environments.

Methods, Procedures and Facilities

Sample Collection. Bottom sediment cores, suspended sediment samples, pore water samples and bulk water samples were obtained from an arsenic contaminated lake in Bryan, Texas. Preliminary samples were obtained from arsenic contaminated sites in the vicinity of Beaumont and Houston, TX. In the field, all samples were collected and maintained in such a manner as to avoid contact with the atmosphere.

Water Analysis and Arsenic Speciation. Water samples were filtered through 0.45 μm pore-size membrane filters and analyzed for pH, Eh, Fe, SO_4 , S^{2-} , As(3+), and As(5+) by electrometric, flame atomic absorption spectroscopy, graphite furnace atomic absorption spectroscopy, ion chromatography, and hydride generation atomic absorption spectroscopy procedures.

Mineralogical Analysis. The sediment samples were split into two fractions. One fraction was maintained in its reduced state in sealed bottles, with care taken to avoid contact with the atmosphere. The other samples were allowed to air dry. The air-dried samples were separated into sand, silt and clay particle-size separates, the particle-size distribution was determined, and the mineralogy of each fraction was determined by x-ray diffraction procedures. Particle size and morphology of selected sediment samples were evaluated by scanning electron microscopy (SEM) at the Electron Microscopy Center at Texas A&M University for the possible occurrence of pyrite. Amorphous Fe oxide, total Fe oxide and total Mn oxide were determined by extraction with ammonium oxalate in the dark at pH 3.0, citrate dithionite, and hydroxylamine hydrochloride, respectively. Carbonate and organic C were determined by a modification of the Allison wet-digestion procedure. The total arsenic content of both the oxidized and reduced sediments was determined by digestion of the soil in $\text{HNO}_3/\text{HF}/\text{H}_2\text{O}_2$ and analysis of the digest by hydride generation atomic absorption. Reduced sediment samples were analyzed by selective extraction procedures to obtain estimates of reactive or acid volatile sulfide (AVS) and total sulfide contents.

Selective Extraction Procedures. Selective extraction procedures for arsenic are utilized to obtain information concerning the dominant bonding modes for the various arsenic species, based on the suspected mode of action of the specific reagents. Selective extractions also give clues concerning the role that suspected biological agents may have on the mobilization and uptake of arsenic. Selective extractions were performed on both oxidized and reduced sediments. Selective extractants included H_2O , dilute HCl , CaCl_2 , $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, NaH_2PO_4 , DTPA, oxalic acid and citric.

Since the heavy metals are predominantly concentrated at the surfaces of the suspended and sediment colloids (as surface adsorbed and occluded species or as poorly ordered solid solutions), and since it is these surface layers which control the availability of metals within the biosphere, major emphasis was placed on evaluation of the surface dissolution procedures, e.g., the chelate extraction procedures.

Infrared Spectroscopy. Infrared spectroscopy provides valuable information concerning the mode of bonding (e.g., monodentate, bidentate, binuclear bridging) of oxyanions to colloidal surfaces. Infrared procedures have been available for several decades to evaluate bonding mechanisms in dried (dehydrated) systems, but only over the past few years has the technology evolved to enable the evaluation of bonding mechanisms in wet systems. Over the past year, we evaluated the application to horizontal attenuated total reflectance Fourier-transform infrared spectroscopy (HATR-FTIR) to determination of the mechanism of retention of phosphate and arsenate to sediment colloids in wet systems. Phosphate was used since this is an ion with which we have previous experience concerning molecular symmetry in dissolved and adsorbed states. These studies have significant implications to the factors influencing retention and release of arsenic in sediments and the possible modes of biological action which may influence arsenic mobilization.

Arsenic Retention and Release. Arsenic retention and release was evaluated in selected natural sediments and synthetic colloidal systems. The synthetic minerals provided analogs to the colloidal components of natural sediments and allowed us to test hypotheses of specific bonding and release mechanisms under controlled conditions. The minerals of predominant interest were ferrihydrite (an amorphous Fe oxide) and poorly ordered FeS, which represent the most reactive mineral phases under oxidized and reduced conditions, respectively. These are also the two mineral phases which are likely to control arsenic adsorption, release and solubility under oxidized and reduced conditions, respectively. The adsorption and release of arsenic was evaluated under changing redox regimes, i.e., during the reduction of oxidized sediments or the oxidation of reduced sediments. During these experiments, pH, redox potential, and dissolved As(3+), As(5+), Fe(2+), S²⁻ and SO₄²⁻ were monitored.

Principal Findings and Significance

Arsenic retention and release from sediments

The chemical and mineralogical compositions of the principal sediments for this study were determined. The sediments differed considerably in their native sulfur contents, as well as in their native Fe contents. In the oxidized state, the sulfur probably existed predominately in the SO₄ form, as dissolved SO₄, gypsum (CaSO₄) or barite (BaSO₄), and the Fe was present predominantly as Fe oxides as determined by selective dissolution procedures. Under extended reduced conditions, a significant proportion of the sulfate was apparently reduced to S²⁻. The arsenic was not readily extracted from reduced sediment by deionized water or neutral salts (KCl or MgCl₂) when oxygen was excluded during the actual extraction. Considerable arsenic was released from similarly reduced sediments when oxygenated extractants were utilized. In reduced sediments high in total sulfur, the arsenic was likely held predominately in association with S²⁻, probably as As(III), in either a mixed Fe/As sulfide phase or as As₂S₃. Upon exposure to air, the sulfide rich phases were rapidly oxidized (with concomitant increases in dissolved Fe²⁺ and SO₄²⁻), suggesting that the precipitated sulfide phases were predominantly fine grained and very reactive. When the sediments were exposed to oxidizing conditions for short periods of time, e.g., less than 1 hr., the concentration of dissolved arsenic and that extractable by neutral salts (KCl or MgCl₂) increased rapidly to values considerably above the EPA drinking water standard. The rate of achievement of the maximum dissolved arsenic concentration was highly dependent on the availability of O₂ and the rate of oxidation of S²⁻. Following the achievement of maximum dissolved As concentrations, there was a gradual reduction in the concentration of dissolved arsenic as well as of dissolved Fe²⁺, due to adsorption of As(3+) and As(5+) on the surfaces of the precipitating Fe oxide phase. The transformation of As(3+) to As(5+), as assessed by determination of solution As speciation, was remarkably fast in these systems. In spite of the relatively high total As concentrations, solution concentrations of arsenic were quite low following long term oxidation, i.e., longer than 48 h, indicating that arsenite and arsenate were

strongly bound to the Fe oxide surface. Most of the total arsenic (> 75 %) was extracted from the oxidized sediments by the relatively mild 0.1 M NaH₂PO₄ reagent, probably due to replacement of arsenate and arsenite by phosphate from the ligand binding sites at surfaces of the Fe oxides. The fact that not all of the bound arsenic was displaced by the ligand-exchange reagent indicates that some of the arsenic may have been bound or occluded at inaccessible (or slowly accessible) sites. Plant and microbially produced complexing reagents, such as citrate and oxalate, were also competitive with arsenate and arsenite for ligand binding sites. These results have significant implications to the possibility of a biologically induced desorption of arsenate and arsenite from soils and sediments. Results of this study indicate that arsenic is tightly bound in reduced sediments (though this reaction is highly dependent on the Fe/S ratios), but is readily released and then bound again upon oxidation of the reduced sediments. Arsenic is readily released from oxidized sediments by the action of competitive ligand exchange reagents. The major release of arsenic to the pore water occurs during the transformation between oxidizing and reducing conditions. The presence of native inorganic sulfur strongly influences the retention of arsenic under reduced conditions.

Arsenite and Arsenate Adsorption on Fe Oxides

Adsorption is one of the processes that affects the bioavailability and mobility of As in the environment. In oxidized systems, the oxide minerals, predominantly the Fe oxides, control the retention and release of As(III) and As(V). The objectives of this aspect of the study were to evaluate (i) the kinetics, equilibria, and H⁺ and OH⁻ release stoichiometry, and surface charge stoichiometry for the adsorption of arsenite and arsenate on ferrihydrite, and (ii) the pH dependence of arsenate and arsenite adsorption on this Fe oxide. Ferrihydrite was selected because of its high surface area and surface reactivity, and because this is a dominant Fe oxide phase which strongly influences the retention of arsenic in hydromorphic systems. A pH-stat unit was used to keep the pH constant during the reaction and to simultaneously monitor the net stoichiometry of H⁺ or OH⁻ released. Kinetic studies were carried out over time periods up to 96 h. Adsorption isotherms were obtained by equilibrating As at initial solution concentrations up to 26.7 mM, with 2 g L⁻¹ 2-line ferrihydrite suspensions. The adsorption reactions were relatively fast, with the reactions almost completed within the first few hours. Arsenite reacted faster than arsenate with the ferrihydrite at relatively high As concentrations, but arsenate adsorption was faster at low As concentrations and low pH. The best simple model to describe the kinetics of As adsorption was the parabolic diffusion equation. Adsorption maxima of approximately 0.60 (0.58) and 0.25 (0.16) mol_{As} mol_{Fe}⁻¹ were achieved for arsenite and arsenate, respectively, at pH 4.6 (pH 9.2 in parentheses). The very high arsenite retention, which precludes its retention entirely as surface adsorbed species, indicates the likelihood that ferrihydrite was transformed to a ferric arsenite phase, though this possibility has yet to be confirmed by spectroscopic studies. The general trend at initial arsenic concentrations ≥ 0.27 mol_{As} kg⁻¹ ferrihydrite within the pH range of 4 to 9, was increasing arsenite adsorption and decreasing arsenate

adsorption with increasing pH. At initial As concentrations of 0.27 to 0.80 mol_{As} kg⁻¹ ferrihydrite, the adsorption envelopes crossed at approximately pH 6 to 7.5, i.e., adsorbed arsenate concentrations were relatively greater than adsorbed arsenite concentrations at lower pH values whereas adsorbed arsenite was greater at higher pH. At the highest initial arsenic concentration studied, a distinct adsorption maximum was observed for arsenite adsorption at approximately pH 9.0, which corresponds closely to the first pK_a (9.2) of H₃AsO₃⁰, whereas there was a continuous drop in arsenate adsorption with increasing pH from 3 to 11. The adsorption isotherms followed either the Langmuir or the Freundlich equation. While arsenate adsorption released OH⁻, arsenite adsorption caused OH⁻ release at high pH and H⁺ release at low pH. The amount of H⁺ or OH⁻ released depended also on the As surface coverage.

Acid-base titration curves were developed for arsenite and arsenate by equilibrating 2 g L⁻¹ ferrihydrite suspensions containing initial As solution concentrations of 0, 0.53, and 1.60 mM with varying amounts of HCl and NaOH at 0.003, 0.01, and 0.1 M ionic strength. The pH in the supernatant was determined after a 24 h equilibration period. Adsorption envelopes were obtained by analyzing the corresponding supernatant solutions for As. Arsenite and arsenate adsorption decreased the charge of the ferrihydrite surface. The effect was more pronounced for arsenate adsorption. The decrease in surface charge was also dependent on pH, ionic strength, and As surface coverage. The pH dependence of the surface charge changes could be explained by surface complexation reactions, but the extent of several possible individual surface adsorption reactions could not be resolved using the surface charge data.

Significance Of Studies

Arsenic was retained by the sediment solid phases in the largest amounts either under strongly reducing conditions or under strongly oxidizing condition. Dissolved arsenic concentrations were greatest under shifting redox conditions, i.e., oxidized→reduced or reduced→oxidized. This observation has important implications to the management of arsenic contaminated sediments. The studies of the influence of pH on adsorption of arsenate and arsenite by ferrihydrite also have important implications to the management of arsenic contaminated sites.

In this study we did not directly assess biomobilization or absorption of arsenic by any organism, but the extraction and transformation studies do have important implications for the assessment of arsenic mobilization potential. Under reduced conditions arsenic is retained predominantly by association with sulfide (i.e., by coprecipitation with FeS, as As₂S₃, or by adsorption as arsenite). The poorly crystalline sulfides and arsenic associated with these phases are readily solubilized by reaction with weak acid, e.g., 0.1 M HCl. Therefore, this extraction (preferably under reduced conditions to prevent the reprecipitation of Fe oxide and resulting readsorption of arsenic) provides a reasonable assessment of arsenic potentially mobilized during the oxidation of reduced sediments.

Under oxidizing conditions, arsenic is predominantly retained by adsorption of arsenate and arsenite at Fe and Mn oxide surfaces. The bound arsenic can be desorbed by ligand exchange with ligands (e.g., phosphate) that are held more tightly than the arsenic. Therefore, KH_2PO_4 (e.g., 0.1 M) is a useful extractant for the assessment of the arsenic release potential from oxidized sediment. The EPA extraction procedure, which determines total arsenic, might also be a reasonable alternative for the determination of potentially mobilizable arsenic, since given the proper conditions, all sulfide and oxide bound arsenic could be potentially mobilized.

Training Accomplishments

<u>Field of Study</u>	<u>Undergraduate</u>	<u>Master's Degree</u>	<u>Ph.D. Degree</u>	<u>Post-Ph.D.</u>	<u>Total</u>
Chemistry	2				2
Agronomy	1	2	1	2	6

Funding Influenced by the Texas Water Resources Project

<u>Funding Agency</u>	<u>Topic</u> (abbreviated)	<u>Dates</u>	<u>Status</u>	<u>Amount</u>
Pantex	Bioaccumulation of P, U and heavy metals by plants	10/95-present	funded	\$ 421,000
Elf Atochem	Biohazard potential of As and heavy metals in stream- and pond-bed sediments	1994-96	funded	\$ 215,488
ARCO	In situ remediation of As contaminated soils	1/96-present	funded	\$ 50,000
DOE	EXAFS beam time for Cr and As studies	7/96-present	funded	\$ 20,000

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