Report for 2005AR77B: Flow and hydrochemical evolution of arsenic in ground water: tracking sources and sinks in the alluvial aquifer of southeastern Arkansas, USA

Publications

- There are no reported publications resulting from this project.

Report Follows

Problem and Research Objectives

Following the accumulation of evidence for the chronic toxicological health effects, including cancer, of arsenic (As) in drinking water, the United States Environmental Protection Agency (USEPA) recently reduced the maximum concentration level (MCL) for As from 50µg/L to 10µg/L (USEPA, 2001). Widespread high concentrations of arsenic in ground water (>10µg/L) have been documented in drinking-water aquifers in the West, the Great Lakes region, and New England. Moderate to high concentrations of As have been found in parts of the central and southern United States (Welch, 2003). The health impact of As to municipal water supply systems in Arkansas is low, based on analyses collected by the Arkansas Department of Health. However, recent publications documenting water quality in the Bayou Bartholomew watershed (Kresse and Fazio, 2002, 2003) revealed that 21 out of 118 irrigation water wells completed in shallow Quaternary alluvial deposits (alluvial aquifer) with a depth of 80-100 feet had As concentrations exceeding 10µg/L. Most municipal water supply wells in eastern Arkansas are advanced predominantly into deeper Tertiary Formations because of the problems associated with the high concentrations of Fe and Mn in the shallow alluvial aquifers. However, domestic wells completed in alluvial deposits may present risks to private well owners not protected by the Safe Drinking Water Act (SDWA).

This proposed study of the hydrogeology and hydrogeochemistry along the flow paths in both areal and vertical dimensions within the alluvial aquifer in southeastern Arkansas has implications for:

1) Understanding the geochemistry of soils, sediments, and ground water, and characterization of the spatial and vertical distribution and mobilization mechanism of As in different geochemical environments (soils, sediments, and ground water).

2) Identifying the temporary and permanent sources and sinks (mineral phases) for as in the aquifer.

3) Identifying the speciation of As in its total, dissolved, adsorbed, and organic forms.

4) Assessing the solubility or saturation indexes of important mineral phases in the aquifer and their relations to As partitioning and solubilities in the environment.

5) Understanding the flow pattern and hydrochemical evolution and fate of As in the ground water.

6) Application of geochemical modeling tools as an aid in predicting source, behavior, distribution, and fate of As in the alluvial aquifer.

7) Evaluation of model capability and sensitivity to model parameters in portraying the true field conditions.

8) Discussion of model limitations as an aid to predict geochemical processes occurring in the aquifer.

There is now considerable evidence that high-As ground water can be associated with reducing conditions, particularly in alluvial and deltaic environments (Smedley et. al., 2002).

The Bengal Basin in Bangladesh and India is the most notable example. While the precise mechanisms responsible for this remain uncertain, it is possible that both reductive desorption and reductive dissolution of As from oxides and clays play a vital role.

Statistical and graphical analysis of ground-water quality data provides strong corollary evidence of reductive dissolution of As bearing Fe oxyhydroxides as the releasing mechanism of elevated (>10µg/L) concentrations of As in the alluvial aquifer (Kresse and Fazio, 2002, 2003) in Arkansas. This conclusion was based solely on the occurrence and geochemical trends of some reduction sensitive parameters (as NO_3-N, NH_4-N, Fe, Mn, etc) in the aquifer. The present study is evaluating the following conceptual models of As mobilization and release mechanisms by interpreting chemical analyses of sediment and ground water, and results of model simulations:

1) As release mechanisms: we will test the three established conceptual models of As release mechanisms.

   a) The oxidation model (Acharyya, 1997; Pearse, 1995; Sinha Roy, 1997) would support the source of As in the aquifer as As-bearing sulfide minerals e.g. arsenopyrite, and that the mechanism of release is by oxidative dissolution. Thetrigger to oxidative dissolution is the anthropogenic factor of extensive groundwater development, which via lowering of the piezometric surface/water table has drawn atmospheric oxygen into a previously anoxic aquifer environment. As a result, an "oxidation front" is created where oxygen meets reduced sediments containing As-bearing pyrite (FeS_2), thus releasing As to the fluid phase.

   b) An alternate model, known as the Fe oxyhydroxide reduction model (Matisoff, 1982; Korte, 1991; BGS, 1999; Nickson et el. 1997, 1998, 2000), is now widely accepted as the principal mechanism of As mobilization in the ground water of the alluvial aquifers in many parts of the world. This model proposes that the As in the ground water derives from reductive dissolution of As-rich Fe oxyhydroxide that exists as a dispersed phase (e.g. as a coating) on sedimentary grains. The reductive dissolution process dissolves Fe oxyhydroxide and releases to ground

water both Fe^{2+} and the sorbed load of the Fe oxyhydroxide, which includes As.

c) The competitive ion exchange model (Acharyya et al., 2000) proposes that the high levels of As in ground water and its enhanced mobility are due to the competitive anion exchange between As-oxyanion and phosphate. Phosphate, which has a very similar adsorptive capacity as arsenate, will compete for the same adsorption sites on metal oxides, clay surfaces, organic matter, etc. This model assumes that the excessive use of fertilizers (artificial phosphate source) to augment agricultural output has affected As sorption, effectively displacing or "knocking" it off adsorption sites. This results in higher concentrations of As in ground water.

2) If the As releasing mechanism supports the reducing model, then we must justify whether the reductive dissolution (Guo et al., 1997; Nickson et al., 1997; Ahmed et al., 2004) or the reductive desorption (Zobrist et al., 2000;) is the prime geochemical process.

3) If the As releasing mechanism supports the reducing model, then we must justify the redox driver for iron oxyhydroxide reduction, as organic matter, such as peat, in the aquifer (Ravenscroft et al., 2001).

4) Organic carbon or its degradation products may quickly mobilize arsenic. Young carbon brought to depth by irrigation pumping plays a role in arsenic mobilization (Harvey et al., 2002).

5) High concentrations of As are localized mostly along the paleochannels (Nickson et al., 1998; Pal et al., 2002; Ghosh and Mukharjee, 2002) and are associated with the presence of sub-aerial peat layers along the paleochannels (Nickson et al., 1998, 2000; Ravencroft, 2001).

Methodology

The direction of groundwater flow in the Bayou Bartholomew aquifer is dominantly southward with the slope of the land within the watershed (Kresse and Fazio, 2002). So, the transect of drilling locations is oriented in an in a triangular pattern to the flow path. Three locations for monitoring wells were selected on the basis of arsenic screening data of Arkansas Department of Environmental Quality (ADEQ), geologic cross sections prepared from well log data of Arkansas Geologic Commission, ground water flow maps of United States Geological Survey (USGS), distribution of upper clay to silty clay aquitard. Three pairs of monitoring wells (each pair within a distance of 5 feet consists of one deep well of about 120 feet and one shallow well of about 30 to 40 feet) were drilled in three locations forming a triangle

Grain size analysis was done by using a micro pipette method (Miller et al., 1987). A five step sequential extraction (Modified from Tessier et al., 1979 and Chao and Zhou, 1983) was done to differentiate the exchangeable, carbonate, amorphous iron and manganese oxide, organic, and acid leachable fractions of arsenic and other chemical compounds. A separate water soluble extraction (Quevauviller, 2002) and a rigorous $HN0_3$- H_2S0_4 acid leachable (Adeloju et al., 1994) extraction were also done. A total of 60 sediments were extracted. Five duplicates, one gravel pack, one bentonite, eight wet sediments, and two coarse (>1mm) sediments were also extracted. The extracted solutions were shipped to ADEQ laboratory in Little Rock, Arkansas for analysis by ion coupled plasma – mass spectrophotometer (CP-MS).

1) Literature review of the present status of arsenic research in USA and in other arsenic affected areas in the world.

2) Sediment samples were collected continuously up to about 35 feet by 5 feet tube (CME spoon) sampler and after 35 feet 18 inches split spoon sampler was used at 5 feet interval. About 150 sediment samples were collected from the six wells. Sub samples of 300g of wet sediment cores were collected in 3 line zip bags to provide fresh sediment for preservation in freezer, and the rest of the collected sediment samples (cores) were archived in aluminum foil. All the sediment samples were transported to the geochemistry laboratory in the Department of Geosciences for further processing. About 100g of archived sediment cores were separated and dried below 40° C in an oven. The sediments were crushed using a conventional porcelain pestle and mortar and passed through a 1mm screen. These sediments were used for several single and sequential extraction procedures for major and trace elements including As.

   Proper sampling collection, handling, and preservation procedures of USGS's National Water-Quality Assessment (NAWQA) Program will be followed (Shelton et al., 1994).

3) After completion of the boring operation, monitoring wells were installed for groundwater quality monitoring and sampling. Standard sample collection and preservation procedures will be followed. A set of 4 samples will be collected in 60 ml high density polyethylene (HDPE) bottles:

   a) filtered and acidified (to 1%HNO_3), (2) filtered but not acidified, (3) not filtered and acidified, and (4) non filtered and non acidified. Another set of non filtered and non acidified samples will be collected in amber glass bottles for dissolved organic carbon. Dissolved ions including Ca^{2+}, Mg^{2+}, Na^+, K^+, SiO_2, As, Fe, Mn, PO_4^{3-}, SO_4^{2-} will be measured on the acidified samples. Dissolved $NO_3^-$and Cl^- will be measured on non acidified samples. Both filtered and non filtered samples will be run to find differences in concentrations, if any methods, sampling, and analytical protocols of

USGS's National Water-Quality Assessment (NAWQA) programs will be followed http://water.usgs.gov/nawqa/).

Parameters to be studied

1) Ground water chemistry: major ions, metals/metalloids including different forms of As (total, water soluble, adsorbed, and organic), Dissolved Oxygen (DO), Redox Potential (Eh), Total Organic Carbon (TOC), Organic Carbon (OC), Inorganic Carbon (IC), alkalinity, other possible redox indicators (e.g. Fe^{2+}, Fe^{3+}, Mn^{2+}, S^{2-}) pH, temperature (T), etc.

2) Sedimentology of soil and aquifer sediments: mineralogy, grain size, etc. Thin section petrography using binocular microscope, polarizing microscope, and scanning electron microscope) will be done to determine the characteristic detrital modes and to infer their provenance. If resources permit, mineral species in the sediments will be identified using X-ray diffraction (XRD), scanning electron microscopy – energy dispersive spectrometer (SEM-EDS) and electron probe micro analysis (EPMA) technology.

3) Chemistry of aquifer sediments: major ions, metals/metalloids including different forms of As (total, water soluble, adsorbed, and organic), DO, Eh, pH, EC, TOC, other possible redox indicators (e.g. Fe^{2+}, Fe^{3+}, Mn^{2+}, S^{2-}), pH, T, etc.

4) Soil pretreatment for a series of selective partial extractions will be carried out to separate the different As species. Separate extraction procedures will be run for other chemical parameters in sediment samples. Procedures of extraction will be those described by Ito (2001). The extractions for chemical forms and leaching agents will be as follows: (i) acid soluble form (As mainly fixed in carbonates), which will be leached using 0.1 M acetic acid; (ii) reducible form (As fixed in Fe- and /or Mn-oxides), which will be leached using 0.1 M hydroxylamine hydrochloride solution, adjusting pH to 2 using HNO_3 acid; (iii) organic form, which will be first decomposed by 0.1 M sodium pyrophosphate solution heated on a hot plate and dissolved into 1 M ammonium acetate solution; and (iv) insoluble form (As fixed mainly in sulfide and rarely in silicate minerals), which will be dissolved by a mixture of concentrated HNO_3 and $HClO_4$ acid if appropriate ventilation equipment is available to work with the $HCLO_4$.

5) Hydraulic properties: hydraulic conductivity and/or transmissivity, porosity, saturated thickness, water table elevations, etc.

<u>Geochemical Modeling</u>

Expertise with two geochemical modeling tools of PHREEQCI (Parkhurst 1995) and MINTEQA2 (Allison et al., 1991) was developed. These two geochemical modeling tools will be used to predict the solid phase partitioning of arsenic having a ratio of unity for modeled (solid phase arsenic derived from model simulation) to calculated (solid phase

arsenic derived by different extraction techniques) arsenic found in sediments. These modeling tools will also be used to predict the speciation of liquid phases and solubilities of mineral phases and their relation to As mobility in the aquifer. A 1 D-reactive transport geochemical model along the flow path for a considerable time interval will be simulated to predict future scale of arsenic contamination in the alluvial aquifer.

Forward modeling is used to predict water chemistry after completion of predetermined set of equilibrium reactions. Whereas, inverse modeling is used to suggest which geochemical processes take place along the flow path. Prediction of As behavior needs a combination of forward models with speciation and surface complexation capabilities. The program PHREEQC (Parkhurst, 1995), a forward model, has been extensively used to model evolution of ground water chemistry along a flow path. MINTEQA2 can be operated in forward and inverse modes. This model requires accurate ground water flow direction and the mineralogy of the sediments. If the necessary data are available, then MINTEQA2 model will be run in inverse mode.

Speciation Modeling

Speciation modeling provides a "snapshot" of the assumed equilibrium state of a dynamic system. That is, the chemical composition of a ground-water sample is provided, and assuming that the chemical species in the solution are at mutual equilibrium, the concentrations and activities of the various ionic species present are calculated. Speciation calculation can be used to indicate if some As bearing minerals can precipitate. Another application includes determination of saturation indices for minerals, which could be a sink for dissolved Fe (the highly suspected sink for As). Chemical analyses results of water and sediment collected from the 3 monitoring wells will be used as input into the speciation module of the PHREEQC program to achieve speciation and solubilities of mineral phases and their relation to As mobility in the aquifer.

Surface Complexation Modeling

Surface Complexation Models (SCM's) provide a rational interpretation of the physical and chemical processes of adsorption and are able to simulate adsorption in complex geochemical systems (Stollenwerk, 2003). The importance of oxides in controlling the concentration of As in natural water is well established (Matisoff et al., 1982). Iron oxyhydroxides are probably the most important adsorbents in sandy aquifers because of their greater abundance and the strong binding affinity (Smedley et al., 2001). The SCM module of PHREEQC considers hydrous ferrous oxide to be the single most important adsorbents of As in aquifers. A perfect simulation of the partitioning of arsenic would reveal all samples having a ratio of unity for modeled to calculated arsenic found on sediments. The first stage of the surface complexation modeling is to determine the model parameters:

1) Determination of the quantity of solid phase (iron oxides present in the aquifer sediments) concentration can be derived from petrographic analysis of sediment samples. Bulk sediment extraction data for total iron will be used as surface concentrations of iron.

2) Determination of surface site density of the solid phase (iron oxides) present in the aquifer. Literature values (Dzombak and Morel, 1990) will be used as a first approximation.

3) Determination of surface area of the solid phase (iron oxides). The best approach is to use literature values (Dzombak and Morel, 1990) of surface area as an initial estimate.

4) Determination of equilibrium constants for the mass action equations describing all relevant adsorption reactions. Dzombak and Morel (1990) database are used for PHREEQC.

Reasonable estimates of surface site density are important for accurate modeling of solute adsorption (Davis and Kent, 1990). Natural systems contain complex mixtures of minerals and it is difficult to quantify the concentration of surface sites for individual minerals. For consistency in applying the surface complexation modeling approach to natural systems, Davis and Kent (1990) recommended that equilibrium constants for strongly binding solutes be derived using the site density from Dzombak and Morel (1990) of 3.84 μmoles/m^2.

Inverse Mass Balance Modeling

Inverse mass balance modeling shows that if the chemistry of the start and end solutions along a flow path are known, possible mass transfer reactions that have produced the compositional difference may be determined. The extent to which these reactions have taken place, can be deduced from mass balance principles. So, this modeling approach will indicate which processes take place along the flow path. Inverse modeling is generally used to verify hypotheses on the origin of As (Sracek et al., 2004). The basic prerequisites of inverse modeling are the knowledge of flow pattern and information about mineralogy, including As mineral phases together with a full suite of chemical composition of ground water along the flow path. Results from mineralogical analysis and chemical analysis of ground water of the three wells, and aquifer properties (e.g. flow pattern) from existing flow models of southeastern Arkansas (Czarnecki et al., 2003) and data together with water-level data of the proposed three wells, will be used as an input into the Inverse Mass Balance module of PHREEQC to infer the geochemical processes occurring along the flow path.

Research To Be Completed

The following steps will be done to complete the research:

1) Mineral species in the sediments will be identified by using XRD. Surface properties of specific minerals (hosts minerals for arsenic as iron oxides, pyrites, etc.) will be identified by scanning electron microscopy – energy dispersive spectrometer (SEM-EDS).

2) More precise ground-water level measurement by survey grade GPS (Fast Static GPS Survey) will be conducted for investigating ground-water flow direction, particle movement, and physical ground water modeling.
3) Water samples will be collected from the six monitoring wells for total analysis of major, trace, and dissolved organic matter.
4) Arsenic speciation will be done on the six monitoring wells using an ion-exchange chromatography method modified after Grabinski (1981).
5) Three more extraction procedures to determine the FeII/FeIII ratio (the ratio of amorphous iron oxides to crystalline iron oxides), sediment sulfide contents, and total digestion for chemical elements in the sediments.
6) Geochemical model run (forward modeling)and sensitivity analysis. Compilation, analysis, and interpretation of chemical data from geochemical model run.
7) Finally, assessment of geochemical model findings, identification of source and sinks (permanent and temporary) for arsenic, releasing mechanism of As to ground water, prediction of future nature of As contamination problem, dissertation writing, writing papers for publication, etc.

Principal Findings and Significance

According to the grain size analysis results, available As screening data, and spatial distribution of upper clay to silty clay layer, the high As site is more sandy to a depth of approximately 25 feet from surface than the other two low As sites. Average level of the water table in the 3 sites varies from 18.5 to 24 feet. This observation suggests that high As sites are getting more recharge than the other two low As sites. One possible explanation for this observation is that vertical recharge has a relationship to As mobilization in the aquifer system. Our speculation is that As is being released from the sediments in a specific zone of the aquifer where seasonal water table fluctuation brings successive oxidation and reduction conditions. As is being released due to the complex interplay between redox reactions and microbial activities. The releasing As is going down due to recharge water and spatially distributed due to local flow dynamics. More detailed investigation will be followed for the conclusion.