

Arsenic Monitored Natural Attenuation: Successful Application and Current Research by IST

David R. Burris and H. James Reisinger
Integrated Science & Technology, Inc.

Arsenic is one of the most frequently encountered contaminants in soils and ground water at hazardous waste sites. There are a number of sources for arsenic in the environment, some due to man's activities and others that are naturally occurring. The U.S. Environmental Protection Agency has recently lowered its arsenic drinking water standard to 10 micrograms per liter ($\mu\text{g/L}$) due to a re-evaluation of health concerns. Lowering of the arsenic drinking water standard will likely place an added emphasis on the potential threats posed by arsenic at contaminated sites and remedial options to address those potential threats.

Anthropogenic sources for arsenic include a range of human activities including disposal of ash from the burning of coal or oil, arsenical pesticides, and mining and smelting operations. Mobilization of arsenic from these anthropogenic sources can lead to ground-water contamination. Arsenic in soils can also be derived from natural geologic sources, resulting in low milligram per kilogram (mg/kg) levels of naturally occurring arsenic. Arsenic that is naturally occurring in soils can be mobilized by human activities to cause ground-water contamination. For example, landfills or subsurface spills of organic liquids such as petroleum can alter geochemistry and mobilize arsenic. This mobility feature of arsenic geochemistry raises the possibility that some sites with organic plumes may also have unsuspected, though potentially significant dissolved arsenic issues.

Any potential human health threat caused by arsenic contamination of ground water, by either anthropogenic arsenic or mobilization of naturally occurring arsenic must be addressed. Arsenic monitored natural attenuation (MNA) is an important and cost-effective remedial option to be considered along with other possible, appropriate remedial actions.

Remediation approaches for arsenic-contaminated sites can vary depending upon site conditions. If there is no immediate hazard to human health and the environment, mitigation of arsenic ground-water contamination by natural attenuation processes (primarily involving sequestration or immobilization) may be an appropriate remedial option in combination with long-term monitoring (*i.e.*, MNA). Evaluation of MNA for arsenic at a specific site entails substantial site characterization to establish if the plume has reached steady state or is decreasing in size (or will likely decrease) and to assess which natural attenuation processes are occurring at the site.

MNA for organic contaminants such as petroleum hydrocarbons and, to a lesser extent, chlorinated solvents has become a widely accepted remediation option. Biodegradation is a dominant natural attenuation pathway for many organic contaminants, which is attractive since the contaminant goes away, along with its associated risk (if its degradation products are non-toxic). An inorganic contaminant like arsenic has its risk associated with the element itself (*i.e.*, it can not be degraded); however other natural attenuation processes may

mitigate arsenic's risk if ground-water concentrations are decreased (and arsenic mobility and/or bioavailability reduced) as a result of those operational natural attenuation processes.

Although MNA for arsenic is an appropriate remedial option at many sites, there has been limited regulatory acceptance to date. Improvements in our conceptual understanding of the relevant arsenic MNA processes and successful demonstrations of MNA for arsenic at contaminated sites should increase its regulatory acceptance and allow broader application of this remediation approach at appropriate sites.

IST is a leader in the development of arsenic MNA approaches, having gained regulatory approval for and having successfully applied MNA for arsenic at an industrial site in Georgia. In addition, IST is a key participant in a Federal, Strategic Environmental Research and Development Program (SERDP)-funded research effort examining arsenic sequestration processes in aquifers. This article briefly describes IST's activities in advancing the understanding regarding the appropriate application of arsenic MNA as a remediation option.

Successful Application of Arsenic MNA

The site where IST successfully applied arsenic MNA is an industrial plant located in Georgia. In the early 1960s, a low wetland area was filled with ash from the plant's steam boilers. The ash was produced by thermal oxidation (combustion) of coal, wood, and heavy oil. In 1984, a solid waste landfill was designed and built on top of the previously placed ash. The landfill was permitted by the state of Georgia and was used to dispose of cellulosic materials such as wood and paper waste as well as primary water treatment plant grit and sludge. The landfill is still active, and, at this point, the fill material has reached a height of approximately 30 feet above the ash surface. It is operated under a permit issued by the state, which requires ground-water monitoring per U.S. EPA Resource Conservation Recovery Act specifications. In the course of monitoring a series of monitoring wells that surrounded the landfill, data were generated that showed that the landfill impacted underlying ground water with arsenic at concentrations exceeding the then-accepted primary drinking water standard (50 µg/L).

The site is in the Georgia Coastal Plain Physiographic Province. It is topographically relatively flat and is underlain with interlayered silty and clayey sands. The water table is approximately 10 to 15 feet below ground surface. Ground-water flow is toward a river adjacent to the plant under a gradient of approximately 0.08 and an estimated average hydraulic conductivity of 3.4×10^{-4} feet per second, giving an estimated ground-water flow velocity in the 1,000-feet-per-year range; thus, the travel time from the landfill to the river can be estimated as less than 1 year. The surficial aquifer at the site is approximately 15 feet thick and is underlain by a confining unit of dense clay.

After it was determined that the landfill had impacted the site ground water with arsenic, state regulators mandated that the source of the arsenic in the landfill be determined. We hypothesized that the source of the arsenic was the ash on which the landfill was constructed. We set about testing our hypothesis through installation of ceramic cup vacuum lysimeter and piezometer pairs in the landfill, with the lysimeters placed in the

cellulosic waste and twinned piezometers in the underlying ash (the ash is primarily in the saturated zone) at selected locations. Samples of liquid from the waste and ash interstices were collected and analyzed for total and dissolved arsenic, pH, oxidation-reduction potential (ORP), dissolved oxygen (DO), specific conductance, and temperature. The results indicated that leachate from the cellulosic material contained nearly no detectable arsenic but was devoid of oxygen and strongly reducing. Samples of interstitial water from the underlying ash, however, contained arsenic concentrations in the milligrams per liter (mg/L) range.

Arsenic commonly exists in the environment in two oxidation states, pentavalent (relatively oxidized) and trivalent (relatively reduced) depending on several geochemical factors, two of the most important being Eh and pH. Further, the valence state of arsenic has profound effects on its behavior in the subsurface, including sorption potential, solubility, and aqueous mobility. Conducting a conceptual biogeochemical evaluation, we deduced that arsenic in the ash at the time of placement was likely in the pentavalent oxidation state as a result of generation in an oxygen-rich combustion environment. The data indicate that overlying cellulosic material in the landfill was producing highly reduced leachate due to microbial metabolism of dissolved organic material. Reduction of arsenic to its trivalent form would tend to increase its mobility. In addition, reduction of iron and manganese oxides on the ash could also have facilitated the mobility of arsenic, since arsenic is often associated with those minerals. Slightly higher pH in leachate samples may also have been a factor in arsenic mobility. Furthering the biogeochemical conceptual model of the site, it was hypothesized that a return to oxidizing conditions downgradient would reduce the arsenic mobility and thus reduce dissolved arsenic concentrations. Oxidizing conditions could return arsenic to its less mobile pentavalent state. Also, solubilized iron and manganese could oxidize and coat the aquifer matrix with hydrous metal oxide minerals, which are good sorbents for arsenic. Lowering of pH would also reduce arsenic mobility.

After the source of the arsenic had been identified, state guidance required that we delineate the horizontal and vertical extent of the dissolved plume. This was accomplished through sampling and analysis of ground-water samples from monitoring wells installed downgradient of the plume. Total and dissolved arsenic, pH, ORP, DO, and temperature were determined in each sample. The arsenic and ORP results for this initial 1999 sampling event are shown on Figures 1 and 2, respectively. Results of the analysis showed that the dissolved arsenic plume persisted to the point that the aquifer transitioned from reducing to oxidizing, and from relatively anoxic to oxygen-rich. Downgradient from this transition zone, little or no arsenic was detectable, consistent with the biogeochemical conceptual model developed for the site. Arsenic was not detected in a deep well installed downgradient in the aquifer beneath the confining unit, suggesting that the arsenic plume is limited to the surficial unconfined aquifer.

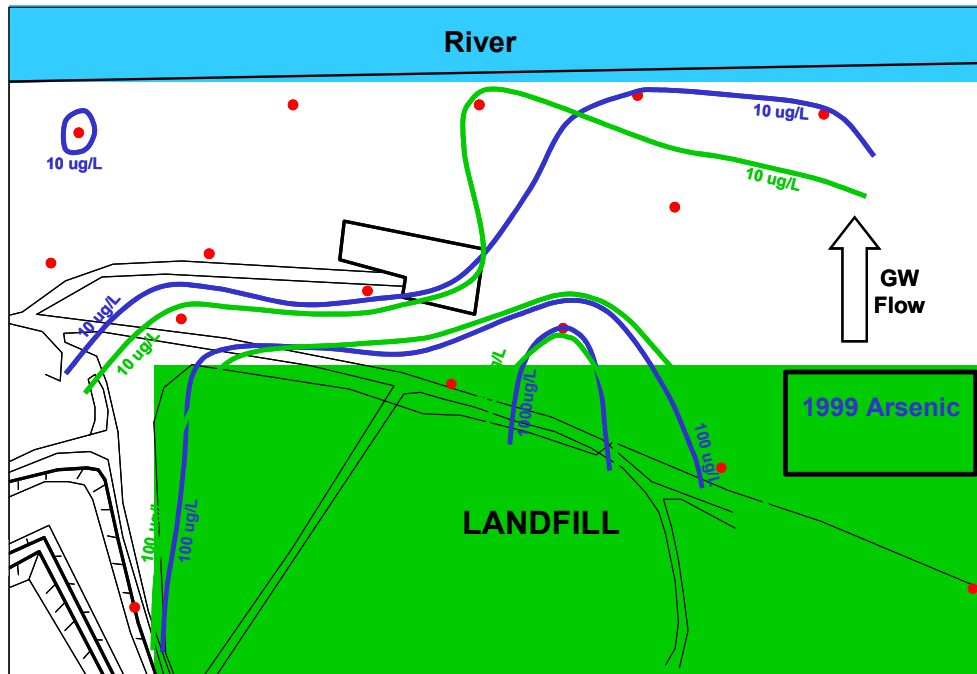


Figure 1. Dissolved arsenic ground-water concentrations in surficial aquifer during 1999 and 2004 sampling events.

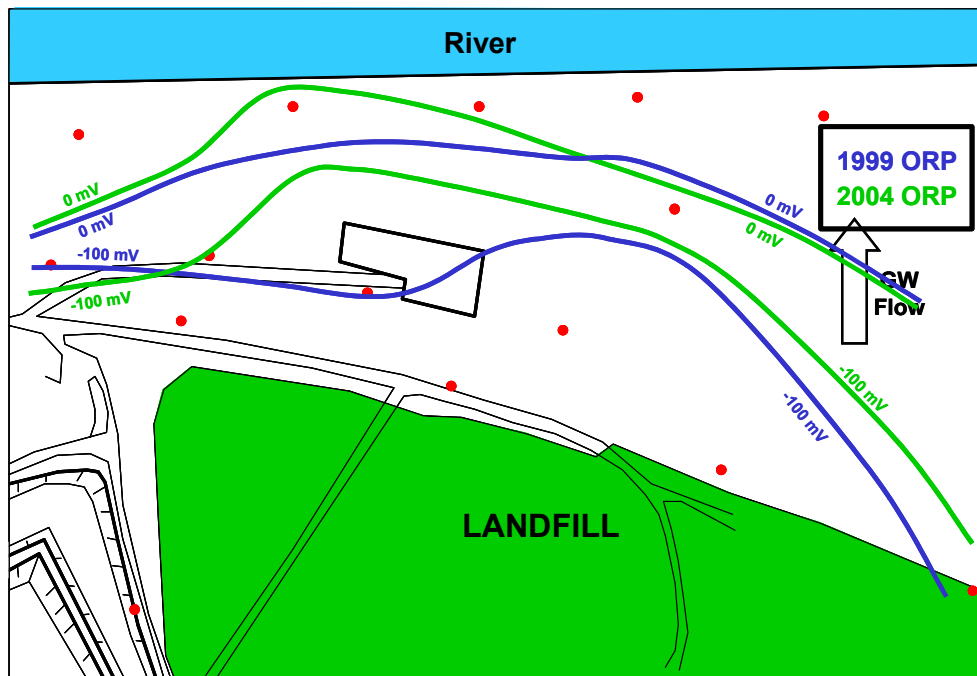


Figure 2. Oxidation-reduction potentials in surficial aquifer during 1999 and 2004 sampling events.

After the dissolved-phase arsenic plume was delineated, state guidance required that potential remedies be identified and evaluated, and an appropriate remedy selected. As well, the selected remedy had to be protective of human health and the environment. The sensitive receptor that served as the focus of the project was the river (ground-water discharge zone) located about 500 feet from the landfill. Screening and evaluation of remedial options led to the selection of MNA as the remedy best suited for the site. The state regulatory agency approved MNA as the remedy; however, the regulatory agency stipulated that approval was contingent upon landfill capping to minimize landfill leachate and implementation of an active remediation remedy (aeration trench) in the event that the plume grew in size.

Monitoring of the arsenic plume has been conducted since selection of the MNA remedy. The 2004 sampling results for arsenic and ORP are also shown on Figures 1 and 2. Results indicate that the plume is indeed stable and that MNA is an appropriate and effective remedy for this site. IST's successful experience at this site helps to demonstrate that arsenic MNA may be an appropriate remedy at specific sites where subsurface conditions are conducive to effective natural attenuation processes that sequester arsenic, making it less mobile and thus reduce arsenic concentrations in ground water.

Current Research on Arsenic MNA

IST's successful experience with arsenic MNA at the industrial site discussed in the previous section led us to collaborate with Dr. Janet Hering of the California Institute of Technology in submitting a proposal entitled "Environmental Fate and Exposure Assessment for Arsenic in Groundwater" to SERDP, a Department of Defense (DoD) program in cooperation with the U.S. EPA and the Department of Energy (DoE). With Dr. Janet Hering as principal investigator and IST as a key research participant, our SERDP proposal was accepted for funding. A project fact sheet can be found at: www.serdp.org/research/CU/CU_1374.pdf. This SERDP research project is anticipated to be completed in 2008.

The objective of this project is to develop a conceptual model for arsenic mobilization and sequestration that can be coupled with site characterization to demonstrate whether natural attenuation processes are operative at sites containing arsenic in ground water. Critical to this effort is the establishment of methods for demonstrating arsenic sequestration. Complementary laboratory studies will investigate strategies for augmenting natural sequestration processes.

As part of this project, an arsenic-specific conceptual model will be developed using the United States Geological Survey (USGS) code PHREEQC for geochemical modeling. Two DoD field sites have been chosen for study: 1) a site in Florida where the source is an arsenic-based herbicide (*i.e.*, anthropogenic arsenic site) and 2) a site in New England where the source of arsenic is naturally-occurring but was mobilized by anthropogenic activities (*i.e.*, mobilization of naturally occurring arsenic site). Site characterization studies will be performed to assess the speciation of arsenic in soils and aquifer sediments using selective extraction and X-ray absorption spectroscopy (XAS). Arsenic occurrence and speciation will

be determined by separation of As(III) and As(V) by ion-exchange and quantification by inductively coupled plasma mass spectrometry (ICP-MS).

Column studies will be performed with arsenic-contaminated soils to assess the effects of varying conditions on arsenic mobility and with uncontaminated soils to assess the effectiveness of arsenic sequestration processes. Column studies will be extended to include augmentation by altering conditions to promote arsenic sequestration through barium-based precipitation of As(V), iron-based sorption of As(III) and/or As(V), and oxidant-based sequestration of As(III) and/or As(V) with oxidation and precipitation of co-occurring Fe(II).

Results of this project will serve as the basis for determining the potential human health impacts of arsenic contamination at DoD and private sector sites (*i.e.*, exposure assessment). In appropriate circumstances, rigorous monitoring of plume movement coupled with identification and demonstration of operative natural attenuation processes may be sufficient to ensure the protection of human health. It is critical that the processes leading to arsenic natural attenuation and the factors governing their effectiveness are identified and that procedures are developed to determine whether such processes are operative at a given site and whether they could be made more effective by various augmentation strategies.

IST is proud to be a key participant in this exciting research effort. Our hope is to promote collective understanding of arsenic natural attenuation processes and the appropriate application of arsenic MNA on a site-specific basis.