FINAL REPORT

Environmental Fate and Exposure Assessment for Arsenic in Groundwater

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Acronyms

AFB	Air Force Base
As	arsenic
BRAC	Base Realignment and Closure
CA	California
Caltech	California Institute of Technology
DoD	Department of Defense
EPA	Environmental Protection Agency
ERD	enhanced reductive dechlorination
EXAFS	Extended X-ray absorption fine structure
Fe	iron
FL	Florida
ft	feet
Ft.	Fort
g	gram
g/L	gram per liter
h	hour
IST	Integrated Science and Technology, Inc.
JBF	Jackson Bluff Formation
kg	killogram
m	meter
M	molar
MA	Massachusetts
mg	milligram
mg/kg	milligram per killogram
mg/L	milligram per liter
mL	milliliter
mL/h	milliliter per hour
mM	millimolar
Mn	manganese
MNA	monitored natural attenuation
MW	monitoring well
NA	natural attenuation
nd	non-detect
NDSEG	National Defense Science and Engineering Graduate
NPL	National Priority List
SERDP	Strategic Environmental Research and Development Program
SON	Statement of Need
UC	University of California
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
µg/L	microgram per liter

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Executive Summary

The fate and transport of arsenic were examined at two Department of Defense (DoD) sites. At Tyndall Air Force Base, Florida arsenic contamination is the result of application of arsenical herbicides. At the Devens Reserve Forces Training Area (Ft. Devens), Massachusetts, naturally-occurring arsenic has been mobilized by application of enhanced reductive dechlorination (ERD) technology, designed to remediate contamination by chlorinated solvents. These two sites were compared with respect to plume evolution, mechanism of arsenic mobilization in the source areas, and potential sequestration mechanisms.

At both sites, groundwater was collected from existing monitoring wells and one or more new wells were drilled. Drilling was also performed at both sites to obtain sediment core samples for characterization and laboratory experiments. Groundwater collected at both sites was analyzed for a suite of chemical constituents and was also used in some mobilization experiments. Other mobilization experiments were conducted using synthetic groundwater solutions (based on the composition of background groundwater collected at the sites). Sediments were used for chemical and spectroscopic characterization, for batch and column studies of arsenic (As) mobilization and sequestration, and for batch studies of augmentation of arsenic sequestration.

At Tyndall, elevated levels of arsenic persist in the source area soils, decades after herbicide use was discontinued. Arsenic concentrations in groundwater near the source area exceed 1 mg/L. A plume of arsenic-contaminated groundwater was delineated based on groundwater collected from existing monitoring wells. Comparison with historical monitoring data suggests that the plume of arsenic contamination is stable or even retreating. Contaminated soil in the source area soils was partially excavated in 2003. Laboratory experiments examining arsenic mobilization and sequestration were conducted with source area soils and sediments from the surficial aquifer and the Jackson Bluff Formation (JBF), a presumed confining layer. Substantial mobilization of arsenic was observed under near-ambient conditions in column experiments and in selective extraction under mild conditions that would not be expected to result in dissolution of the solid matrix. Sorption experiments with both surficial aquifer and JBF sediments indicated that significant accumulation of arsenic in the sediments occurred only at very elevated dissolved arsenic concentrations. Thus sorption was excluded as an effective mechanism for arsenic sequestration at this site. The persistence of arsenic in the source area soils was attributed to limited infiltration and leaching (i.e., hydrologic control) rather than to geochemical constraints on arsenic mobility. The basis for the apparent stability of the arsenic plume could not be established based on the available field data. The laboratory results, however, suggest that the assumption that the arsenic contamination is confined to the surficial aquifer by the JBF should be tested by further field investigations.

At Devens, the low concentrations of arsenic in groundwater upgradient of the ERD treatment zone and in the farthest downgradient wells indicated that the naturally-occurring arsenic is immobile under ambient conditions (i.e., in the absence of anthropogenic inputs of organic bioavailable carbon). Laboratory experiments in which background sediments were inoculated with a known arsenic- and iron-reducing bacterium and amended with lactate confirmed that the arsenic and iron in the sediments are subject to microbially-mediated mobilization. Comparison of historical monitoring data suggested that the extent of migration of organic carbon, arsenic, iron (Fe), and manganese (Mn) at the field site was slower than would be expected based on estimates of groundwater flow velocities. Attenuation of organic carbon could be attributed to microbial mineralization, but the attenuation of inorganic species would require that they be sequestered into the solid phase. Selective extraction of Fe(II) from the sediments did provide some direct evidence for Fe(II) sequestration along the transect of groundwater wells, but the putative sequestration of arsenic, (total) iron, or manganese did not result in any enrichment in these elements detectable against the background concentrations. Examination of the sediments by X-ray absorption spectroscopy (XAS) did not show any evidence of As(III) adsorption under *in situ* conditions, although sorbed As(III) could be detected spectroscopically in sediments used in batch and column sequestration studies. Sorption of arsenic onto Devens sediments appeared to be enhanced in the presence of Fe(II). The Devens sediments were found to possess some (limited) natural capacity for As(III) and Fe(II) oxidation; oxidative precipitation of Fe(III) oxyhydroxides would be expected to enhance arsenic sequestration. Experiments examining possible strategies for augmentation of the natural attenuation of arsenic demonstrated that the oxidative capacity of the native sediments could be increased by amendment with synthetic birnessite (nominally an Mn(IV) oxide). Birnessite amendment substantially increased arsenic sequestration but only in the presence of Fe(II), suggesting that the *in situ* formation of Fe(III) oxyhydroxides is important for the effective sequestration of arsenic. Arsenic sorption is more favorable at the Devens site than at the Tyndall site due to the higher iron content of the native sediment. This difference would be even more pronounced if fresh Fe(III) oxyhydroxide surfaces are formed by the *in situ* precipitation of Fe(II).

The comparison of the two sites provides insight into the conditions under which monitored natural attenuation (MNA) can be relied upon to protect downgradient receptors from exposure to arsenic contamination. The results of the Tyndall study do not support reliance on MNA despite the observed persistence of arsenic in the source area and the apparent stability of the plume. Further investigations to determine the integrity of the JBF as a confining layer are needed.

The Devens study suggests that MNA may be an effective remedial option for sites where naturally-occurring arsenic has been mobilized due to localized introduction of organic carbon. The zero-order question relevant to these sites is whether As was immobile under ambient conditions (i.e., before the introduction of organic carbon). This question can be answered affirmatively if dissolved arsenic concentrations in groundwater are low upgradient of the organic carbon inputs and/or in the far-field downgradient of the influence of the organic carbon plume. The first-order questions that must be subsequently addressed include: (1) Is arsenic in the plume undergoing attenuation? (2) What is the capacity for arsenic sequestration in the far-field? and (3) What is the long-term stability of arsenic sequestered in the far-field? Ultimately, the capacity for arsenic sequestration must be assessed in the context of the organic carbon loading to the site.

Objectives

Concentrations of arsenic in groundwater at many Department of Defense (DoD) facilities exceed the U.S. drinking water standard of 10 µg/L. Known sources of arsenic contamination at DoD facilities include disposal of fly ash and past usage of arsenical biocides. In addition, naturally-occurring arsenic present in soils at DoD sites can be mobilized by the inadvertent release or intentional introduction of organic carbon. Arsenic-contaminated groundwater may not, however, pose a threat to human health if the arsenic plume is effectively attenuated before it intercepts a drinking water source. In such cases, monitored natural attenuation (MNA) may be a viable strategy for the management of sites with arsenic-contaminated groundwater.

Acceptance and implementation of MNA as a remedy requires a mechanistic understanding of the processes by which arsenic may be sequestered in the subsurface environment and of the conditions that favor sequestration or that might allow subsequent remobilization of sequestered arsenic. The overall objective of this project is the development of a sound scientific basis for the evaluation of MNA for arsenic, particularly with regard to DoD facilities. The specific objectives of this work are:

1. development of a conceptual model for arsenic attenuation in the subsurface environment that can be coupled with site characterization to determine whether attenuation processes are operative at a given site,
2. assessment of methods for demonstrating arsenic sequestration,
3. laboratory investigation of strategies for augmentation of natural arsenic sequestration, and
4. application of this paradigm to assess the environmental fate and exposure for arsenic at two DoD sites representing situations where arsenic was either introduced or mobilized as a result of human activities.

MNA offers a potential cost-effective alternative to *ex situ* or *in situ* methods for active groundwater remediation. Thus, this research represents an innovative response to SERDP's Statement of Need (SON).

Background

The Superfund Information Site (http://cfpub.epa.gov/supercpad/cursites/srchsites.cfm) lists arsenic as a contaminant of concern at 54 DoD facilities and 18 BRAC (Base Realignment and Closure) sites with contaminated groundwater that are active sites on the National Priority List (NPL). Arsenic-contaminated groundwater poses a threat to human health if the contaminated groundwater is used as a drinking water supply without adequate treatment (Smith et al. 2002). Arsenic is a known human carcinogen, and consumption of arsenic-contaminated groundwater is associated with many adverse health effects including cancer of the skin and internal organs. The U.S. drinking water standard for arsenic is 10 µg/L (FR 2001a).

Arsenic contamination of groundwater at DoD sites can derive either from the anthropogenic introduction of arsenic (most commonly through disposal of fly ash or use of arsenical biocides) or from the mobilization of naturally-occurring arsenic associated with the anthropogenic introduction of organic carbon. This introduction of organic carbon may be either inadvertent (e.g., release of fuel hydrocarbons from spills or leaks in pipelines or storage facilities or organic-rich leachates generated within sanitary landfills) or intentional (i.e., associated with biostimulation of *in situ* remediation). Such biostimulation has been implemented at a number of DoD facilities for the remediation of chlorinated solvents (i.e., enhanced reductive dechlorination, ERD) and could also be applied for the remediation of perchlorate. The potential for mobilization of naturally-occurring arsenic as an undesirable side-effect of biostimulation has been demonstrated in laboratory studies (McLean et al. 2006) but has not previously been observed in a field setting.

The biogeochemical processes that can lead to the mobilization or sequestration of arsenic in the subsurface (Reisinger et al. 2005; USEPA 2007b) are shown schematically in Figure 1. Since naturally-occurring arsenic in many soils and aquifer sediments is associated with iron-bearing minerals (McMahon and Chapelle 2008; Welch et al. 1988; Welch et al. 2000), the destabilization of these carrier phases under reducing conditions can result in arsenic mobilization (Cummings et al. 1999; Lee et al. 2005; Zobrist et al. 2000). Conversely, conditions that favor the oxidative precipitation of iron(III) oxyhydroxides would promote the sequestration of arsenic through sorpion and/or co-precipitation (Cozzarelli et al. 2001; Radloff et al. 2007). Although arsenic can also be sequestered in the form of authigenic sulfide minerals, this removal mechanism is limited, in most freshwater aquifers, by sulfate availability (Beak et al. 2008; Kirk et al. 2004; O'Day et al. 2004).

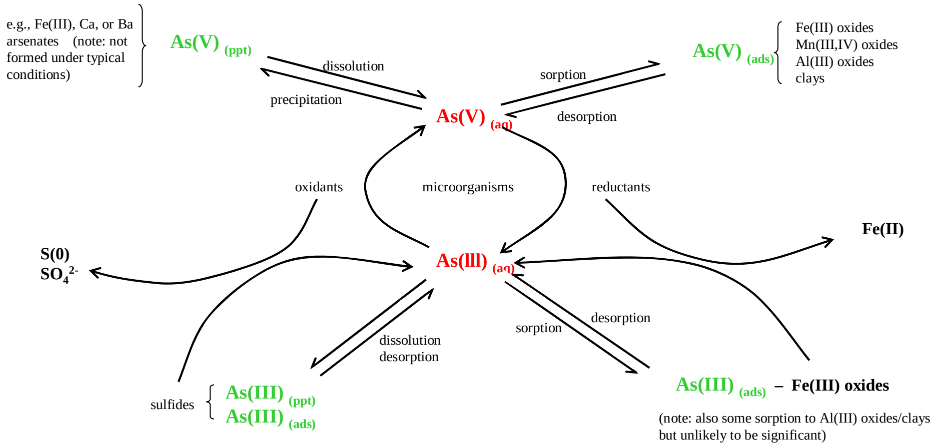

Figure 1. Biogeochemical Processes that can Transform Arsenic from Immobile to Mobile Species. (green) Immobile Species, (red) Mobile Species. After Reisinger et al. 2005.

A number of technologies are highly effective for the removal of arsenic from contaminated water (Garelick et al. 2005; Mohan and Pittman 2007) and these can be applied as *ex situ* (i.e., pump-and-treat) methods for arsenic-contaminated groundwater. These methods include coagulation (i.e., with ferric chloride or alum) and adsorption on packed bed media (e.g., granular ferric hydroxide or activated alumina). Particularly for aluminum-based coagulants and sorbents, the efficiency of arsenic removal can be dramatically enhanced by pre-oxidation of As(III) to As(V). With greensand filtration, the filter media itself is an oxidant and removal of arsenic, whether it occurs in the groundwater as either As(III) or As(V), is enhanced if the groundwater also contains elevated concentrations of Fe(II) (Viraraghavan et al. 1999). Even the oxidative precipitation of Fe(II) in groundwater can, in some cases, be sufficient to accomplish effective arsenic removal (Lytle et al. 2005). With *ex situ* methods, however, the need for long-term operation and maintenance of pump-and-treat facilities can result in very substantial costs.

In situ methods, most commonly permeable reactive barriers, can be an attractive and cost-effective alternative to *ex situ* methods. Zero valent iron, Fe(0), has been widely used in permeable reactive barriers for groundwater contaminated with chlorinated solvents. Both As(V) and As(III) can be removed from water by iron wire or filings in batch systems or columns; removal has been attributed to sorption and/or surface precipitation of As onto iron corrosion products at the metal surface (Farrell et al. 2001; Lackovic et al. 2000; Leupin and Hug 2005; Leupin et al. 2005; Yu et al. 2006). Zero valent iron has not, however, yet been applied in a permeable reactive barrier system for *in situ* treatment of arsenic-contaminated groundwater.

An alternative *in situ* strategy, MNA, has been successfully exploited in the management of sites where groundwater contains petroleum hydrocarbons and other biodegradable organic contaminants. MNA relies on “natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a timeframe that is reasonable compared to that offered by other more active methods” (EPA 1999). Natural attenuation processes include “a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, volume, or concentrations of contaminants in soil or groundwater” (Bekins et al. 2001). Recently, the EPA has described the conceptual and technical basis for the application of MNA to inorganic contaminants, including arsenic (EPA 2007a, 2007b). This application relies in part on prior successful applications to organic contaminants in groundwater but must account for the different types of natural attenuation processes applicable to inorganic and organic contaminants (Rittmann et al. 2007). Despite the prior lack of guidance for application of MNA for inorganics, MNA has been accepted on an *ad hoc* basis as a remedy for several sites with arsenic-contaminated groundwater (Reisinger et al. 2005). Nonetheless, it is clear that further work is needed to support the evaluation of MNA as a suitable remedy for specific sites, which requires careful and comprehensive site assessment based on a conceptual site model that relates the processes of arsenic mobilization and sequestration to the conditions prevailing at the site.

Approach

Two study sites were identified for the study based on historical monitoring records, one with anthropogenic arsenic contamination and the other with naturally-occurring arsenic mobilized by the anthropogenic introduction of organic carbon. At each site, groundwater was collected from existing monitoring wells and one or more new wells were drilled. Drilling was also performed at each site to obtain sediment core samples for characterization and laboratory experiments. Groundwater from each site was analyzed for a suite of chemical constituents and was also used in some mobilization experiments. Other mobilization experiments were conducted using synthetic groundwater solutions (based on the composition of background groundwater collected at the sites). Sediments were used for chemical and spectroscopic characterization, for batch and column studies of arsenic mobilization and sequestration, and for batch studies of augmentation of arsenic sequestration. Experimental details of field and laboratory investigations of the anthropogenic arsenic sites, Tyndall Air Force Base (Florida), are described elsewhere (Fitzmaurice et al. in prep.). Various aspects of the investigations at the naturally-occurring arsenic site, Devens Reserve Forces Training Ares (Massachusetts), are described in separate reports: field and batch laboratory studies (He et al. in prep.), batch and column studies (Choi et al. in prep.), and augmentation studies (He and Hering in prep.). An additional work discusses the conceptual basis for application of MNA at Devens and similar sites (Hering et al. in prep.).

Results and Accomplishments

The fate and transport of arsenic in groundwater were examined at two DoD sites. At one of these sites, Tyndall Air Force Base, FL, arsenic contamination was due to the use of As_2O_3 as an herbicide. At the other site, Devens Reserve Forces Training Area, MA (Ft. Devens), naturally-occurring arsenic was mobilized by the anthropogenic introduction of organic carbon designed to stimulate the microbial degradation of chlorinated solvents through enhanced reductive dechlorination (ERD). Field work was performed at each site and laboratory investigations were conducted with groundwater and sediments collected from both Tyndall (Fitzmaurice et al. in prep.) and Devens (Choi et al. in prep.; He et al. in prep.; He and Hering in prep.). Here, the two sites are compared with respect to plume evolution, mechanism of arsenic mobilization in the source areas, and potential sequestration mechanisms, and an assessment is made regarding the feasibility of MNA at the sites. Possibilities for augmentation of natural attenuation are also examined.

Historical evidence suggesting natural attenuation

Both sites, Tyndall and Devens, were chosen partly because historical monitoring data suggested that arsenic might be subject to natural attenuation at the site. At Tyndall, the plume appeared to be stable or even retreating (Figure 2). This monitoring data was confirmed by additional groundwater measurements conducted as part of this project in August 2006. A new well (MW-1R) was drilled immediately downgradient of the source area to replace well MW-1 (which was removed during the (partial) excavation of source area soil). The arsenic concentration in groundwater collected at MW-1R was 1.16 mg/L, somewhat lower than previously measured at well MW-1 (e.g., 2.4 mg/L in 1993). This difference may reflect a decrease in the source strength due to the partial excavation of contaminated soil.

At Devens, the plume of arsenic-contaminated groundwater increased in extent over the period 2003-2006, consistent with the continued monthly injections of organic carbon (i.e., a molasses solution) (Figure 3). Over this period, the leading edge of the arsenic plume migrated approximately 12 m (40 ft); the estimated groundwater movement over the same period was approximately 290 m (950 ft). This observed retardation of arsenic suggests that the dissolved arsenic at the leading edge of the plume is undergoing sequestration, but the migration from 2003 to 2006 also suggests that sequestered arsenic can be remobilized under continued loading of organic carbon to the system.

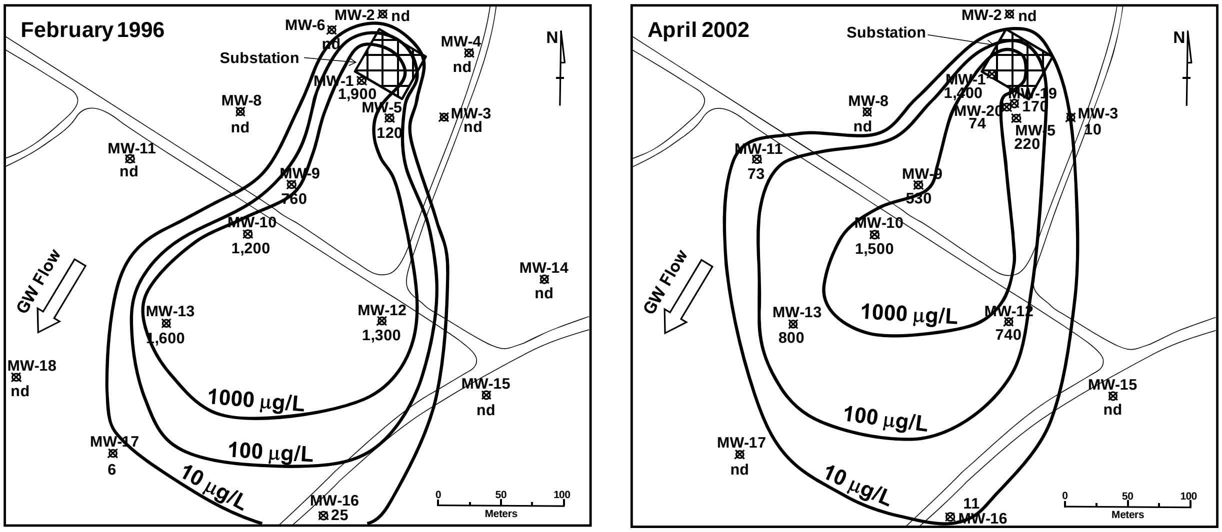

Figure 2. Plume of Arsenic Contaminated Groundwater at Tyndall. Measurements made at Monitoring Wells (MW) in February 1996 (left panel) and April 2002 (right panel). Note that Contaminated Soil in the Source Area (cross-hatched square) was Partially Excavated in 2003. On the Basis of these Data, the Plume Appears to be Stable (or even retreating) Over this Time Period. Data from Reports Issued by Southern Company Services and Gulf Power.

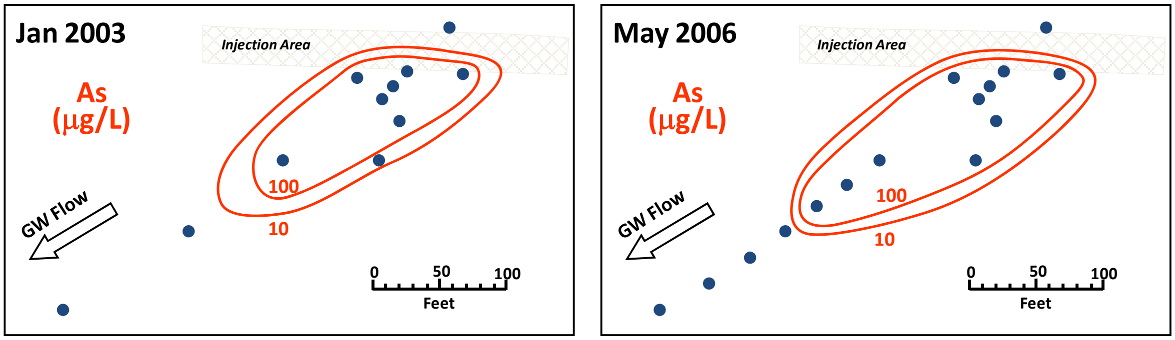

Figure 3. Plume of Arsenic Contaminated Groundwater at Devens. Measurements made at Monitoring Wells (•) in January 2003 (left panel) and May 2006 (right panel). Injection Area is Indicated by Cross-hatched Box. Note that Additional Wells were Installed in May 2006 as Part of this Project. Data for 2003 from Arcadis, Inc.

Arsenic in the source areas and its mobilization

The most obvious contrast between the two sites is the nature of the source area of arsenic contamination. At Tyndall, application of As_2O_3 as an herbicide was discontinued in the 1970's but arsenic persists at elevated concentrations (up to 280 mg/kg) in source area soils. Because the source area is an operating electrical substation, contaminated soil could only be partially excavated; an estimated 30-70% of the arsenic contamination in the source area was removed by excavation in 2003. In sediments obtained from borings at the site away from the source area, however, the arsenic content was generally <10 mg/kg (determined both by a commercial laboratory and by extraction following EPA method 3050B (EPA 1996) performed at Caltech). Thus, a pronounced gradient was observed in arsenic content between soil in the source area and sediments either upgradient of the source area or within the plume of arsenic-contaminated groundwater downgradient of the source area.

In contrast, there is no known source of anthropogenic arsenic at the specific study area at the Devens site; elevated concentrations of arsenic in groundwater are observed only downgradient of the site of organic carbon injection. The arsenic content in Devens sediments (determined by 3050B extraction) was 16.25±3.50 mg/kg in 15 sediment samples collected both up- and downgradient of the organic carbon injection area. No systemic gradient in the arsenic content of the sediment was observed with distance from the organic carbon injection area.

No distinct arsenic-bearing mineral phases could be identified in soil or sediment samples from either the Tyndall or Devens site. In all samples (with the exception of a single sample from Devens), bulk X-ray absorption spectroscopy (XAS) indicated that arsenic was present in the +V oxidation state. In the anomalous Devens sample, quantitative analysis of the Extended X-ray Absorption Fine Structure (EXAFS) spectrum indicated the presence of arsenic associated with pyrite, which was presumed to be detrital.

Selective extractions of the Tyndall source area soil and Devens sediment indicated markedly different lability of arsenic in the solid phase. With the Devens sediments, <10% of the 3050B-extractable arsenic was released by extraction with ammonium sulfate or phosphate, suggesting that dissolution of the solid matrix is required for arsenic mobilization. With the Tyndall source area soil, the proportion of 3050B-extractable arsenic released by extractants that do not dissolve the matrix (i.e., ammonium sulfate and phosphate) was substantially greater (approximately 40%). In addition, repeated extractions of the Tyndall source area soil with background groundwater collected at the site released >90% of the 3050B-extractable arsenic.

The results of the selective extractions suggest that, at the Tyndall site, arsenic could be readily released from the source area soils under ambient conditions. This is consistent with the elevated arsenic concentrations (1.2 mg/L) observed in groundwater immediately downgradient of the source area and was confirmed in static and flow-through column experiments in which source area soils were exposed to background groundwater (or a synthetic equivalent). Arsenic concentrations similar to those observed at well MW-1R were observed in the effluent from the static columns (2.1±0.2 mg/L) and flow-through columns (Figure 4). Note that variations in effluent arsenic concentrations with flow rate are attributed to mobilization of colloids at higher flow rates.

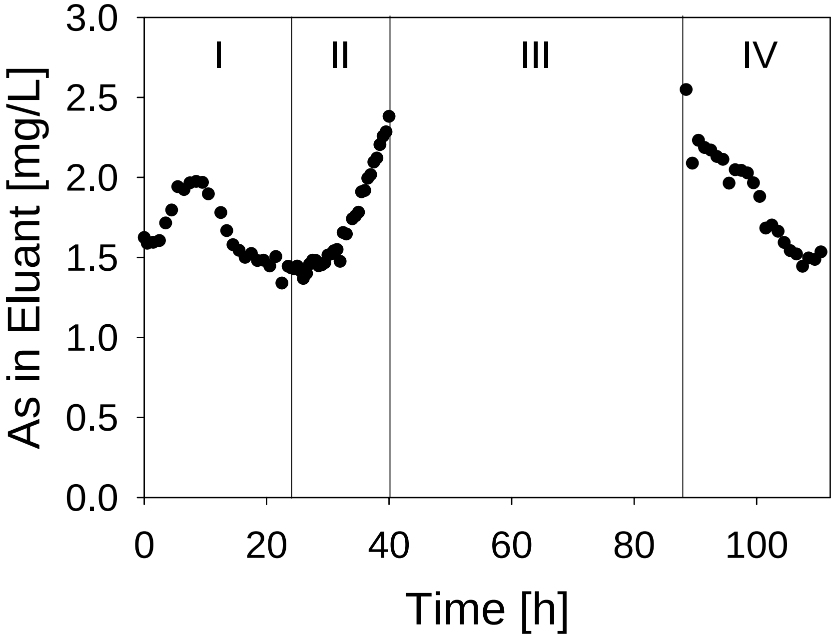

Figure 4. Column Experiments Conducted with Tnydall Source Area Soil. Concentrations of As in the Eluant of a Column Packed with 220 g soil (0-250 μm size fraction) and Eluted with Simulated Groundwater (44 μM NaCl, 75 μM $CaSO_4$, and 82 μM $MgSO_4$, buffered to pH 5.2 with 10 mM pyridine) under Saturated up-flow Conditions. The Column was Run at 12.5^{o}C in the Dark at Flow Rates of 5 mL/h for 24 h (region I), 20 mL/h for 16 h (region II), at no Flow for 48 h (region III), and at 5 mL/h for 24 h (region IV).

In contrast, the selective extractions of Devens sediments indicate that the naturally-occurring arsenic in these sediments would be immobile under ambient conditions (i.e., conditions prior to the anthropogenic introduction of organic carbon). This supposition is confirmed by the low concentrations of arsenic (<10 μg/L) observed upgradient of the organic carbon injection area and in the far-field, downgradient of the influence of the organic carbon input. Release of arsenic from Devens sediments requires at least partial dissolution of the matrix, which is accomplished with chemical reductants in the laboratory extractions. The potential for arsenic mobilization from Devens sediments by microbial reductive dissolution of the matrix (presumably Fe(III) oxyhydroxides) was examined in laboratory experiments in which Devens sediments were inoculated with a known Fe(III)- and As(V)-reducing bacterium, *Shewanella* sp. strain ANA-3. Substantial release of arsenic over the course of the experiment was observed only when lactate was added to stimulate microbial activity; addition of lactate had only a minor effect in the presence of formaldehyde, which effectively inhibits microbial activity (Figure 5). These experiments confirm that arsenic in the Devens sediments is bioavailable and could be mobilized under the conditions generated by the anthropogenic introduction of organic carbon at the site.

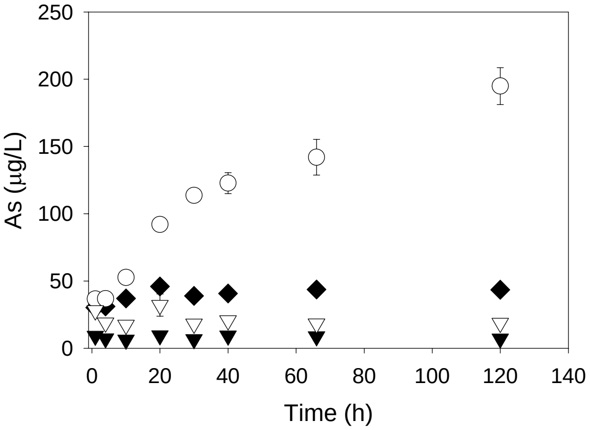

Figure 5. Release of Arsenic Over Time in Simulated Mobilization Experiments with Devens Sediment. Conditions: 1 g Wet Sediment (21.5% water content) Incubated with *Shewanella* sp. Strain ANA-3 in 20 mL Synthetic Groundwater. Symbols: (○) 10 mM Lactate, (◆) No Lactate, (▽) 2% Formaldehyde, 10 mM Lactate, (▼) 2% Formaldehyde, No Lactate. Error Bars Correspond to Standard Deviation of Triplicate Samples.

The principle contrasts between Tyndall and Devens with regard to the source of arsenic and its lability under ambient conditions may be summarized as follows:

- The source of arsenic is anthropogenic at Tyndall and geogenic (i.e., naturally-occurring) at Devens.
- A strong gradient in the arsenic content of soils/sediments is observed at Tyndall but not at Devens.
- At Tyndall, arsenic in the source area is mobile under ambient conditions (i.e., geochemically labile), whereas at Devens, the naturally-occurring arsenic is immobile under ambient conditions (i.e., in the absence of anthropogenically-introduced organic carbon).

Potential mechanisms and evidence for natural attenuation of arsenic

If arsenic mobilized in some source area is to undergo natural attenuation, then there must be some gradient along the flowpath of the arsenic-contaminated groundwater that results in favorable conditions for arsenic sequestration. For arsenic, the likely mechanisms for sequestration are sorption, precipitation, and co-precipitation (EPA 2007b). The extent of arsenic sequestration by one or more of these mechanisms will depend on the geochemical conditions, which govern the solubility of both arsenic-bearing mineral phases and carrier phases for arsenic sorption. The oxidation state of arsenic, which will also depend on the geochemical conditions, can strongly affect the extent of arsenic sorption in systems dominated by aluminum- or aluminosilicate based sorbents, though this effect is less pronounced in iron-dominated systems (Hering and Dixit 2005).

At Tyndall, the only gradient that would favor arsenic sequestration is that of the concentration gradient of arsenic in the solid phase. However, laboratory sorption experiments conducted with uncontaminated aquifer sediment materials resulted in significant accumulation of arsenic in the solid phase only at quite elevated concentrations of dissolved arsenic (Figure 6). Note that greater sorption was observed with sediments from the Jackson Bluff formation (JBF), a presumed confining layer, than in the overlying surficial aquifer sediments. The very limited sorption observed with the surficial aquifer sediments is consistent with the observation that surficial aquifer sediments collected from within the plume of arsenic-contaminated groundwater are not enriched in arsenic relative to sediments collected upgradient of the source area. A slight enrichment in arsenic content was observed in JBF sediments collected downgradient of the source as compared with sediments collected upgradient, though this may be within the range of the natural variability of the samples. It is, however, presumed that the JBF acts as a confining layer, which would necessarily limit the contact between the contaminated groundwater and the JBF sediment.

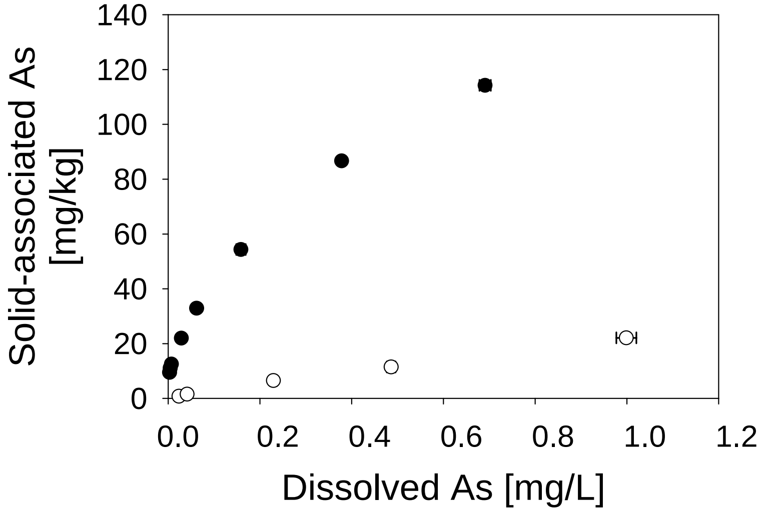

Figure 6. Batch Sorption Experiments Conducted with Tyndall Sediments. Concentrations of Solid-associated As as a Function of Dissolved As Concentrations in Suspensions of Tyndall Sediments Collected Upgradient of the Source Area and Equilibrated in Background Groundwater Spiked with As(V). Symbols: (○) Surficial Aquifer Sediment, (●) JBF Sediment. Experimental Conditions: 0.75 g in 25 mL, Rotated at 20 rpm at 12.5°C in the dark for 36 h in Triplicate.

At Devens, a strong gradient in geochemical (specifically redox) conditions exists at the site due to the anthropogenic introduction of organic carbon. Upgradient of the organic carbon injection area, the groundwater is relatively oxidizing (E_h ~ +100 mV, sulfate ~ 16 mg/L, and low or undetectable concentrations of dissolved arsenic, iron, and manganese). Similar conditions are also observed in the far-field, downgradient of the influence of the organic carbon injection.

The extent of the plumes of elevated organic carbon at Devens is similar to that of the arsenic plumes shown in Figure 3. Similar to arsenic, the plume of organic carbon shows an expansion of the affected area over the period 2003-2006 but not as much as would be expected if the injected organic carbon were behaving conservatively. Attenuation of the anthropogenically-introduced organic carbon by microbial respiration is expected and is, indeed, the basis of ERD technology. As the organic carbon is mineralized, the leading edge of the plume comes into contact with uncontaminated groundwater and unaltered aquifer sediments, resulting in a strong gradient in redox conditions.

As mentioned above, sorption, co-precipitation, and precipitation are the most likely mechanisms for arsenic sequestration in the subsurface environment. Arsenic could sorb onto the native aquifer sediment or onto Fe(III) oxyhydroxides if such phases form *in situ* upon contact with uncontaminated groundwater or native aquifer sediment at the leading edge of the plume.

With Devens sediments, an extraction targeting Fe(II) did suggest enrichment of Fe(II) in sediments collected downgradient of the observed maximum in the total dissolved iron concentrations (present predominantly as Fe(II)) in groundwater (Figure 7). No significant variations in the sediment content of arsenic, iron, or manganese along the transect could be detected by 3050B-extractions. It is possible that the background concentrations (and intrinsic variability) of these elements in the sediments is too high to allow the detection of any enrichment associated with sequestration.

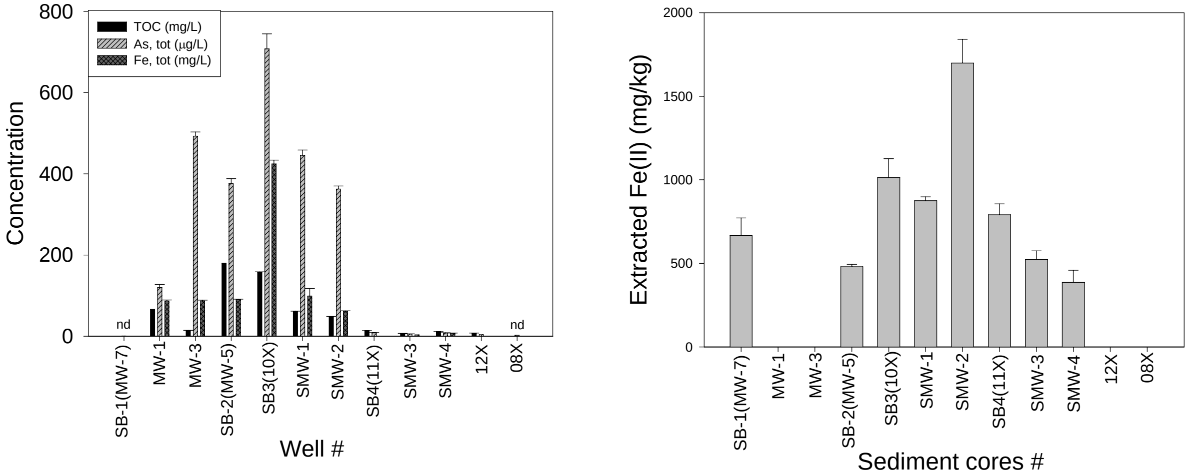

Figure 7. Comparison of Groundwater Composition and Fe(II) Extracted from Cores Collected Along the Transect of Monitoring Wells at Devens. (left panel) Concentrations of Total Organic Carbon (TOC) and Total Dissolved Arsenic and Iron, (right panel) 0.5 M HCl-extractable Fe(II) in cores. Note the Apparent Enrichment in HCl-extractable Fe(II) at the Location SMW-2. (nd = not detected. Error bars correspond to standard deviation of riplicate samples.)

Both As(III) and As(V) were detected in Devens groundwater, but interrogation of the aquifer sediments by XAS provided no evidence for As(III) sorption. With the exception of a single sample in which some arsenic appeared to be associated with detrital pyrite, only As(V) was detected in the solid phase. The absence of a signal for sorbed As(III) might indicate preferential sorption of As(V) under *in situ* conditions or oxidation of As(III) to As(V) upon sorption, or sorbed As(III) below the detection limit of the method (< ~5 mol % of total As present)..

In batch and column experiments conducted in the laboratory with native aquifer sediments, sorption of both As(III) and As(V) was observed. In systems spiked only with As(III), examination of the solid by XAS indicated partial oxidation of As(III) to As(V), which was detectable against the background concentration of As(V) in the native aquifer sediment (Figure 8). Examination of the X-Ray absorption near edge stricture XANES of Mn and Fe in As(III)-reacted sediments suggested that Mn(III,IV) present in the sediments may be a source for abiotic oxidation of As. It is important to note, however, that sorption of As(III) onto aquifer sediments could be detected by XAS for sediment samples exposed to As(III) in the laboratory but not for aquifer sediments that had been exposed to As(III)-contaminated groundwater in the field.

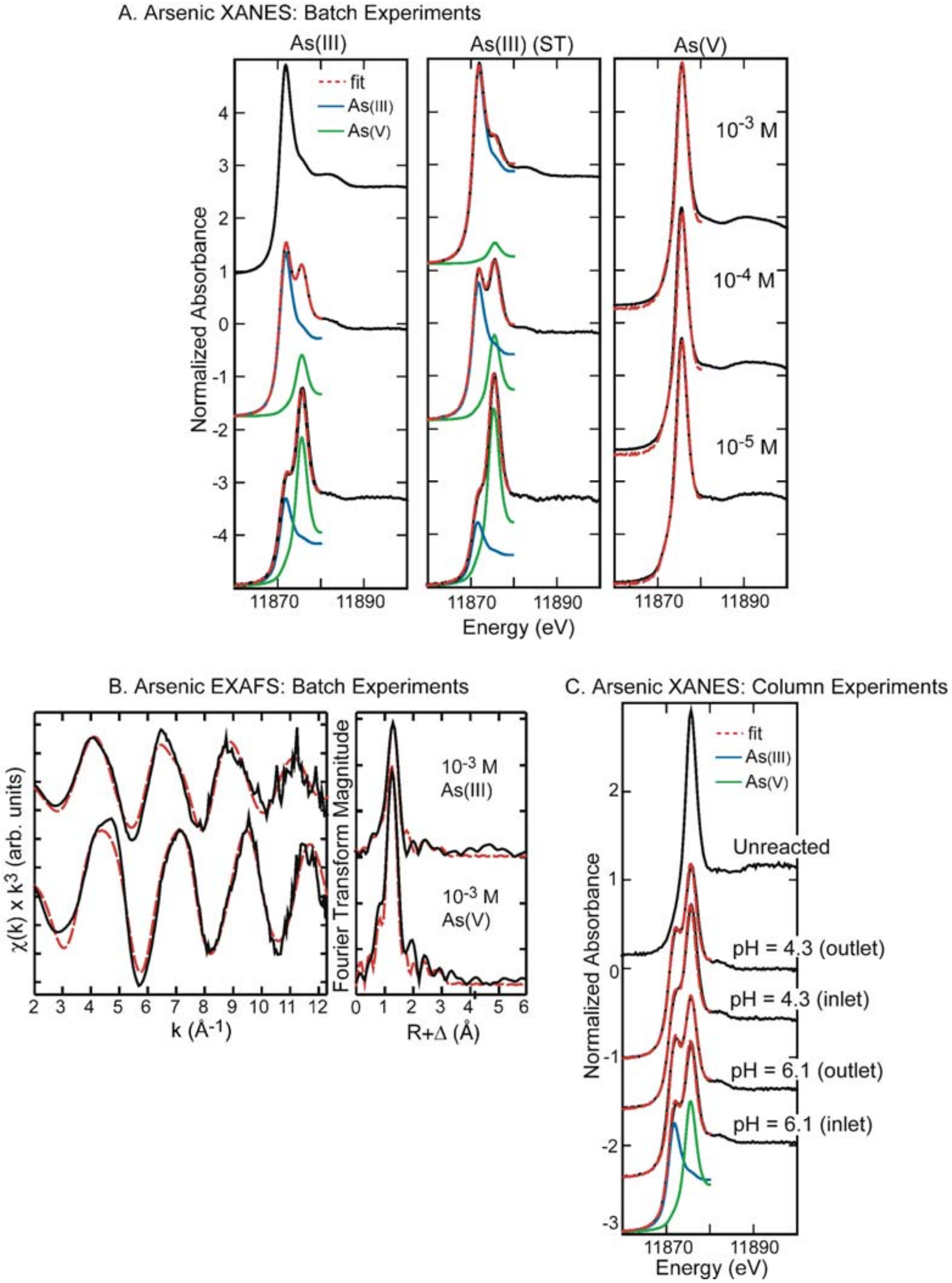

Figure 8. Spectroscopic Data for Devens Sediment. A. Normalized As XANES Spectra and Quantitative Fit Deconvolutions with Reference As(III) and As(V) Spectra for Batch Sediments Reacted with As(III) or As(V) Solutions (10^{-3}, 10^{-4}, 10^{-5} M); ST: Samples Sterilized with 2% Formaldehyde. B. Arsenic EXAFS Spectra and Fourier Transforms of Batch Sediments Reacted with 10^{-3} M As(III) or As(V). Dashed Line is the Non-linear Least-squares Best Fit. Numerical Fit Results Reported in Supporting Information. C. Normalized As XANES Spectra and Quantitative Fit Deconvolutions with Reference As(III) and As(V) Spectra for Column Sediments Reacted with 10^{-4} M As(III) + 10^{-3} M Fe(II) Solution: Column 2 (pH 4.3) and Column 3 (pH 6.1).

Column experiments in which Devens was exposed to influent synthetic groundwater spiked with As(III) indicated that retention of arsenic was enhanced in the presence of Fe(II) (Figure 9). Note, however, that the retained arsenic was also more readily desorbed (i.e, by arsenic-free influent) when Fe(II) was present in the initial influent solution.

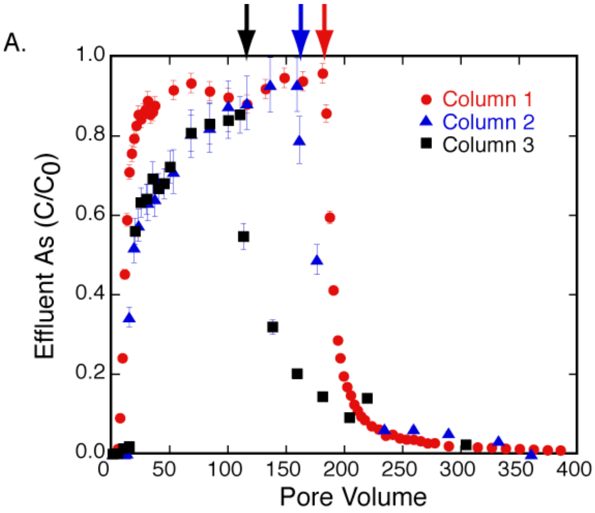

Figure 9. Column Experiments Conducted with Devens Sediments. Effluent Arsenic Concentrations Normalized to the Influent Concentration of 10^{-4} M As(III) as a Function of Pore Volume. Column 1: As(III) only; Column 2: As(III) + Fe(II), unbuffered (pH 4.3); Column 3: As(III) + Fe(II), Buffered (pH 6.1). Arrows Indicate Start of Column F lushout with As- and Fe-free Background Pore Water Solutions.

The difference in apparent sorption capacity between Devens and Tyndall sediments is likely to be related to their iron content. Florida soils in general are very low in iron compared to average soils and sediments (Chen and Ma 1998). On the basis of 3050B-extractable Fe content, Devens sediments are approximately 1400-fold enriched in iron compared with the Tyndall JBF sediments (which are themselves substantially enriched in iron compared with the Tyndall surficial aquifer sediments and source area soils).

Although *in situ* oxidation of Fe(II) present in the contaminated groundwater at Devens could, in principle, contribute to sorption of arsenic in this system, the Devens sediments appear to have a quite limited oxidative capacity. Some *in situ* Fe(II) oxidation may occur at the leading edge of the plume due to the contact between contaminated and uncontaminated groundwater, but it is unlikely that this can be captured in field sampling, particularly due to the dynamic nature of the plume front as organic carbon injections are continued.

Arsenic sorption is more favorable at the Devens site than at the Tyndall site due to the higher iron content of the native sediment. This difference would be even more pronounced if fresh Fe(III) oxyhydroxide surfaces are formed by the *in situ* precipitation of Fe(II).

Possible augmentation of natural attenuation

The potential for augmentation of arsenic sequestration by Devens sediments was examined as a complement to the assessment of the oxidative capacity of the sediments. Since the oxidative capacity of the native sediments was found to be rather low, amendment with synthetic birnessite (nominally MnO_2) was examined as a means of increasing the oxidative capacity. Comparison of arsenic sequestration in the presence and absence of Fe(II) allowed assessment of the potential contribution of *in situ* Fe(II) oxidation to arsenic sequestration.

Suspensions of native sediment were amended with synthetic birnessite ($MnO_{1.7}$) containing manganese in a mixed oxidation state. In the absence of Fe(II), oxidation of As(III) to As(V) was observed in suspensions spiked with As(III) but arsenic removal from solution was quite limited. In contrast, in the presence of Fe(II), arsenic removal increased with increasing amounts of birnessite (Figure 10). This increased arsenic removal coincided with an increase in the amount of Fe(III) that could be extracted from the solid phase. Essentially all arsenic that remained in the dissolved phase was present as As(III). Measurements of dissolved manganese (not shown) indicated that the added birnessite was reduced concurrent with the oxidation of As(III) and/or Fe(II).

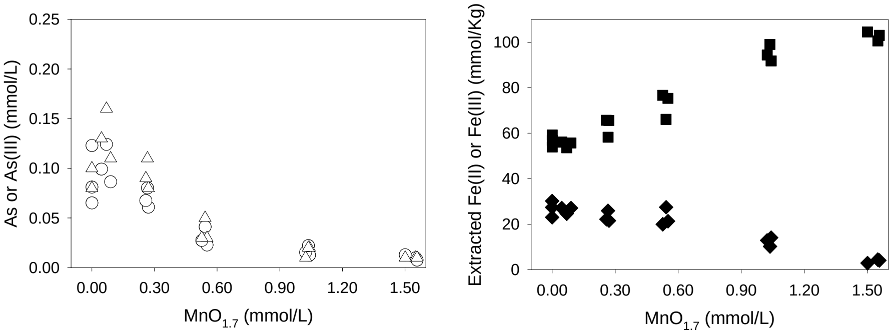

Figure 10. Augmentation Experiments Conducted with Devens Sediments. Effect of Synthetic Birnessite on the Sequestration of Arsenic and the Oxidation of Fe(II) and As(III) in Devens Sediment Suspensions. (left panel) Concentrations of Total As (○) and As(III) (△) in Supernatants as a Function of Added $MnO_{1.7}$, (right panel) Fe(II) (◆) and Fe(III) (■) Extracted from the Solid Phase as a Function of Added $MnO_{1.7}$. Conditions: Initial As(III) Concentration 0.25 mM, Initial Fe(II) Concentration 2.0 mM, Sediment Concentration 50 g/L, pH 6.1, 24-h Reaction Time.

These results demonstrate that amendment with solid Mn(III,IV) oxides could be an effective strategy to augment natural attenuation for arsenic plumes that also contain elevated concentrations of Fe(II). Solid Mn(III,IV) oxides could be used in a permeable reactive barrier, but this technology is limited to relatively shallow plumes of contaminated groundwater (Powell et al. 1998; Puls 1997). Injection of nanoparticulate Mn oxides, if this material could be produced at a reasonable cost, might allow the formation of an *in situ* reaction zone for the sequestration of arsenic and iron.

Assessment of MNA

For both the Tyndall and Devens sites, groundwater monitoring data suggested that natural attenuation could be contributing to the observed plume stability. In addition, at Tyndall, arsenic was observed to persist in the source area for several decades after the application of arsenical herbicides was discontinued. This preliminary evidence for natural attenuation was examined in the context of further site characterization, chemical and spectroscopic characterization of soils and aquifer sediments, and laboratory experiments on arsenic mobilization and sequestration.

The most obvious distinction between the two sites is that arsenic derives from anthropogenic input at Tyndall, but is naturally occurring at Devens. There are three other distinctions between the sites that are likely to have as much, if not more, bearing on the effectiveness of natural attenuation processes. First, there is a strong gradient in geochemical conditions at Devens (due to the anthropogenic input of organic carbon) but not at Tyndall. Second, the iron content of the Devens sediments is higher than at Tyndall (which affects the sorption capacity of the sediment). Third, the dissolved iron is higher in the Devens groundwater (maximum concentration ~400 mg/L) than in the Tyndall groundwater (maximum concentration ~0.09 mg/L), thus there is a greater opportunity for *in situ* oxidative precipitation of Fe(III) oxyhydroxides at Devens than at Tyndall.

Since a strong case cannot be made for natural attenuation of arsenic in the surficial aquifer at Tyndall, alternative explanations must be sought for the persistence of arsenic in the source area and the apparent stability of the arsenic plume. We suggest that the leaching of arsenic from the source area soils due to infiltration of rainwater is limited by two mechanisms: (1) under heavy and/or long duration rain events, a significant proportion of precipitation may contribute to overland flow rather than to infiltration and (2) under light and /or short duration rain events, evaporation and capillary rise of As-contaminated water within the shallow vadose, particularly during the warmer months, might retard the transport of As from the source area. Thus we suggest that persistence of anthropogenic arsenic in the source area alone should not be interpreted as evidence that arsenic is not labile under ambient geochemical conditions.

The apparent stability of the plume is predicated on the integrity of the JBF as a confining layer. One well was drilled through the JBF into the underlying Intracoastal Formation near the source area, where the observed thickness of the JBF was 2.5 m. If the integrity of the JBF were compromised farther downgradient, penetration of the plume into the underlying Intracoastal Formation could provide an explanation for the absence of detectable arsenic in groundwater collected at the farthest downgradient wells drilled into the surficial aquifer. This hypothesis requires confirmation by further field investigations.

This study illustrates the importance of evaluating potential sequestration mechanisms in assessing whether observed plume stability can be attributed to natural attenuation processes. It also highlights the difficulty of detecting direct evidence of arsenic sequestration in field samples. Laboratory experiments conducted with sediment samples from the field site can provide insight into potential sequestration mechanisms and information that can be useful in interpreting field observations.

Conclusions

The application of MNA for inorganics such as arsenic is gaining recognition and acceptance from regulatory agencies. The mechanisms for natural attenuation of arsenic are, in the general case, well understood, but the effectiveness of these potential mechanisms at a specific site can be difficult to assess. Continued groundwater monitoring and analysis of plume stability (Aziz et al. 2003) are necessary to ensure protection of downgradient receptors and to trigger implementation of contingency measures if needed.

The study of the fate and transport of arsenic at two field sites – anthropogenic arsenic at Tyndall and naturally-occurring arsenic at Devens – illustrates that observations of plume stability (based on groundwater monitoring) should be supplemented by laboratory evaluation of potential sequestration mechanisms. Direct evidence for arsenic sequestration (i.e., by examination of the soils or sediments obtained from field sites) may be difficult to demonstrate depending on the background arsenic concentrations.

The Devens study suggests that MNA may be an effective remedial option for sites where naturally-occurring arsenic has been mobilized due to localized introduction of organic carbon. The zero-order question relevant to these sites is whether As was immobile under ambient conditions (i.e., before the introduction of organic carbon). This question can be answered affirmatively if dissolved arsenic concentrations in groundwater are low upgradient of the organic carbon inputs and/or in the far-field downgradient of the influence of the organic carbon plume. The first-order questions that must be subsequently addressed include: (1) Is arsenic in the plume undergoing attenuation? (2) What is the capacity for arsenic sequestration in the far-field? and (3) What is the long-term stability of arsenic sequestered in the far-field? Ultimately, the capacity for arsenic sequestration must be assessed in the context of the organic carbon loading to the site.

Transitioning: Publications and Presentations

Publications

Choi, S., P. A. O’Day, and J. G. Hering. in prep. Natural Attenuation of Arsenic by Sediment Sorption and Oxidation.

Fitzmaurice, A. G., A. A. Bilgin, P.A. O’Day, D. Burris, H. J. Reisinger, and J. G. Hering. in prep. Geochemical and hydrologic controls on the mobilization of arsenic derived from herbicide application.

He, Y. T., A. G. Fitzmaurice, A. A. Bilgin, S. Choi, P. A. O’Day, J. Horst, J. Harrington, D. Burris, and J.G. Hering. in prep. Geochemical processes controlling arsenic mobility in groundwater: A case study of arsenic mobilization and natural attenuation.

He, Y. T., and J. G. Hering. in prep. Enhancement of arsenic(III) sequestration by manganese oxides in the presence of iron(II).

Hering, J. G., P. A. O’Day, R. G. Ford, Y. T. He, A. A. Bilgin, H. J. Reisinger, and D. R. Burris. in prep. MNA as a Remedy for Arsenic Mobilized by Anthropogenic Inputs of Organic Carbon.

Presentations

Bilgin, A. A., Hering, J. G., Harrington, J., Horst, J., Burris, D., Reisinger, H. J. Geochemical Controls on Natural Attenuation of Arsenic Solubilized by Human-Induced Alterations, Oral presentation at the Fall meeting of the American Geophysical Union, San Francisco, CA, Dec. 5-9, 2005

Choi, S., Beals, D. A., Hering, J. and O'Day, P. A. (2007) Sequestration Mechanisms of Arsenic Mobilized during In Situ Bioremediation of Chlorinated Solvents, poster presentation, American Geophysical Union, Fall Meeting 2007, Dec. 10-14, San Francisco, CA. Eos Trans. AGU, 88(52), Fall Meet. Suppl.

Fitzmaurice, A. G, Bilgin, A. A., Hering, J. G., O’Day, P., Burris, D., Reisinger, H. J. Geochemical and Hydrologic Controls on the Mobilization of Arsenic Derived from Herbicide Application, Oral presentation at the American Chemical Society 232nd National Meeting, Geochemistry Division, 10-14 September 2006, San Francisco, CA.

Hering, J. G., Bilgin, A., O’Day, P., Root, R., Illera, V., Clark, J., Reisinger, H. J., Burris, D. Investigation of Arsenic Mobility at an Arsenic-Contaminated DoD Facility, poster presented at the SERDP/ESTCP Partners in Environmental Technology Technical Symposium and Workshop, Washington, DC, Nov. 29-Dec 1, 2005.

Hering, J., Bilgin, A., Fitzmaurice, A., He, Y., Harrington, J., Horst, J., Burris, D., Reisinger, H. J. Fate and Transport of Naturally-Occurring Arsenic Mobilized during In Situ Bioremediation of Chlorinated Solvents, poster presented at the SERDP-ESTCP Partners in Environmental Technology Technical Symposium & Workshop, 28-30 November 2006, Washington, DC.

O'Day, P. A., Illera, V., Root, R., Choi, S. and Vlassopoulos, D. (2007) Mechanisms of Arsenic Mobilization and Attenuation in Subsurface Sediments. Oral presentation, American Geophysical Union, Fall Meeting 2007, Dec. 10-14, San Francisco, CA Eos Trans. AGU, 88(52), Fall Meet. Suppl.

O'Day, P. A., Hering, J. He, Y., Burris, D. R., and Reisinger, H. J. (2007) Possible Sequestration Mechanisms for Naturally-occurring Arsenic Mobilized During In Situ Bioremediation of Chlorinated Solvents, poster presentation, SERDP-ESTCP Partners in Environmental Technology Technical Symposium and Workshop, 4-6 December 2007, Washington, DC.

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