

Landfill-Stimulated Iron Reduction and Arsenic Release at the Coakley Superfund Site (NH)

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Arsenic is a contaminant at more than one-third of all Superfund Sites in the United States. Frequently this contamination appears to result from geochemical processes rather than the presence of a well-defined arsenic source. Here we examine the geochemical processes that regulate arsenic levels at the Coakley Landfill Superfund Site (NH), a site contaminated with As, Cr, Pb, Ni, Zn, and aromatic hydrocarbons. Long-term field observations indicate that the concentrations of most of these contaminants have diminished as a result of treatment by monitored natural attenuation begun in 1998; however, dissolved arsenic levels increased modestly over the same interval. We attribute this increase to the reductive release of arsenic associated with poorly crystalline iron hydroxides within a glaciomarine clay layer within the overburden underlying the former landfill. Anaerobic batch incubations that stimulated iron reduction in the glaciomarine clay released appreciable dissolved arsenic and iron. Field observations also suggest that iron reduction associated with biodegradation of organic waste are partly responsible for arsenic release; over the five-year study period since a cap was emplaced to prevent water flow through the site, decreases in groundwater dissolved benzene concentrations at the landfill are correlated with increases in dissolved arsenic concentrations, consistent with the microbial decomposition of both benzene and other organics, and reduction of arsenic-bearing iron oxides. Treatment of contaminated groundwater increasingly is based on stimulating natural biogeochemical processes to degrade the contaminants. These results indicate that reducing environments created within organic contaminant plumes may release arsenic. In fact, the strong correlation (>80%) between elevated arsenic levels and organic contamination in groundwater systems at Superfund Sites across the United States suggests that arsenic contamination caused by natural degradation of organic contaminants may be widespread.

Introduction

Arsenic contamination is widespread, both internationally (1–4) and within the United States, where nearly one-fifth of public groundwater supplies contain detectable levels of arsenic (5). The environmental risks associated with arsenic depend on its dissolved concentration and speciation.

Unfortunately, solid-phase concentrations do not effectively predict aqueous concentrations because a variety of factors may impact solubility. As a result, arsenic contamination frequently is identified in regions containing little or no known anthropogenic or natural arsenic source. Considerable effort has thus been expended to better understand the geochemical factors that regulate arsenic concentrations in the environment.

Three principal mechanisms of arsenic mobilization associated with geochemical conditions have been identified: desorption in alkaline conditions, competitive sorption, and reductive release, especially as associated with the dissolution of iron oxides. Of these, the reductive release of arsenic and/or arsenic-bearing minerals appears to be the primary cause of elevated arsenic levels under most conditions (6–9). Of particular importance are iron(III) (hydr)oxides, which strongly retain arsenic under oxic conditions (10–12). Elevated arsenic levels result from the reduction of arsenic-bearing iron (hydr)oxides under reducing conditions (6–9), conditions common in aquifers in Bangladesh and West Bengal (8, 13).

Iron reduction and the associated release of arsenic is frequently a dissimilatory microbial process (3, 6–9, 14). As a dissimilatory process, it must be coupled to the oxidation of an energy source, most commonly organic carbon. Several carbon sources have been proposed in Bangladesh, including dissolved organic carbon (13) and peat (15), although there is considerable disagreement concerning the mechanism by which these carbon sources are introduced into the aquifer (a prerequisite for iron reduction). Other issues including the role of humans in inducing arsenic contamination, the history and duration of potential arsenic contamination, and the reasons that reduction does not universally create arsenic contamination remain to be determined.

Arsenic contamination also is observed in more localized areas. In fact, more than one-third of the National Priorities List (Superfund) sites have excessive arsenic levels (16). While some of this contamination results from introduced arsenic, there is no known anthropogenic source for the arsenic at many of these arsenic-contaminated sites. The introduction of organic matter, which can stimulate biogeochemical processes such as metal reduction and thereby arsenic release, is one possible mechanism to explain the source of dissolved arsenic in some of these systems. Most arsenic-contaminated Superfund sites (81%) also have organic co-contaminants (e.g., benzene and other aromatic hydrocarbons) that could also serve as energy sources for iron reduction. However, relatively few studies have examined the role of these contaminants in arsenic release. Several recent studies (e.g., 17, 18–20) have suggested a linkage between contaminant-induced iron reduction and arsenic release, but more work remains to conclusively link contaminant degradation to arsenic release in these environments.

Here, we report a combination of field and laboratory-based investigations of arsenic contamination at an arsenic-contaminated Superfund site in Coakley, NH. This landfill site is typical in that it contains elevated levels of arsenic, other heavy metals, and organic contaminants. We use monitoring well data collected over the last 10 years to directly correlate changes in arsenic concentrations to geochemical processes such as reduction. By comparing modern concentrations with historical and background levels, we establish a quantitative link between field arsenic concentrations, iron reduction, and the attenuation of organic contaminants. Furthermore, we confirm this linkage using mechanistic information gleaned from X-ray absorption

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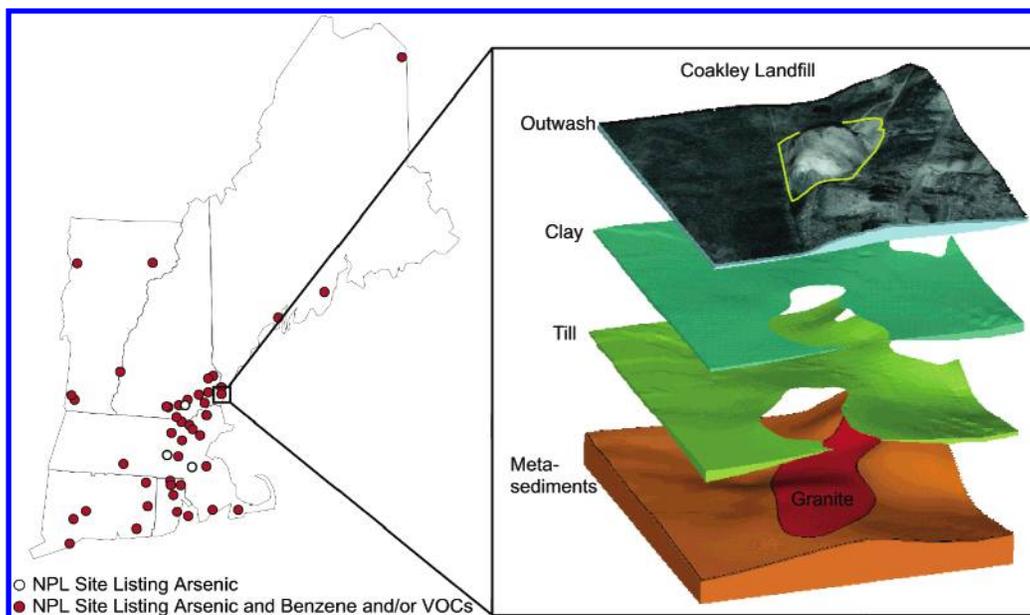


FIGURE 1. Location and subsurface geology of the Coakley Superfund site (outlined in yellow) in New Hampshire. Of the 45 federally remediated groundwater contamination (NPL) sites in the Northeast U. S. listing arsenic as a contaminant of concern, all but two also list volatile organic contaminants (VOCs) and/or benzene.

spectroscopic analysis and batch incubations in which arsenic release is stimulated by dissimilatory iron reduction.

Materials and Methods

Site Selection, Sampling, and Characterization. The Coakley Landfill Superfund site in North Hampton, New Hampshire (Figure 1) contains elevated levels of As, Cr, Pb, Ni, Zn, and benzene (and other volatile organic carbon species). The site was operated as a landfill from 1971 to 1983, when it was put on the National Priorities List. Remediation for VOC contamination called for consolidation of waste, landfill capping, and monitored natural attenuation (5). Testing performed on monitoring wells in 1991 showed that As, Cr, Pb, and Ni were the only inorganic parameters in excess of their maximum contaminant level (MCL). Manganese was also listed as a contaminant of concern. Construction of the landfill cap, emplaced as a part of a monitored natural attenuation (MNA) remediation plan, was completed in the summer of 1998.

The site today consists of a mounded, mixed-waste former landfill on thin layers of glacial outwash, glaciomarine clay, and till overlying bedrock. The bedrock consists of two major geologic units: the Rye Formation, which is a group of Silurian–Ordovician metasedimentary and metavolcanic rocks, and the Devonian Breakfast Hill Granite, which forms an intrusion running parallel to the Rye Formation. The glaciomarine clay is much finer than either the outwash or till, and has a correspondingly low hydraulic conductivity (7×10^{-7} cm/s) that impedes water flow and creates a boundary to oxygen exchange.

The pH, temperature, redox potential (E_h), conductivity, and dissolved oxygen levels were determined using electrochemical probes at each well in the field. The pH and E_h prior to landfill use are estimated using porewaters from clay samples in an uncontaminated region approximately 1 km west of the landfill site. The pH of these uncontaminated clays is circumneutral (between 6.5 and 7.1) and the E_h (about +400 mV) is indicative of oxidizing conditions.

The concentrations of contaminants and selected other elements were determined quarterly for a series of 27 monitoring wells, sampling wells, and landfill leachate from 1993 to the present. Sample collection was performed in acid-cleaned polyethylene bottles in accordance with EPA

low flow guidelines. Well locations, water level, and elevation reading were recorded at each well. The availability of this long-term concentration data is particularly beneficial to correlate changes in geochemical conditions and arsenic loading over time and as a result of MNA.

Groundwater Concentration Analysis. Filtered ($0.45 \mu\text{m}$) groundwater samples were analyzed for metals (Fe, Mn, Ca, Mg, Ni, Cr, Pb, Zn), anions (NO_2^- , NO_3^- , SO_4^{2-} , Cl^- , PO_4^{3-}), total organic carbon (TOC) and inorganic carbon (TIC), and total As. Samples to be used for metals analysis were acidified in the field with $100 \mu\text{L}$ of concentrated nitric acid, and total arsenic was treated on site with 0.125 M ethylenediaminetetraacetic acid (EDTA) to help preserve speciation. Dissolved metal concentrations were usually determined by inductively coupled plasma–mass spectrometry (ICP–MS), which has detection limits of about 20 ng/L, and analytical uncertainties of 4% or better. Anion concentrations were determined for un-acidified, filtered samples using ion chromatography. TIC was determined by acid titration, and TOC was determined using a Sievers TOC analyzer.

Elemental Analysis of Solids. The elemental concentration of a suite of metals and nonmetals (approximately 40 elements) was determined for small (5 g), homogenized samples of soils, sediments, and rocks from in and around the Coakley site. These solids were digested in concentrated HNO_3 followed by aqua regia. Elemental concentrations of the resulting solutions were determined by ICP–MS.

Extended X-ray Absorption Fine Structure Spectroscopy. Extended X-ray absorption fine structure (EXAFS) spectra were collected from clay-rich samples from -200 to $+1000$ eV about the K-edge of As (11867 eV) and Fe (7112 eV). Spectral processing was performed using WinXAS (21). Spectra were background corrected using a first-order polynomial fit, and normalized to unity. Linear combination fitting of normalized EXAFS spectra was used to determine the relative fractions of various iron mineral phases. Standards used for linear combination of Fe spectra were hematite, magnetite, ferrihydrite, goethite, lepidocrocite, chlorite, and pyrite. Arsenic reference spectra included sodium arsenate sodium arsenite, orpiment, realgar, and arsenopyrite.

The local coordination environment of As and Fe was determined by fitting EXAFS spectra. Normalized spectra were converted from energy to momentum (k -space) space

using a Fermi Level (E_f) of 11 868 eV for As and 7120 eV for Fe. A seven-point cubic spline was fit to the spectra and weighted by k^3 to amplify the upper k -range. A Fourier transform was applied to the spectra to produce a radial structure function ($3-14 \text{ \AA}^{-1}$). Fits were simulated using theoretical phase and amplitude functions derived using FEFF 8 (22) to determine the local coordination, including the element (Z), coordination number (CN), distances (R), and Debye–Waller factor (σ^2). Such fitting determines interatomic distances within 0.02 \AA , but may have considerable errors ($\pm 20-30\%$) in CN due to correlation with σ^2 .

Selective Sequential Extractions. Selective sequential extractions are commonly used to provide information about the phase associations of arsenic and other trace metals (23, 24). Triplicate samples (2 g) were extracted first with 1 M MgCl_2 solution for 1 h to remove the soluble As species. Second, the carbonate phases were extracted with 1 M sodium acetate/acetic acid for 5 h. The sample was then split into two subsamples for the determination of noncrystalline oxides and acid-volatile sulfides (AVS) fractions. Noncrystalline (hydr)oxides and AVS were extracted with 1 M HCl in one subsample, and ammonium oxalate (AOD) was used to extract amorphous oxides in the other. Sodium hypochlorite was reacted with residual solids from the HCl extraction at 95°C to remove organic-matter-associated As. A heated hydroxylamine/acetic acid (HH) extraction dissolved the crystalline (hydro)oxides. Residual silicates were removed by reflux with 10 M HF. It should be noted that sequential extractions separate trace elements into operationally defined mineralogical fractions, which may vary from actual speciation. Nevertheless, selective sequential extractions provide a useful, albeit approximate, method of estimating trace metal speciation.

Benzene Adsorption. The distribution coefficient for benzene adsorption on samples of the glaciomarine clay was determined by oscillation adsorption. Approximately 30 g (dry weight) of clay was placed into a 500-mL glass jar, and 100 mL of benzene solution of concentrations 1, 25, 50, 100, and 250 ppm was added. Jars were purged with nitrogen gas and filled completely to prevent excess volatilization into headspace, capped, and sealed to prevent air exchange. Samples were shaken for 5 h at 175 rpm, and centrifuged at 4000 rpm to separate fluids from clay. This step was repeated multiple times until no solid remained in the pellet. Supernatants were filtered ($0.45\text{-}\mu\text{m}$ filter), preserved with HCl, refrigerated, and analyzed by GC–MS. The mass of adsorbed benzene was determined by difference.

Batch Anaerobic Incubations. To stimulate the creation of a reducing environment, approximately 50 g of the glaciomarine clay from an uncontaminated site was suspended in a 250-mL solution containing 0.02 M CaCl_2 , 1% (w/v) D-glucose, and 0.33% (w/v) ammonium chloride (25). Glucose- and nutrient-free controls were also prepared. These samples were continuously purged with nitrogen gas, covered, and placed in a nitrogen atmosphere at room temperature. Samples were stirred and incubated for 3–14 days. The redox potential and pH were measured at 15-min intervals throughout the duration of the experiment. Every 2 days, filtered subsamples (10 mL, filtered with $0.2\text{-}\mu\text{m}$ filters) were collected and preserved with 100 μL of concentrated HNO_3 . The As, Fe, and S concentrations in these solutions were determined by ICP-MS.

Results and Discussion

Landfill Leachate Composition. A series of leachate samples were taken in August 2002 from a spring in the rip-rap drainage swale on the northwest perimeter of the landfill, each with varying levels of contributions from both groundwater and uncontaminated surface water sources. Arsenic concentrations in the leachate were relatively low ($23 \mu\text{g/L}$),

TABLE 1. Pre- and Post-Cap Average Contaminant Concentrations^a

location	contaminant	pre-cap mean	post-cap mean	change	p-value ^b
overburden	As	16.2	43.7	+169%	0.03
bedrock	As	10.7	9.5	-11%	0.76
all	As	13.8	21.9	+58%	0.16
overburden	benzene	10.9	2.6	-76%	0.02
bedrock	benzene	8.6	4.7	-46%	0.11
all	benzene	10.3	3.6	-65%	0.01
all	Mn	3160	107	-97%	0.001
all	Ni	2.5	<0.04	-99.8%	<0.0001
all	Cr	1.3	<0.04	-99.9%	<0.0001
all	Zn	2.2	0.2	-92%	<0.0001
all	Pb	25	4	-84%	0.02

^a Contaminant concentrations are reported as $\mu\text{g/L}$. ^b The p-value is the probability of significant difference for log-normalized concentrations. Smaller values are more significant; comparisons of means with p-values <0.05 are significantly different at $>95\%$ probability.

while samples collected following mixing with groundwater were significantly elevated (to $170 \mu\text{g/L}$ in a nearby spring), presumably as a result of As originating from groundwater sources. The glaciomarine clay that underlies much of the site is within 1–2 m of the surface at this string, thus arsenic contamination may originate within that layer. Following mixing with surface waters, As levels dropped off to 35 and then $17 \mu\text{g/L}$, as would be expected from dilution from uncontaminated sources.

Effects of Landfill Remediation. Following landfill capping in 1998, concentrations of Cr, Ni, Pb, and Zn declined significantly, while arsenic levels increased modestly (Table 1). Organic contaminants such as benzene also decreased significantly during this time, due in part to natural attenuation/biodegradation (26, 27). The effective remediation of Cr, Ni, and Pb with capping is consistent with these metals being derived from landfill leachate. The increase in arsenic after capping, combined with the lack of a gradient in arsenic concentrations with distance from the landfill, suggest that the leachate is not the primary source of the arsenic and points to an alternative, potentially natural, source of contamination.

Both the bedrock and overburden could serve as natural arsenic sources. Elevated arsenic concentrations elsewhere in the region have been attributed to bedrock pegmatites near the contacts between granitic and metasedimentary bedrock (28, 29). At these contaminated bedrock sites, arsenic is mobilized by desorption at high (>7) pH. While such a contact exists under this site (Figure 1), bedrock arsenic concentrations in both the contact region and adjoining bedrock are low (<1 ppm) and the pH is generally slightly acidic. In addition, concentrations of arsenic in wells screened in the bedrock have shown no significant change in arsenic concentration with remediation (Table 1). We thus conclude that neither the bedrock, nor contacts with it, are major sources of arsenic at this site.

We propose the arsenic at the Coakley site is derived from a glaciomarine clay layer in the overburden underlying the landfill (Figure 1). Typical arsenic concentrations in this clay layer (~ 20 ppm) are appreciably higher than other lithological units in the area but not unusually high. In fact, the clay layer contains arsenic levels similar to those of uncontaminated soils and sediments (30). The presence of an arsenic source within the overburden is further supported by the presence of significantly higher arsenic concentrations within wells screened within the overburden relative to wells located within the bedrock (Table 1). Given the propensity for arsenic retention within this clay layer, geochemical processes that promote arsenic desorption are likely responsible for its mobilization. Additionally, the geochemical release of arsenic

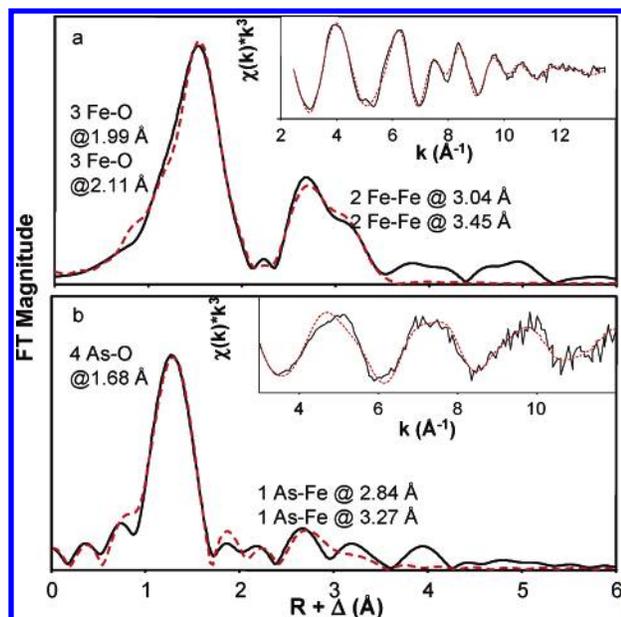


FIGURE 2. Iron (a) and arsenic (b) EXAFS spectra of the clay layer. The coordination environment is determined by fitting spectra (solid black lines) with theoretical spectra (red dotted lines). These data indicate that iron is present as ferrihydrite, while the arsenic is retained as AsO_4^{3-} bound to the ferrihydrite surfaces as both double corner sharing and edge sharing complexes. XANES spectroscopy confirmed that most arsenic was present as As(V). Similar spectra were identified in triplicate samples. Errors in interatomic distance (0.02 \AA) are small compared to the errors in coordination number ($\pm 20\text{--}30\%$).

in low arsenic environments (e.g., Bangladesh) is well chronicled.

Clay Layer Mineralogy. The clay layer is primarily composed of illite and chlorite; two clay minerals with relatively low affinity for arsenic (31, 32). However, the layer also contains approximately 5% total iron, much of which may be present in more reactive forms. Sequential extractions (23, 24) suggested that much of the iron is associated with reactive (amorphous) iron oxides (Supporting Information, Figure S1). Subsequent XAS analysis also indicates that Fe in this clay layer is predominantly ferrihydrite, $\text{Fe}(\text{OH})_3$, an amorphous iron oxide that strongly retains arsenic (33, 34). The Fe K-edge spectra contain Fe–Fe features suggestive of ferrihydrite (Figure 2), and linear combination fitting (Supporting Information, Figure S2) of this spectra indicates that at least 70% of the Fe is present in this phase.

The arsenic oxidation state and its association with ferrihydrite in the clay was also examined by XAS (Figure 2). XANES data (Supporting Information, Figure S3) indicates that all (within error) adsorbed As is present as As(V), a fact confirmed by the short As–O bond (1.68 \AA) measured in EXAFS. The EXAFS spectra identify As–Fe interactions indicative of adsorption to iron oxides (two As–Fe shells at distances of 2.83 and 3.24 \AA). These measured distances are similar to those observed for As(V) adsorbed on ferrihydrite (35–37), but also are similar to the distances measured on goethite and lepidocrocite (37, 38). However, the preponderance of ferrihydrite in the clay layer and its reactivity toward As and other ions suggests that arsenic is indeed associated with ferrihydrite. The association of As with ferrihydrite is confirmed by the concomitant extraction of As and Fe in amorphous oxide fraction (Supporting Information, Figure S1). The measured partition coefficient (K_d , determined using the field-measured concentrations of arsenic in the aqueous and solid phases) is high, and ranges between 400 and 1000 L/kg. This range is consistent with other environments rich

in ferrihydrite (e.g., 39). Under reducing conditions, this partition coefficient is expected to decrease measurably.

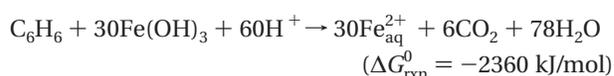
Iron Reduction Coupled to Arsenic Release at Coakley.

Arsenic associated with poorly crystalline iron oxides may be mobilized as a result of dissimilatory iron reduction by microorganisms (6–9, 13, 40). Dissimilatory iron reduction involves the oxidation of a carbon source coupled with the reduction of ferric iron as the primary electron acceptor (41). This process is ubiquitous in submerged aqueous environments, particularly in systems containing poorly crystalline iron oxides that undergo facile biogeochemical reduction (42, 43). At Coakley, the clay layer is fully saturated to impede oxygen flow, and the landfill provides a source of organic carbon.

Batch experiments consisting of the arsenic-rich clay and added carbon source (glucose) under a nitrogen atmosphere confirm that microbially mediated iron reduction could release arsenic in this system. Dissolved Fe (II) concentrations increased over time and were tied to decreasing redox potentials and pH (Figure 3). The release of iron required an organic carbon source and nutrients; thus, iron reduction in this system was microbially driven. Appreciable arsenic was also released over the course of these experiments and was strongly correlated to Fe(II) production. Some arsenic release also may be stimulated by a decrease in pH (from 7 to about 5) associated with biogeochemically mediated reduction over the course of the incubation. Arsenic and, to a lesser extent, iron are also released in batch incubations of other soils and sediments (e.g., 44, 45). Thus, batch reactions with the clay layer indicate that arsenic levels increase significantly as a result of microbial iron reduction.

At many mixed waste sites, there are a range of organic substrates which could facilitate iron reduction. At Coakley, benzene is entirely derived from the landfill and the predominant organic contaminant. Thus, changes in benzene concentrations are indicative of biogeochemical processes involving benzene, but also these other organics. Furthermore, benzene serves as an effective tracer for landfill-derived organic contamination because the landfill is the only major source of benzene. Benzene strongly partitions into the clay layer ($K_d = 220 \text{ L kg}^{-1}$) and thus, prior to capping, leachate-derived benzene likely accumulated in the clay layer. The accumulated benzene and other organics may then be oxidized by microbes through natural attenuation, releasing the sorbed arsenic (27). Consistent with this hypothesis, benzene concentrations in the overburden have decreased and arsenic concentrations increased (Table 1). It is possible to establish the coupling between benzene oxidation and arsenic release at the Coakley site by examining the *relative changes* in benzene and arsenic concentrations in specific wells over time that result from the decomposition of benzene and reductive release of arsenic, respectively. In fact, changes in dissolved benzene concentrations in the overburden after capping are well correlated ($R^2 = 0.86$) with changes in arsenic concentrations (Figure 3). Direct correlations between benzene and arsenic concentrations, however, show little or no trends because of the influence of the initial concentration and an apparent decoupling between the extent of benzene degradation and its initial concentration.

Theoretically, it should also be possible to use the change in benzene concentrations with the known stoichiometry of benzene oxidation to estimate the fraction of iron oxides that were reduced.



Given that 30 mol of Fe(III) are reduced per mol of benzene oxidized (assuming complete utilization of benzene, complete

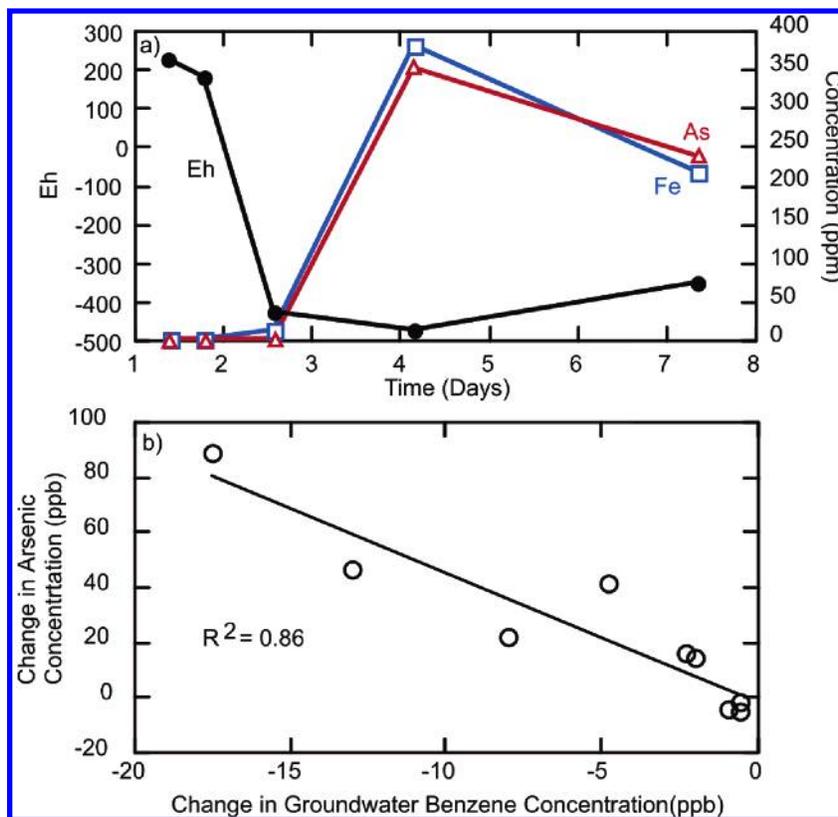


FIGURE 3. (a) Coupling of As release to Fe reduction in a batch experiment under a nitrogen atmosphere. Upon the addition of glucose and nutrients to the system, redox potential dropped, leading to the release of dissolved Fe and As. (b) Changes in groundwater dissolved benzene concentrations in overburden wells before and after landfill capping are well correlated with corresponding changes in arsenic concentrations.

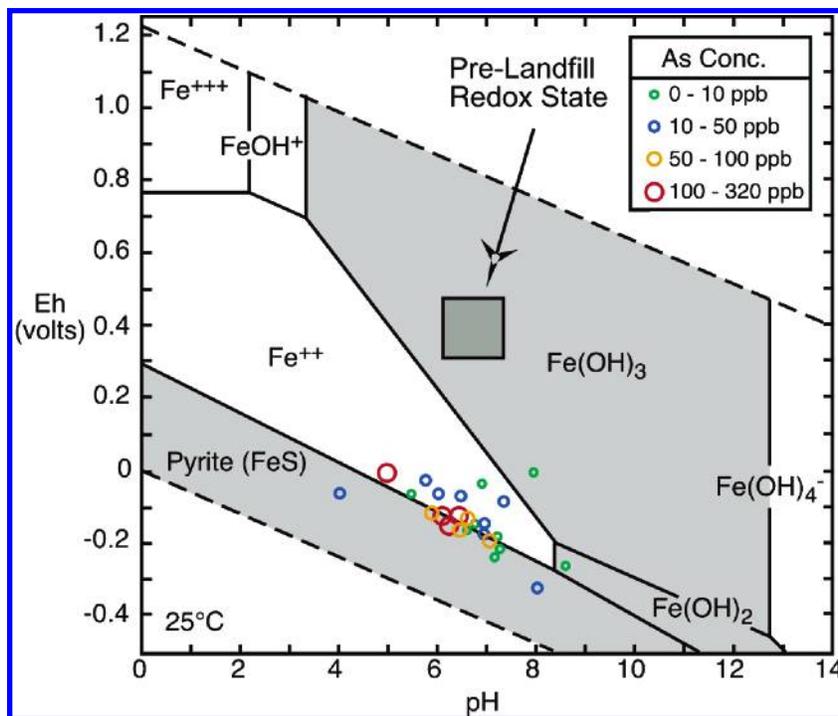


FIGURE 4. Iron stability diagram. Prior to the Coakley landfill, the redox potential and pH of groundwater in the clay layer was within the stability field of ferrihydrite (indicated by the dashed box). Measured redox potential (E_h) and pH of present-day As-contaminated samples from the site are indicative of Fe(III) reduction to dissolved Fe(II). The most reduced samples exhibit the highest arsenic concentrations.

oxidation, and no Fe(II) precipitation), a 10 $\mu\text{g/L}$ decrease in dissolved benzene concentrations corresponds to no more than 0.3 mg/L increase in Fe(II) concentrations. This relatively modest increase in Fe concentrations is not large enough to

explain the observed iron concentrations, thus, additional organic carbon sources, either other contaminants or landfill-derived organic matter, also are involved in dissimilatory iron reduction. However, if desorption of adsorbed benzene

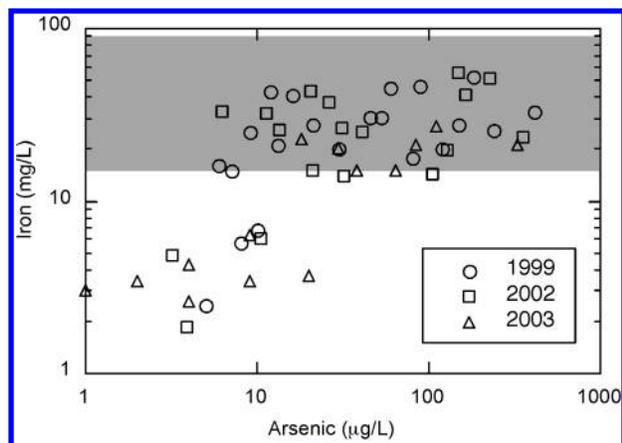


FIGURE 5. Correlation between dissolved total As and Fe concentrations after cap construction. Arsenic concentrations generally correlate with iron concentrations until siderite solubility limits Fe levels, as indicated by shaded region.

replenishes dissolved benzene, then the change in benzene levels could explain the reduction of a considerably larger quantity of iron(III) hydroxide.

Considerable field evidence indicates that active reduction of arsenic-bearing iron (hydr)oxides occurs at Coakley. For example, the relationship between the pH and redox potential identifies the active redox transformations of iron, and arsenic concentrations. The pH of the uncontaminated glaciomarine clay is circumneutral and the redox potential (about +400 mV) is indicative of oxidizing conditions (Figure 4) favoring strong retention of arsenic (34, 46). Current arsenic-contaminated groundwater at Coakley exhibits more reduced potentials (0 to -200 mV) within the dissolved Fe^{2+} stability field, indicative of iron-reducing conditions. The relationship between dissolved iron and arsenic levels can also be compared to better establish the reductive release of arsenic from iron oxides. Dissolved arsenic and iron concentrations are correlated at lower concentrations, but the relationship breaks down at higher dissolved iron concentrations (Figure 5). The iron levels are limited by siderite solubility when the iron concentration is above about 14 mg/L; dissolved iron levels are broadly in equilibrium with siderite given the near neutral pH (~6) and measured alkalinity (at least 200 mg/kg CaCO_3) of contaminated groundwater at the Coakley site (Figure 5). Siderite formation also would serve to moderate pH changes associated with the oxidation of dissolved organics. These data are consistent with iron concentrations in other groundwater systems, which are frequently saturated with respect to ferrous mineral phases such as vivianite and siderite (13, 14, 47). We therefore conclude that iron reduction is the primary mechanism by which arsenic is released from sedimentary environments at Coakley.

The elevated arsenic concentrations suggest that the reduced environment is relatively recent; the mobilized arsenic would have long since been flushed from the clay if reducing conditions were present prior to landfill emplacement. Redox conditions should now remain poised until all available iron oxide is reduced or the organics are oxidized. Thus, sulfide produced through sulfate reduction is not likely to accumulate at this time. Additionally, arsenic retention in sulfidic minerals such as arsenopyrite or orpiment is not likely due to a lack of reduced sulfur in the system.

Implications. The mechanism of As mobilization demonstrated at this site is similar to that suggested for the catastrophic contamination occurring in Bangladesh, West Bengal (e.g., 8, 14) and elsewhere. While the scale of As contamination elsewhere may be larger than that seen at Coakley, our results have broad implications regarding the identification and treatment of arsenic-contaminated sites. The natural

process of microbial degradation occurs whenever groundwater is contaminated by most commonly occurring organic contaminants. In fact, microbial degradation is the cornerstone of the increasingly common remediation practice of monitored natural attenuation (MNA). Prior to 1990, MNA was selected as a remediation strategy less than 5% of the time at Superfund sites; in 1998, MNA was selected almost 30% of the time (48). When microbial degradation of organics occurs under reduced conditions, groundwater may become contaminated by naturally occurring arsenic—even when the levels of naturally occurring arsenic are not elevated. Reducing conditions are enhanced when, as is common practice with MNA, the landfill is capped and the supply of oxygenated water to the subsurface is diminished. Among groundwater contamination sites being remediated by the U.S. Environmental Protection Agency, those employing MNA are nearly 50% more likely to have excessive arsenic contamination (48). This strong correlation between elevated arsenic levels and organic contamination in groundwater systems has not been recognized previously and suggests that arsenic contamination caused by natural degradation of organic contaminants may be a widespread phenomenon. Additionally, mobilization of arsenic via natural attenuation may greatly prolong or exacerbate the remediation process. Thus, care must be exercised when evaluating the suitability of natural attenuation to ensure that arsenic contamination is not worsened by remediation nor the cleanup time greatly increased.

Acknowledgments

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Supporting Information Available

Additional figures detailing extraction data and linear combination EXAFS fitting. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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