Geochemical and hydrologic controls on the mobilization of arsenic derived from herbicide application

Arthur G. Fitzmaurice¹, A. Azra Bilgin¹, Peggy A. O'Day², Virginia Illera², David R. Burris³, H. James Reisinger³, Janet G. Hering^{1}*

¹Department of Environmental Science and Engineering, California Institute of Technology,
1200 E. California Blvd., MC 138-78, Pasadena, CA 91125, USA

²School of Natural Sciences, University of California, Merced, 5200 N. Lake Road, Merced, CA
95343, USA

³Integrated Science & Technology, Inc., 1349 Old Highway 41, Suite 225, Marietta, GA 30060,
USA

*Corresponding author: Eawag, Swiss Federal Institute of Aquatic Science & Technology,
Ueberlandstrasse 133, CH-8600 Dübendorf, Switzerland

FAX: +41 (0)44 823 5398; Janet.Hering@eawag.ch

submitted to *Applied Geochemistry*, February 2009

revised version submitted September 2009

This document is the accepted manuscript version of the following article:
Fitzmaurice, A. G., Bilgin, A. A., O'Day, P. A., Illera, V., Burris, D. R., Reisinger, H. J., & Hering, J. G. (2009). Geochemical and hydrologic controls on the mobilization of arsenic derived from herbicide application. *Applied Geochemistry*, 24(11), 2152-2162. <http://doi.org/10.1016/j.apgeochem.2009.09.019>

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Abstract

The fate and transport of arsenic (As) was examined at an industrial site where soil- and groundwater contamination are derived from the application of As_2O_3 as an herbicide.

Application of arsenical herbicides was discontinued in the 1970's and soils in the source area were partially excavated in 2003. Arsenic contamination (up to 280 mg/kg) remains in the source area soils and a plume of As-contaminated groundwater persists in the surficial aquifer downgradient of the source area with maximum observed As concentrations of 1,200 $\mu\text{g/L}$ near the source area. The spatial extent of As contamination as defined by the 10 $\mu\text{g/L}$ contour appears to have remained relatively stable over the period 1996 to 2006; the boundary of the 1,000 $\mu\text{g/L}$ contour has retreated over the same time period indicating a decrease in total As mass in the surficial groundwater.

In column experiments conducted with source area soil, the As concentrations in the column effluent were comparable to those observed in groundwater near the source area. A substantial fraction of the As could be leached from the source area soil with ammonium sulfate and ammonium phosphate. Exhaustive extraction with background groundwater removed most of the total As. These results indicate that As in the source area soils is geochemically labile. Source area soils are low in extractable iron (Fe), manganese (Mn), and aluminum (Al), and characterization by X-ray absorption spectroscopy and electron microscopy indicated that As is present primarily as arsenate sorbed to (alumino)silicate minerals.

Batch sorption experiments showed much less sorption on surficial aquifer sediments than on sediments from the Jackson Bluff Formation (JBF), a presumed confining layer. This limited capacity of the surficial aquifer sediments for As sorption is consistent with the similar As contents observed for these sediments within and upgradient of the As plume. The apparent

stability of the As plume cannot be explained by sequestration of As within the surficial aquifer. Sorption to JBF sediments may contribute to As sequestration, but As enrichment in JBF sediments within the plume (i.e., as compared with JBF sediments upgradient) was not observed.

These results indicate that neither the persistence of As in the source area soils or the apparent stability of the plume of As-contaminated groundwater at this site can be explained by geochemical controls on As mobility. The absence of demonstrable geochemical bases for such observations suggests that possible hydrologic controls should be further investigated at this site.

Keywords: groundwater contamination, natural attenuation, sorption, XAS

1. Introduction

Arsenical pesticides and herbicides were widely used in the United States throughout the 20th century until arsenic (As) was placed on the U.S. Environmental Protection Agency's (USEPA) Priority List of Hazardous Substances. In 2001, concerns regarding the toxicity and carcinogenicity of As prompted the USEPA to lower the maximum contaminant level (MCL) for As in drinking water from 50 to 10 $\mu\text{g/L}$ (USEPA, 2001). The leaching of As from soils previously treated with arsenical pesticides poses a potential threat to human health through contamination of drinking water supplies.

Arsenical pesticides are known to be effective for years after application (Norman et al., 1950), suggesting that they are not easily leached from soils. After the cessation of pesticide application, As has persisted at high concentrations in some soils despite decades of rainfall and irrigation (Sadler et al., 1994; McLaren et al., 1998; Folkes et al., 2001; Robinson and Ayuso, 2004; Smith et al., 2006; Yang and Donahoe, 2007). Leaching of As applied in organic form has, however, been inferred from the accumulation of As in the sediments of lakes receiving surface runoff or groundwater discharge from treated soils (Whitmore et al., 2008).

Immobility of As in soils under oxic conditions is often attributed to the association of As with Fe-bearing solid phases through sorption or co-precipitation (Smedley and Kinniburgh, 2002; Stollenwerk, 2003). Evidence has also been reported for precipitation of As(V)-containing salts in soils (Bothe and Brown, 1999; Yang and Donahoe, 2007). Mobilization of As from such solids can occur when the solids or the association of As with them are destabilized due to changes in geochemical conditions. Such geochemical control of As mobility is often assumed when As is persistent in soils over long periods.

In this study, we examine the mobilization of As from a sandy soil where it has persisted for three decades after the use of arsenic trioxide (As_2O_3) as an herbicide was discontinued. The controls on As mobilization have implications both for the occurrence of As in groundwater and the fate and transport of As in the subsurface environment.

2. Site Description

Tyndall Air Force Base (AFB) is located in the Florida Panhandle between Panama City and Mexico Beach on a strip of barrier land that separates East Bay (the eastern portion of St. Andrew's Bay) from the Gulf of Mexico (Figure 1). An electrical substation was constructed on the base in 1960. Arsenic trioxide was applied as an herbicide at the substation until the mid-1970's.

In 1992, As contamination in groundwater was identified at the Tyndall site with a maximum As concentration of 1,700 $\mu\text{g/L}$ measured at a monitoring well (MW-1) located at the substation and screened from the water table at 1.5 m below ground surface (bgs) to 4.5 m; an even higher As concentration (2,400 $\mu\text{g/L}$) was observed at MW-1 in 1993 (SCS, 1999). By 1996, 18 monitoring wells were installed at the site (2 additional wells were installed later); all wells were screened over 3-m intervals at varying depths as indicated in Figure 2. Groundwater monitoring in 1996 showed a plume of As-contaminated groundwater extending southwest from the substation in the direction of groundwater flow.

In 2003, soil within the substation was partially excavated to depths ranging from 0.6 to 1.5 m. Approximately 800 t of contaminated soil was removed from the site and replaced with clean soil (SCS, 2003). Some areas of the energized substation could not be safely excavated

and thus those soils remained in place. Crushed gravel covers the entire substation ground surface where equipment is not positioned, allowing for infiltration of rainwater.

The stratigraphy of the study site is defined by three primary units: recent sands (surficial aquifer), the Jackson Bluff Formation (JBF), and the Intracoastal Formation (Schmidt and Clark, 1980; SCS, 1999). The surficial aquifer sediments are well-sorted fine- to medium-graded sands. A distinct peaty zone, 15-30 cm thick, occurs at an approximate depth of 0.9-1.5 m. Below this, the sands are tan to grayish-white, well-sorted, slightly silty, and fine-grained. At a depth of approximately 14 m, the sands grade into the JBF, which is characterized by dark greenish-gray, very fine-grained, clayey, silty sand. The thickness of the JBF varies but appears to be approximately 2.5 m thick near the substation. The JBF is underlain by the upper Intracoastal Formation, which is dark greenish-brown, fine-grained, clayey, silty sand.

Groundwater flow is generally in the southwest direction. The water table is typically within 0.9-1.5 m of the land surface, and the aquifer is recharged by direct infiltration into the porous sands. Groundwater is lost by discharge into springs and streams or drainage ditches, subsurface flow to the ocean, evaporation, transpiration, and withdrawal. In addition, some groundwater may flow downward through the intermediate leaky aquitard. The average hydraulic conductivity estimated from 6 slug tests (Brouwer-Rice method) is 0.02 cm/s (MW-2, 3, 5, 8, 9, and 10), and the effective porosity is estimated to be 0.2. The estimated horizontal flow rate toward the Gulf of Mexico in the surficial aquifer is 0.8 m/d based on a gradient of 0.01, but this hydraulic gradient is not uniform across the site (SCS, 1999).

3. Methods

3.1 Chemicals and analytical methods

All chemicals used were reagent grade or higher, and used without further purification: OmniTrace Ultra HNO₃, HNO₃, HCl, H₂SO₄, pyridine, and CertiPUR ICP standards were obtained from EMD Chemicals; NaAsO₂ and CaSO₄ from J.T. Baker; NaOH, (NH₄)₂SO₄, and NH₄H₂PO₄ from EM Science; Na₂HAsO₄·7H₂O, EDTA, MgSO₄·7H₂O, and NaCl from Sigma; NH₄CH₃COO, CH₃COOH, and CH₃OH from BDH; 1,10-phenanthroline and H₂O₂ from Alfa Aesar; NH₂OH·HCl from Fisher Scientific.

Solutions were prepared with 18.2-MΩ·cm deionized water (Millipore Milli-Q 18.2-MΩ system) and stored in plastic containers that had been washed with 10% HCl. All volumetric flasks were washed with 10% HCl and rinsed several times with deionized water prior to use. All analyses were conducted in triplicate, including instrument and field blanks.

Dissolved As, aluminum (Al), manganese (Mn), and silicon (Si) were determined by inductively-coupled plasma-mass spectrometry (ICP-MS, Hewlett-Packard 4500). Samples were diluted with Ultra HNO₃ (OmniTrace) to 1% acid.

Iron was determined as Fe(II) and total Fe using the colorimetric 1,10-phenanthroline method without boiling (adapted from Eaton et al., 2005) with a UV-Visible Spectrophotometer (Cary 480) at 510 nm.

Arsenic speciation was determined by quantifying As(III) and As(V) using coupled liquid chromatography (LC) and ICP-MS, in which As(III) and As(V) were separated by an HPLC column (Hewlett Packard 1100 series) with a 3-mM phosphate mobile phase (pH 6.0) at 0.9 mL/min flow rate and HPLC outflow was directly connected to ICP-MS for As measurement.

Major cations and anions were quantified by ion chromatography (Dionex Model DX-500) following standard methods (Eaton et al., 2005). Colorimetric determinations of phosphorus by USEPA Method 365.1 (USEPA, 1993) and determinations of total and dissolved organic carbon (TOC, DOC) by combustion/catalytic oxidation (Eaton et al., 2005) were performed by MWH Environmental Laboratories (Pasadena, CA). To avoid excessive holding times, analyses of nitrate and nitrite by ion chromatography were performed by Quality Analytical Laboratories (Panama City, FL).

Specific surface areas of selected samples were determined using the Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption method (Gemini 2360 surface area analyzer, Micromeritics).

3.2 Sample collection

Three types of samples were collected at the Tyndall site: surface area soils, aquifer sediment cores, and groundwater. Drilling was performed at the site in August 2005 using a direct-push drill rig to collect sediment cores and to install a new monitoring well, MW-1R, replacing well MW-1, which was removed during excavation of the source area. Well MW-1R was installed immediately downgradient of the substation boundary and screened from 1.5-4.5 m bgs.

3.2.1 Source area soils and aquifer sediment cores. Surficial soil samples were collected by hand trowel from 0.3 to 0.6 m bgs from two locations (denoted S3 and S27) within the substation in April 2005. An additional sample was collected at location S27 in July 2006. Soil samples were shipped on ice and stored in the dark at 4°C until analysis or frozen for later use.

In August 2005, sediment cores were collected within the arsenic plume (ASB-1, ASB-2, ASB-3) and in background areas cross- and up-gradient of the substation (BSB-1, BSB-2, BSB-3). Upon collection, cores enclosed in acetate core sleeves were cut into intervals of 0.3-0.6 m and sealed with plastic end caps secured with duct tape; selected sections were shipped on ice and stored in the dark at 4°C until they were sectioned into 0.15 m intervals, homogenized under nitrogen in a glove box, and frozen until use.

3.2.2 Groundwater samples. In April 2005, background groundwater was collected up-gradient of the substation from MW-2. Samples were shipped on ice, stored at 4°C until analysis (which was conducted within 10 d of sample collection), and then frozen until used in leaching experiments. Additional groundwater was collected at MW-2 in July 2006 for use in leaching experiments. In August 2005, groundwater samples were collected from 18 monitoring wells using low-flow sampling techniques. Field parameters including pH, dissolved oxygen (DO), temperature, turbidity, and oxidation-reduction potential (ORP) were measured at the time of collection. Samples for analysis of nitrate plus nitrite were analyzed at a local commercial laboratory. Other samples were preserved appropriately for the intended analyte (USEPA, 1983) and shipped on ice. Note that unpreserved samples were used for determination of As speciation. Some samples were filtered through a 0.22 µm mixed cellulose ester (Millipore) filters before analysis.

3.3 Characterization of source area soils and aquifer sediment samples

3.3.1 Sample handling. Source area soil samples collected in April 2005 and July 2006 were stored frozen. Samples were thawed and homogenized without drying (April 2005) or after air-drying in the dark for 1 d (July 2006). Samples were then sieved successively through 18-

mesh (1 mm), 32-mesh (500 μm), 60-mesh (250 μm), and 250-mesh (63 μm) sieves. Water content was determined gravimetrically for the April 2005 samples. Sub-samples of whole and sieved soils collected in July 2006 were freeze-dried for 2 d.

For aquifer sediments (collected August 2005), frozen samples were similarly homogenized, dried, and sieved, but under nitrogen atmosphere in the glove box. Sub-samples were transferred to 15-mL centrifuge tubes and loosely capped in the glove box before being freeze-dried for 2 d.

3.3.2 Scanning electron microscopy (SEM). A soil representative of the source area (S3, collected April 2005) was ground to a powder and allowed to dry under nitrogen in a glove box. A dried sample was mounted on carbon tape and imaged in a FEI Quanta 200 SEM with an EDAX Genesis 2000 energy dispersive spectrometer (EDS) for elemental analysis. The microscope was operated at an accelerating voltage of 20 kV, with a working distance of 10 mm and magnifications of 600-5000 $\times$.

3.3.3 X-ray absorption spectroscopy (XAS). Two representative source area soils (S3 and S27, collected April 2005) were analyzed by X-ray absorption spectroscopy (XAS) (performed in June 2005). Arsenic K-edge absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 11-2 at cryogenic temperature (~ 4 K) under dedicated conditions (3 GeV, 70-100 mA) using an unfocused beam. Powdered samples were loaded into 2-mm-thick Teflon sample holders and sealed with Kapton film. Arsenic K-edge and EXAFS fluorescence spectra (S3 only) were collected using a Si(220) monochromator crystal and a 30-element solid-state Ge array detector. Beam energy was calibrated on As foil at 11,867 eV. Multiple scans (6-8) were collected and averaged for each sample. Structural information was determined by non-linear least-squares fitting of the

normalized EXAFS of sample S3 with the program EXAFSPAK (George and Pickering, 2000) using theoretical phase-shift and amplitude functions for single and multiple-scattering calculated with the program FEFF (Rehr et al., 1992).

3.3.4 Total elemental analysis. Freeze-dried samples of source area soil (S3 and S27, collected April 2005, and the 0-250 μm size fraction of S27, collected July 2006) and whole and size-fractionated aquifer sediment (collected August 2005) were sent to SGS Minerals Services (Toronto, Ontario) for total elemental analyses. Major elements were determined by X-ray fluorescence (XRF) after meta/tetraborate fusion (method XRF76Z) and reported as % oxides. Total As content was determined for source area soils by XRF on pressed pellets (method XRF75V) and for aquifer sediments by hydride generation atomic absorption spectroscopy after sodium peroxide fusion (method HAS90A).

3.3.5 Method 3050B extractions. Sub-samples of homogenized source area and aquifer soil (whole and size-fractionated fractions) were extracted following Method 3050B, a strong acid digestion that mobilizes solid-associated “environmentally available” metals (USEPA, 1996). Elements bound in silicate structures are not extracted by this method. In brief, 1.0-g samples were reacted in 50-mL tubes in triplicate at 95-99 °C on a heating block with 35% HNO_3 for 15 min, ~50% HNO_3 for 4.5 h, and ~5% H_2O_2 for 4 h.

3.3.6 Sequential extractions. For source area soil (S27, collected July 2006), 1.0-g sub-samples of 0-250 and 63-250 μm size fractions were sequentially extracted twice with 25 mL solutions of 50 mM $(\text{NH}_4)_2\text{SO}_4$ for 4 h and twice with 50 mM $\text{NH}_4\text{H}_2\text{PO}_4$ for 16 h following a method adapted from Wenzel et al. (2001) and then subjected to 3050B extraction. Extractions were performed in triplicate. For each extraction step, samples were shaken on a shaker table at

20°C and subsequently centrifuged for 15 min at 2,000g. The supernatant was filtered and retained for measurement, while the solid was subjected to successive extraction steps.

3.4 Mobilization and sequestration experiments

3.4.1 Exhaustive extraction with groundwater. Using the 0-250 µm size fraction of source area soil (S27, collected July 2006), a 100-g sample was leached with 1 L of background groundwater (MW-2, collected July 2006). The suspension was divided into four opaque bottles which were shaken on a shaker table at room temperature for at least 24 h and subsequently centrifuged at 3,500 g for 10 min. The supernatant was decanted, and background groundwater was replaced. This process was repeated 14 times. The soil was air-dried, and aliquots were extracted in triplicate following Method 3050B.

3.4.2 Batch leaching experiments. Batch leaching experiments were performed with 0-250 and 63-250 µm size fractions of source area soil (S27, collected July 2006) using a synthetic groundwater based on the composition of background groundwater (well MW2). The synthetic groundwater consisted of 44 µM NaCl, 75 µM CaSO₄, and 82 µM MgSO₄ buffered to pH 5.2 with 10 mM pyridine. Soils were leached in 15-mL centrifuge tubes at solids concentrations of 5, 40, 100, 250, and 500 g/L. Suspensions were mixed by end-over-end rotation in the cold room (dark, 12.5°C) for 3 d and then centrifuged at 14,000 g for 10 min. Supernatants were filtered through 0.2 µm Acrodisc nylon-membrane syringe filters (Pall) and acidified before analysis. Experiments were performed in triplicate.

3.4.3 Static column leaching experiments. Using the 63-500 µm size fraction of source area soil (S27, collected April 2005), 300 g of soil was distributed evenly into three 11-cm long Plexiglas cylindrical reactors with a 9-cm inner diameter (ID) fitted with a medium porosity (10-

16 μm) fritted filter disc (Chem Glass, NJ) to retain soil. The outlet (outer diameter (OD) 90 mm) was located at the bottom of the column on the side. Approximately 100-150 mL of background groundwater (MW2, collected April 2005) was added to the reactors and allowed to saturate the soil. The reactors were left in the cold room (dark, 12.5°C) for 4 d. The leachate was then pumped out, discarding the first 50 mL, filtering and retaining the next 15 mL, and discarding the remaining leachate. The reactors were then left in the cold room for 1 d. This process of wetting for 4 d and drying for 1 d was performed six times.

3.4.4 Flow-through column leaching experiments. Using the 0-250 μm size fraction of source area soil (S-27, collected July 2006), 220 g of soil was distributed evenly into two 20-cm long Plexiglas cylindrical reactors (5-cm ID) with outlet holes (OD, 90 mm). Nylon mesh was used to retain the soil. Columns were eluted with synthetic groundwater (see section 3.4.2) in an upflow direction under the following flow conditions: 5 mL/h for 24 h, 20 mL/h for 16 h, no flow for 48 h, 5 mL/h for 24 h. Columns were kept in the cold room (dark, 12.5°C) throughout the experiment and samples were collected with an automatic fraction collector.

3.4.5 Sorption experiments with aquifer sediments. Sediment samples (0.75 g) were added to 25 mL of background groundwater (MW-2, collected July 2006) spiked at $t = 0$ h with As(V) at initial concentrations ranging from 0.5 to 170 μM in 50-mL centrifuge tubes in a glove box. Note that, for experiments with ASB-1 sediments, 0.50 g of sediment was added to 16.67 mL solution. Suspensions were prepared in triplicate and rotated end-over-end in the cold room (dark, 12.5°C) for 36 h before centrifugation at 14,000 g. Supernatants were filtered and acidified for analysis. At $t = 36$ h, the pH of the filtered supernatants was measured before acidification. Solid-associated As was calculated as the difference between the total As in the suspension (i.e., As spike plus the ambient As content of the solid) and the measured, dissolved

As concentration. Sorption experiments were performed with whole and size-fractionated sediments from cores obtained within and upgradient of the As plume.

4. Results and Discussion

4.1 Groundwater composition

Groundwater sampling conducted in August 2005 confirmed the extent of As contamination as observed in previous monitoring events (Figures 2 and 3). The As concentration measured at the newly-installed well MW-1R located at the substation boundary (and replacing well MW-1) was 1,160 µg/L. This value is lower than that previously measured at well MW-1 (e.g., 2,400 µg/L in 1993) before its removal in 2003, which may reflect the decrease in the source strength due to the partial excavation of contaminated soil.

Determination of As speciation demonstrated that As is present in the groundwater primarily in the +V oxidation state (Figure 3). The highest As(III) concentration measured was 108 µg/L at well MW-10 corresponding to 13% of the total, dissolved As; As(III) was undetectable in 15 of the 18 wells sampled. In a previous study conducted at Tyndall, groundwater discharging into a ditch was collected approximately 1 m below the surface using shallow piezometers. The observed ratio of As(III):As(V) was roughly 1:1 with approximately 10% of the total, dissolved As present as methylated species (Miller, 2001). Since only As₂O₃ was applied at the site, these observations indicate that both As(III) oxidation and, to a lesser extent, methylation occurred *in situ*.

In general, the Tyndall groundwater was moderately acidic with relatively low conductivity and a major ion composition dominated by calcium (Ca), magnesium (Mg), and sulfate (SO₄) (Tables 1 and 2). Dissolved organic carbon (DOC) measured at MW2 was high

(10.2 mg/L) for groundwater, possibly due to the influence of the peaty organic layer in the subsurface. It is likely that DOC contributes to the observed acidity of the groundwater.

Comparison of Fe (and Mn) concentrations within the zone of As contamination (Table 2) and outside it (Table 1) does not suggest that As mobilization is associated with the reductive dissolution of Fe-containing carrier phases despite the importance of this mechanism for As mobilization in many other locations (Ravenscroft et al., 2009 and ref. cit.)

4.2 Soil and sediment characterization

Soils collected from the source area (i.e., the substation) and sections of sediment cores collected both within and upgradient of the As plume were analyzed.

4.2.1 Source area soils. The mineralogy of the source area soils is dominated by quartz, which was observed by SEM/EDS to occur as euhedral grains (~10-50 μm) with sparse surface coatings containing mostly Al, Si, and Ca (example grain shown in Figure 4). Notably, no Fe was detected by EDS, although Fe is commonly present as a surface coating on soil minerals. Microscale observations are generally consistent with the bulk soil composition, which was determined to be 95% SiO_2 with 1.4% CaO , 0.7% Al_2O_3 , 0.6% Fe_2O_3 , and 0.44% MgO . The amount of 3050B-extractable Fe, Al, and Mn in the source area soils were low compared with a NIST reference sandy soil, similar to a previous survey that also found Florida soils to be depleted in these elements (Chen and Ma, 1998) (Table 3).

Total As contents (determined by XRF) in two source area soil samples were 180 (S27) and 280 (S3) mg/kg, consistent with previous measurements. These values are substantially elevated relative to background As levels in Florida soils, which are characterized by a geometric

mean of 0.4 mg/kg with an estimated upper limit for the background As content of 7.0 mg/kg (Chen et al., 2001).

Concentrations of 3050B-extractable As were approximately 80% of the total As concentrations determined by XRF on whole soils (Table 4). In a modified sequential extraction, a substantial fraction of the As associated with the solids was extracted by ammonium sulfate and ammonium phosphate, indicating that dissolution of the solid carrier phase is not a prerequisite for As mobilization. The distribution of As released in different sequential extraction steps was similar for the 0-250 and 63-250 μm size fractions, though this comparison is complicated by the incomplete (75%) recovery in the sequential extraction as compared with the single 3050B extraction. Exhaustive batch extractions consisting of 14 consecutive washes with background groundwater (each at a soil-solution ratio of 1:10) resulted in the leaching of 92% of the 3050B-extractable As and 79 and 92% of the 3050B-extractable Fe and Mn.

Comparable results were obtained in a previous study of soils from the southeastern U.S. that had been contaminated by As_2O_3 ; approximately 50% of the total extractable As was released from the soil by extraction with ammonium sulfate and ammonium phosphate (Yang and Donahoe, 2007). Comparison of sequential extraction and (kinetic) leaching of soils with synthetic acid rain (SAR) solution indicated that, in low pH soils, the amount of As leached by SAR corresponded closely to the sequential extraction steps that did not involve any reduction (i.e., reductive dissolution) of the soil matrix (Qi and Donahoe, 2009).

The oxidation state of As in two source area soils was determined by XANES analysis of the bulk soil. The energy of maximum absorption is indicative of As oxidation state (e.g., Foster, 2003). Soil XANES spectra show that As is present predominantly in the +V oxidation state, as indicated by the absorption maximum at 11.875 KeV (Figure 4). There is no evidence in

XANES spectra for adsorption at lower energies that would indicate the presence of other As oxidation states. Quantitative EXAFS analysis of one sample (S3) indicated the arsenate geometry of tetrahedral coordination of As to four oxygen atoms and weak backscattering from atoms beyond the oxygen coordination shell (Figure 4). Second-neighbor features were fit with a combination of multiple scattering from the arsenate tetrahedra and a second shell of Si or Al atoms (which cannot be distinguished as backscatterers). The structural results are consistent with sorbed arsenate on the surface of Al-oxide surface coatings and/or aluminosilicate minerals. A previous study also found that As was generally disseminated on the surface of fine-grained soil particles; analysis of rare As-rich particles by XANES demonstrated the presence of As(V) (Yang and Donahoe, 2007). Thus the speciation of As in the solid phase further supports the hypothesis of *in situ* As(III) oxidation to As(V) and lack of association with Fe-oxide phases. In many other environments, of course, Fe-oxide phases are known to be key contributors to As retention in soils (Smedley and Kinniburgh, 2002; Cances et al., 2005; Cances et al., 2008).

4.2.2 Vertical distribution of As content in sediment cores outside the source area.

In contrast to the source area soils, As contents (as determined by both total elemental analysis and 3050B extraction) in sediments collected both within the area of the As plume (ASB cores) and upgradient of the source area (BSB cores) were generally within the range expected for uncontaminated Florida soils (Figure 5). In the surficial sediments, 3050B-extractable As was actually slightly lower in the ASB than in the BSB cores despite the elevated As concentrations in groundwater at the locations of the ASB cores. This indicates that the surficial aquifer sediments have a limited capacity for As sorption under *in situ* conditions.

Sediments collected within the JBF were enriched in As relative to the surficial sediments both within and upgradient of the plume. Both the 3050B-extractable and total As contents

appeared to be higher in the JBF sediments collected within the plume than in those collected upgradient of the plume. However, these differences were in the range of the variability observed among replicate samples from an individual core. Total As contents were higher than 3050B-extractable As contents; this difference was somewhat more pronounced for the BSB cores than for the ASB cores.

4.3 Batch and column studies of As mobilization from source area soil

Source area soil was equilibrated in batch systems with background groundwater at varying soil-solution ratios for 3 d. Dissolved As concentrations of up to 700 µg/L were observed in the equilibrated groundwater; between 1 and 15 % of the 3050B extractable As was released from the source area soils (Figure 6).

Also shown in Figure 6 are the results of a static column experiment, in which soil was equilibrated with background groundwater for a period of 4 d. The equilibrated solution was then allowed to drain from the column and replaced with fresh background groundwater. In 6 consecutive treatments, the As concentration in the effluent was $2,100 \pm 200$ µg/L with no systematic variation over the course of the experiment. This As concentration corresponds to release of 0.7 ± 0.06 mg/kg of As from the soil (or 0.5 % of the 3050B-extractable As). The As concentrations in the static column effluent are consistent with those observed in the plume near the source area at wells MW-1 and MW-1R.

In flow-through columns run under saturated conditions, As concentrations in the effluent varied depending on the flow conditions (Figure 7). At a flow rate of 5 mL/h (region I), the As concentration in the effluent stabilized at 1,400 µg/L, a concentration comparable to that observed in the groundwater plume near the source area.

With increasing flow rate, the As concentration in the effluent increased over time and did not reach a stable value within 16 h (region II); the maximum As concentration observed in the effluent at a flow rate of 20 mL/h was 2,400 µg/L. This increase in As concentration may be attributable to the increased mobilization of colloidal particles under conditions of increased shear. In contrast, if the release of As from the solid phase were controlled by the kinetics of reaction at the solid-water interface, the As concentration in the effluent would have been expected to have decreased with increasing flow rate as a constant mass flux was increasingly diluted (Schnoor, 1990). Additionally, a constant As concentration in the effluent would have been expected if the release of As from the solid phase were transport-controlled.

After the no-flow period of 48 h (region III), no further increase in the effluent As concentration was observed. This is consistent with the observations in the static column experiments, in which effluent As concentrations were comparable. It would be expected that colloidal particles released by shear forces under the flow conditions of region II would have been recaptured by attachment to the soil under the no-flow conditions of region III. With re-initiation of the flow at 5 mL/h (region IV), the As concentration in the effluent gradually decreased to a concentration of 1,500 µg/L, similar to that observed at the end of the initial flow period (region I).

4.4 Sorption of As onto sediment from the surficial aquifer and the JBF

Batch experiments were conducted to assess the capacity of surficial aquifer and JBF sediments for sorption of As(V), the principal oxidation state of As both in the groundwater and in source area soils. Sediment samples (core BSB-3, 0-125 µm size fraction) were equilibrated for 36 h in background groundwater spiked with As(V). Under these conditions, substantially

greater sorption was observed with the JBF sediment than with the surficial aquifer sediment (Figure 8). Neither sediment exhibited a clear saturation, but the maximum observed value of solid-associated As (for the range of experimental conditions examined) was 114 mg/kg for the JBF sediment and only 22 mg/kg for the surficial aquifer sediment, a ratio of 5.2:1. Notably, the JBF sediment was also enriched in Fe and Al compared with the surficial aquifer sediment at ratios of 3.7:1 for Fe and 30:1 for Al based on total elemental analysis by XRF.

The effect of surface area on As(V) sorption was investigated in batch experiments with size-fractionated JBF sediments (14-15 m, core ASB-1). In sieved fractions, the 0-63 μm fraction had a BET surface area of 10.7 m^2/g and an ambient As content of 24.1 mg/kg. The 63-125 μm size fraction had both a lower BET surface area, 4.8 m^2/g , and lower ambient As content, 4.7 mg/kg. Normalizing for surface area, the 0-63 μm fraction was enriched in As compared to the 63-125 μm fraction by a ratio of 2.3:1. In the sorption experiments, the sorption capacity of the 0-63 μm fraction was substantially greater than that of the 63-250 μm fraction on a per mass basis (Figure 9a) but very similar when normalized for surface area (Figure 9b).

4.5 Hydrologic considerations

Although the hydrology of the Tyndall site is not fully characterized, four aspects of the site hydrology should be considered in the interpretation and integration of the field and laboratory observations. The first aspect is infiltration in the source area, the second is transport within the surficial aquifer, the third is infiltration and dilution downgradient of the source area, and the fourth is the integrity of the JBF as a confining layer.

The topography of the Tyndall site and the corresponding hydraulic gradients are variable across the site. In the source area itself, the topography is quite flat with an estimated hydraulic

gradient of only 0.001. The groundwater table is also shallow (approximately 1.5 m bgs). Thus heavy precipitation would be expected to result in substantial overland flow (i.e., runoff) as well as in infiltration. After a precipitation event, high temperatures, particularly in spring and summer months, would drive evaporation and capillary rise of As-contaminated groundwater. These processes would tend to retard the transport of As from the source area and could be a basis for the observed persistence of As despite the ease of leaching of As from the source area soils observed in the static and flow-through column experiments.

One well immediately downgradient of the source area (MW-7 not shown in Figure 2 but located between MW-1 and MW-5) was drilled through the JBF and into the underlying Intracoastal Formation. Well logs indicate that the JBF is approximately 2.5 m thick at this location. The water table elevation at MW-7 is lower than at nearby wells completed in the surficial aquifer thus indicating a potential downward hydraulic gradient. Low to non-detectable As concentrations at MW-7, however, indicate that As-contaminated groundwater is not penetrating through the JBF near the source area.

Away from the source area, specifically downgradient of well MW-10, the hydraulic gradient increases by about a factor of 10. Between MW-10 and MW-17, the evolution of the 10 and 1,000 $\mu\text{g/L}$ contours in As concentrations over time (Figures 2 and 3) indicate that the extent of As contamination (as defined by the 10 $\mu\text{g/L}$ contour) is stable or even retreating and that the mass of As in the surficial groundwater (corresponding to the 1,000 $\mu\text{g/L}$ contour) has declined. Comparison of the As contents of surficial aquifer sediments within and upgradient of the As plume indicate that As is not being sequestered in the surficial aquifer sediments; this inference is supported by the batch sorption experiments conducted in the laboratory. The apparent reduction in the mass of As in the surficial aquifer may be attributable to the partial excavation

of As-contaminated soils in the source area and a consequent decrease in source strength. Infiltration of rainwater into the aquifer downgradient of the source area could lead to dilution of As concentrations in the plume. It is also possible that, in this area, the integrity of the JBF as a confining layer is compromised. Since the conclusions regarding the stability of the As plume are based only on observations from wells completed in the surficial aquifer (with the exception of MW-7), the possible penetration of the As plume into the Intracoastal Formation could provide an additional explanation for the apparent stability of the As plume in the surficial aquifer.

5. Concluding comments

This study examined potential geochemical controls on As fate and transport, such as kinetic limitation of As mobilization and the sequestration of As through sorption and/or precipitation reactions, at a site with persistent As contamination in soil and groundwater. Such geochemical controls were examined in laboratory experiments to aid in the interpretation of two specific field observations: (1) the persistence of As in source area soils decades after the discontinuation of use of As_2O_3 as an herbicide and (2) the apparent stability of the plume of As-contaminated groundwater.

Experimental results, however, suggest that the persistence of As in the source area cannot be explained by geochemical controls, as is often assumed, but may be the result of limited infiltration (i.e., hydrologic control). Column experiments with source area soil generated aqueous As concentrations comparable to those observed in groundwater near the source area. A substantial fraction of the As could be leached from the source area soil with background groundwater, or moderate leaching conditions, indicating that the As in the source

area soil is geochemically labile. Because the amount of extractable Fe and Mn in source area soils was low compared with typical soils, Fe- or Mn-reducing conditions, which are often responsible for As mobilization (Ravenscroft et al., 2009 and ref. cit.), are not required to mobilize As from the source area.

Likewise, experimental results did not support a geochemical mechanism to explain the apparent stability of the As-contaminated groundwater plume. Batch sorption experiments showed that surficial aquifer sediments sorbed As(V) much less than sediments from the JBF, a presumed confining layer, which suggested that As sorption by surficial aquifer sediments is not a primary retention mechanism. This limited capacity of the surficial aquifer sediments for As(V) sorption is consistent with the similar As contents observed for surficial aquifer sediments within the As plume and upgradient of the plume (i.e., background conditions). Sorption to JBF sediments may contribute to As sequestration, although increased As levels in JBF sediments within the As plume area compared to upgradient background JBF sediments was not observed. The competence of the JBF as a confining unit far downgradient of source area soils has not been examined, and may be a factor in the apparent stability of the As plume.

The assessment of natural attenuation as a remedial option for As contamination in groundwater often focuses on potential geochemical mechanisms for sequestration. Studies at other sites have demonstrated the importance of sorption and precipitation processes involving Fe, Mn, Al, and S for As sequestration and attenuation. This study suggests that possible hydrologic controls should also be carefully considered in assessing the apparent mobility and sequestration of As in the subsurface, particularly in settings that are depleted in the elements that can contribute to the immobilization of As.

Acknowledgements

This work was supported by the Strategic Environmental Research and Development Program (SERDP) Project #ER-1374. AGF was supported by the National Defense Science and Engineering Graduate (NDSEG) Research Fellowship. Assistance provided by Gulf Power Co. and the Southern Co. and support provided by Joe McLernan (Tyndall AFB) are gratefully appreciated. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. Thanks to Rob Root (UC Merced) for assistance with XAS data analysis.

References

- Bothe, J.V., and Brown, P.W. (1999) Arsenic immobilization by calcium arsenate formation. *Environmental Science & Technology* **33**: 3806-3811.
- Cances, B., Juillot, F., Morin, G., Laperche, V., Alvarez, L., Proux, O. et al. (2005) XAS evidence of As(V) association with iron oxyhydroxides in a contaminated soil at a former arsenical pesticide processing plant. *Environmental Science & Technology* **39**: 9398-9405.
- Cances, B., Juillot, F., Morin, G., Laperche, V., Polya, D., Vaughan, D.J. et al. (2008) Changes in arsenic speciation through a contaminated soil profile: A XAS based study. *Science of the Total Environment* **397**: 178-189.
- Chen, M., and Ma, L.Q. (1998) Comparison of Four USEPA Digestion Methods for Trace Metal Analysis Using Certified and Florida Soils. *J. Environ. Qual.* **27**: 1294-1300.

- Chen, M., Ma, L.Q., Hoogeweg, C.G., and Harris, W.G. (2001) Arsenic background concentrations in Florida, USA surface soils: Determination and interpretation. *Environmental Forensics* **2**: 117-126.
- Eaton, A.D., Clesceri, L.S., Rice, E.W., Greenberg, A.E., and Franson, M.A.H. (eds) (2005) *Standard methods for the examination of water and wastewater*. Washington, DC: American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF).
- Folkes, D.J., Kuehster, T.E., and Litle, R.A. (2001) Contributions of pesticide use to urban background concentrations of arsenic in Denver, Colorado, USA. *Environmental Forensics* **2**: 127-139.
- Foster, A.L. (2003) Spectroscopic investigations of arsenic species in solid phases. In *Arsenic in Groundwater*. Welch, A.H., and Stollenwerk, K.G. (eds). Boston, MA: Kluwer Academic Publishers, pp. 27-65.
- George, G.N., and Pickering, I.J. (2000) EXAFSPAK: A suite of computer programs for analysis of X-ray absorption spectra. In. Stanford CA: Stanford Synchrotron Radiation Laboratory.
- Gulf Power (2004) Tyndall Air Force Base project update. Letter from Richard S. Markey. Gulf Power Company. Pensacola, FL.
- McLaren, R.G., Naidu, R., Smith, J., and Tiller, K.G. (1998) Fractionation and distribution of arsenic in soils contaminated by cattle dip. *Journal of Environmental Quality* **27**: 348-354.
- Miller, G.P. (2001) Surface complexation modeling of arsenic in natural water and sediment systems. Ph.D. New Mexico Institute of Mining and Technology. Socorro, NM.
- Norman, A.G., Minarik, C.E., and Weintraub, R.L. (1950) Herbicides. *Annual Review of Plant Physiology and Plant Molecular Biology* **1**: 141-168.

- Qi, Y.Q., and Donahoe, R.J. (2009) Modeling Arsenic Desorption from Herbicide-Contaminated Soils. *Environmental Toxicology and Chemistry* **28**: 1338-1345.
- Ravenscroft, P., Brammer, H., and Richards, K. (2009) *Arsenic pollution a global synthesis*. Oxford: Wiley-Blackwell.
- Rehr, J.J., Albers, R.C., and Zabinsky, S.I. (1992) High-order multiple-scattering calculations of X-ray-absorption fine structure. *Phys. Rev. Lett.* **69**: 3397-3400.
- Robinson, G.R., and Ayuso, R.A. (2004) Use of spatial statistics and isotopic tracers to measure the influence of arsenical pesticide use on stream sediment chemistry in New England, USA. *Applied Geochemistry* **19**: 1097-1110.
- Sadler, R., Olszowy, H., Shaw, G., Biltoft, R., and Connell, D. (1994) Soil and Water Contamination by Arsenic from a Tannery Waste. *Water Air and Soil Pollution* **78**: 189-198.
- Schmidt, W., and Clark, M.W. (1980) Geology of Bay County, Florida. Florida Bureau of Geology. Bulletin No. 57.
- Schnoor, J.L. (1990) Kinetics of chemical weathering: A comparison of laboratory and field weathering rates. In *Aquatic Chemical Kinetics: Reaction Rates of Processes in Natural Waters*. Stumm, W. (ed). New York: Wiley-Interscience, pp. 475-504.
- SCS (1999) Tyndall Field Air Force Base substation remedial action plan for groundwater. Report. Southern Company Services, Inc. Birmingham, AL.
- SCS (2003) Tyndall Field Air Force Base substation, Bay County, Florida soil excavation report. Report. Southern Company Services, Inc. Birmingham, AL.
- Smedley, P.L., and Kinniburgh, D.G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* **17**: 517-568.

- Smith, E., Smith, J., and Naidu, R. (2006) Distribution and nature of arsenic along former railway corridors of South Australia. *Science of the Total Environment* **363**: 175-182.
- Stollenwerk, K.G. (2003) Geochemical processes controlling transport of arsenic in groundwater: A review of adsorption. In *Arsenic in Ground Water*. Welch, A.H., and Stollenwerk, K.G. (eds). Boston: Kluwer Academic, pp. 67-100.
- USEPA (1983) Sample preservation methods. United States Environmental Protection Agency. EPA-600/4-79-020. Cincinnati, OH.
- USEPA (1993) Method 365.1: Determination of phosphorus by semi-automated colorimetry. http://www.epa.gov/waterscience/methods/method/files/365_1.pdf
- USEPA (1996) Method 3050B: Acid digestion of sediments, sludges, and soils. SW-846 test methods for evaluating solid wastes. <http://www.epa.gov/SW-846/pdfs/3050b.pdf>
- USEPA (2001) National primary drinking water regulations; Arsenic and clarifications to compliance and new source contaminants monitoring; Final Rule. 40 CFR Parts 141 and 142. *Fed. Register*. **66**: 6976-7066.
- Wenzel, W.W., Kirchbaumer, N., Prohaska, T., Stingeder, G., Lombi, E., and Adriano, D.C. (2001) Arsenic fractionation in soils using an improved sequential extraction procedure. *Analytica Chimica Acta* **436**: 309-323.
- Whitmore, T.J., Riedinger-Whitmore, M.A., Smoak, J.M., Kolasa, K.V., Goddard, E.A., and Bindler, R. (2008) Arsenic contamination of lake sediments in Florida: evidence of herbicide mobility from watershed soils. *Journal of Paleolimnology* **40**: 869-884.
- Yang, L., and Donahoe, R.J. (2007) The form, distribution and mobility of arsenic in soils contaminated by arsenic trioxide, at sites in southeast USA. *Applied Geochemistry* **22**: 320-341.

Figure Captions

Figure 1. Tyndall Air Force Base, FL and substation study site locations.

Figure 2. Groundwater monitoring data showing extent of As contamination in surficial aquifer in February 1996 and April 2002, prior to the partial excavation of source area soils in 2003. Approximate iso-concentration contours shown based on historical monitoring data for total As concentrations ($\mu\text{g/L}$), which are shown next to the location of the monitoring wells (nd = non-detect). All screened intervals were 3 m starting at depths of 1.4 m (MW-1, 4), 1.6 m (MW-2, 3, 5, 6), 18.1 m (MW-7), 5.4 m (MW-8, -9), 10.6 m (MW-10, -11), 11.5 m (MW-12), 11.3 m (MW-13), 8.1 m (MW-14, -18), 8.4 m (MW-15-17). Source: (SCS, 1999; Gulf Power, 2004).

Figure 3. Concentrations of total, dissolved As and As(III) in $\mu\text{g/L}$ determined in Tyndall groundwater in August 2005; values are shown next to the monitoring wells with As(III) in brackets (nd = non-detect). Approximate iso-concentration contours are drawn for total, dissolved As (solid lines) and As(III) (dashed lines). Location of soil borings within the contaminated zone (ASB-1, -2, -3) and upgradient background area (BSB-1, -2, -3) are shown (open circles).

Figure 4. Characterization of source area soils. Top: Representative SEM image and EDS analyses of sample S3. Left panel: As K-edge XANES of S3 and S27 compared with reference spectra of As(III)-oxide (precipitated with Ca(OH)_2 and CaCO_3) and a natural sample of As(V) in travertine; dashed lines indicate characteristic absorption energies for As(III)-O and As(V)-O bonding. Bottom panel: As EXAFS of S3 (solid line) and least-squares best fit (dashed line). Fit results: 4 oxygen atoms (fixed) at 1.67 Å (varied $\sigma^2 =$

0.0011 Å²) with As-O tetrahedral multiple scattering (MS) at 3.01 Å; 2 Al or Si atoms at 3.22 Å (fixed $\sigma^2 = 0.0045$ Å²).

Figure 5. Distribution of total As content (closed symbols) and 3050B-extractable As content (open symbols) with depth (a) in BSB cores collected upgradient of the source area and (b) in ASB cores collected within the As plume. The depth of the Jackson Bluff Formation (JBF) layer at each boring location is also identified. Symbols: (○, ●) ASB-1 or BSB 1, (▽, ▼) ASB-2 or BSB 2, (□, ■) ASB-3 or BSB-3.

Figure 6. Dissolved As concentrations in suspensions of source area soil (S27) equilibrated with background groundwater at varying soil-solution ratios in batch experiments (●) and static column experiments (▼). Experimental conditions: batch experiments – S27 collected July 2006, 0-250 µm size fraction, synthetic groundwater (44 µM NaCl, 75 µM CaSO₄, and 82 µM MgSO₄, buffered to pH 5.2 with 10 mM pyridine), rotated 28 rpm at 12.5°C in the dark for 3d in triplicate; static column experiments – S27 collected April 2005, 63-500 µm size fraction, MW-2 groundwater collected April 2005, 300 g saturated with 100-150 mL, left 12.5°C in the dark for 4 d, repeated 6 times and in triplicate.

Figure 7. Concentrations of As in the eluant of a column packed with source area soil and eluted with simulated groundwater under saturated conditions. The column was run at 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). Experimental conditions: S27 collected July 2006, 0-250 µm size fraction, synthetic groundwater (44 µM NaCl, 75 µM CaSO₄, and 82 µM MgSO₄, buffered to pH 5.2 with 10 mM pyridine), pumped upward through column packed with 220 g of soil, 12.5°C in the dark.

Figure 8. Concentrations of solid-associated As as a function of dissolved As concentrations for 30 g/L suspensions of background sediments (core BSB-3, 0-125 μm size fraction) equilibrated with background groundwater (MW-2 collected July 2006) spiked with As(V). Solid-associated As was calculated as the difference between the total As concentration in the system (based on the As spike plus the ambient As content of the solid) and the measured dissolved As concentration. Symbols: ($\circ$) surficial aquifer sediment (4.0-4.3 m depth; negligible ambient As content), ($\bullet$) JBF sediment (16.0-16.2 m depth; ambient As content 9.6 mg/kg). Error bars correspond to standard deviations of triplicate analyses. Experimental conditions: 0.75 g in 25 mL, rotated end-over-end at 12.5°C in the dark for 36 h in triplicate.

Figure 9. Concentrations of solid-associated As as a function of dissolved As concentrations for 30 g/L suspensions of JBF sediments (core ASB-1, depth 14.0-14.9 m) equilibrated with background groundwater spiked with As(V). Solid-associated As was calculated from the difference between the total As concentration in the system (based on the As spike plus the ambient As content of the solid) and the measured dissolved As concentration. Symbols: ($\circ$) 0-63 μm fraction (ambient As content 24.1 mg/kg or 2.25 $\mu\text{g}/\text{m}^2$), ($\bullet$) 63-125 μm fraction (ambient As content 4.7 mg/kg or 0.98 $\mu\text{g}/\text{m}^2$). Error bars correspond to standard deviations in triplicate analyses. Experimental conditions: 0.50 g in 16.67 mL, rotated end-over-end at 12.5°C in the dark for 36 h.

Table 1. Groundwater composition for wells outside zone of contamination

analyte ^a	units	MW-2 (Apr 2005)	MW-2 (Aug 2005)	MW-3, 7, 8, 11, 15, 16, 17, 18 (Aug 2005)		
				mean	minimum	maximum
As	µg/L	<1	0.15 ± 0.04	2.6	<1	7
As(III)	µg/L	NM ^b	<1	<1		
Mn	µg/L	9	8 ± 0.07	11	<1	73
Al ^c	µg/L	<1	557 ± 16	86	<1	316
Fe	µg/L	<0.25	11 ± 0.01	45	4	93
Na	mg/L	1.75	1 ± 0.05	5	2	8
Ca	mg/L	NM	3 ± 0.29	5	1	18
Mg	mg/L	NM	2 ± 0.06	1	1	2
K	mg/L	0.38	1 ± 0.02	2	<0.1	4
Cl	mg/L	9.8	2 ± 0.14	10	3	15
SO ₄	mg/L as SO ₄	14	12 ± 0.5	13	6	20
Br	mg/L	<0.1	3 ± 0.1	<1		
TOC	mg/L	NM	18	9	3	30
DOC	mg/L	10.2				
pH (unfiltered)		4.93				
pH (filtered)		4.79	NM	5	4	6

^a All samples (except for TOC, DOC and unfiltered pH samples) were filtered through 0.22 μm mixed cellulose ester (Millipore) filters after delivery to Caltech. Samples for DOC analyses were filtered through 0.2 μm nylon (PALL Life Sciences) filters. Nitrate and nitrite were measured for all samples but were not detected. For MW-2 (August 2005) samples, standard deviations are reported for triplicate analyses.

^b NM = not measured

^c The discrepancy between the Al concentrations in samples collected in April and August may indicate loss of Al from April samples. A previous study at this site reported Al concentrations in filtered groundwater of 2.5 mg/L (Miller, 2001)

Table 2. Groundwater composition for wells within zone of contamination (samples collected Aug 2005)									
analyte^a	units	MW-1R	MW-19	MW-20	MW-5	MW-9	MW-10	MW-12	MW-13
As	µg/L	1155 ± 17	152 ± 2	45 ± 0.7	53 ± 0.5	274 ± 2	845 ± 17	484 ± 5	410 ± 3
As(III)	µg/L	<1	<1	<1	<1	<1	108	10	14
Mn	µg/L	7 ± 0.2	8 ± 0.2	<1	2 ± 0.07	<1	<1	1 ± 0.9	<1
Al	µg/L	165 ± 4	225 ± 6	36 ± 1	225 ± 4	167 ± 22	335 ± 7	109 ± 6	65 ± 2
Fe	µg/L	18 ± 0.01	11 ± 0.01	15 ± 0.01	18 ± 0.01	13 ± 0.01	7 ± 0.01	31 ± 0.01	37 ± 0.01
Na	mg/L	2 ± 0.04	3 ± 0.1	<0.1	2 ± 0.06	11 ± 0.4	15 ± 0.4	5 ± 0.1	4 ± 0.2
Ca	mg/L	21 ± 2	12 ± 1	1 ± 0.5	8 ± 0.9	5 ± 0.5	8 ± 0.8	3 ± 0.2	1 ± 0.09
Mg	mg/L	5 ± 0.14	3 ± 0.1	<0.1	2 ± 0.1	2 ± 0.07	2 ± 0.09	2 ± 0.05	1 ± 0.06
K	mg/L	2 ± 0.05	1 ± 0.06	<0.1	1 ± 0.01	1 ± 0.03	1 ± 0.05	2 ± 0.05	2 ± 0.08
Cl	mg/L	4 ± 0.2	5 ± 0.1	10 ± 1	6 ± 1	20 ± 1.4	27 ± 1.6	11 ± 2	9 ± 0.6
SO ₄	mg/L as SO ₄	20 ± 2	15 ± 0.6	19 ± 1	11 ± 2	9 ± 0.3	18 ± 1.3	17 ± 3	12 ± 0.7
Br	mg/L	2 ± 0.1	5 ± 0.2	<0.1	2 ± 0.4	<0.1	<0.1	<0.1	<0.1
TOC	mg/L	11	12	6	11	21	14	6	5
pH	--	6	6	5	5	5	5	4	NM
^a All samples (except for TOC samples) were filtered through 0.22 µm mixed cellulose ester (Millipore) filters after delivery to Caltech.. Standard deviations are reported for triplicate analyses. Nitrate and nitrate were measured for all samples but nitrate was not detected and nitrite was detected only at MW-19 at 2 mg/L. NM = not measured									

Table 3. 3050B extractable contents of Al, Fe, and Mn in soils (dry weight basis)					
element	units	source area soils		NIST sandy soil ^a	40 FL s
		S27	S3		
Al	g/kg	2.6	14	25.4	1.8
Fe	g/kg	0.006	0.002	30.1	0.83
Mn	mg/kg	97	76	441	26.2
^a (Chen and Ma, 1998)					

Table 4. As contents (mg/kg) in source area soils (dry weight basis)

method		sample					
		S3 (April 2005) whole soil ^a	S27 (April 2005)		S27 (July 2006) ^b		
			whole soil ^a	63-250 µm	63-500 µm	0-250 µm	63-250 µm
XRF		280	180			110	
3050B extraction		206	144	108	105	124	105
sequential extraction	sum all steps					93	79
	ammonium sulfate (step 1)					11 ± 0.6	11 ± 0.8
	ammonium sulfate (step 2)					6.1 ± 0.5	5.3 ± 0.2
	ammonium phosphate (step 3)					8.6 ± 2.4	5.1 ± 0.8
	ammonium phosphate (step 4)					8.2 ± 1.8	4.3 ± 1.1
	3050B on residue					59 ± 5.7	54 ± 5.4

^a samples not size-fractionated before analysis or extraction
^b mean value ± standard deviation for triplicate analyses

Figure 1. Tyndall Air Force Base, FL and substation study site locations.

Figure 2. Groundwater monitoring data showing extent of As contamination in surficial aquifer in February 1996 and April 2002, prior to the partial excavation of source area soils in 2003. Approximate iso-concentration contours shown based on historical monitoring data for total As concentrations ($\mu\text{g/L}$), which are shown next to the location of the monitoring wells (nd = non-detect). All screened intervals were 3 m starting at depths of 1.4 m (MW-1, 4), 1.6 m (MW-2, 3, 5, 6), 18.1 m (MW-7), 5.4 m (MW-8, -9), 10.6 m (MW-10, -11), 11.5 m (MW-12), 11.3 m (MW-13), 8.1 m (MW-14, -18), 8.4 m (MW-15-17). Source: (SCS, 1999; Gulf Power, 2004).

Figure 3. Concentrations of total, dissolved As and As(III) in $\mu\text{g/L}$ determined in Tyndall groundwater in August 2005; values are shown next to the monitoring wells with As(III) in brackets (nd = non-detect). Approximate iso-concentration contours are drawn for total, dissolved As (solid lines) and As(III) (dashed lines). Location of soil borings within the contaminated zone (ASB-1, -2, -3) and upgradient background area (BSB-1, -2, -3) are shown (open circles).

Figure 4. Characterization of source area soils. Top: Representative SEM image and EDS analyses of sample S3. Left panel: As K-edge XANES of S3 and S27 compared with reference spectra of As(III)-oxide (precipitated with Ca(OH)_2 and CaCO_3) and a natural sample of As(V) in travertine; dashed lines indicate characteristic absorption energies for As(III)-O and As(V)-O bonding. Bottom panel: As EXAFS of S3 (solid line) and least-squares best fit (dashed line). Fit results: 4 oxygen atoms (fixed) at 1.67 Å (varied $\sigma^2 = 0.0011 \text{ Å}^2$) with As-O tetrahedral multiple scattering (MS) at 3.01 Å; 2 Al or Si atoms at 3.22 Å (fixed $\sigma^2 = 0.0045 \text{ Å}^2$).

Figure 5. Distribution of total As content (closed symbols) and 3050B-extractable As content (open symbols) with depth (a) in BSB cores collected upgradient of the source area and (b) in ASB cores collected within the As plume. The depth of the Jackson Bluff Formation (JBF) layer at each boring location is also identified. Symbols: (○, ●) ASB-1 or BSB 1, (▽, ▼) ASB-2 or BSB 2, (□, ■) ASB-3 or BSB-3.

Figure 6. Dissolved As concentrations in suspensions of source area soil (S27) equilibrated with background groundwater at varying soil-solution ratios in batch experiments (●) and static column experiments (▼). Experimental conditions: batch experiments – S27 collected July 2006, 0-250 μm size fraction, synthetic groundwater (44 μM NaCl, 75 μM CaSO₄, and 82 μM MgSO₄, buffered to pH 5.2 with 10 mM pyridine), rotated 28 rpm at 12.5°C in the dark for 3d in triplicate; static column experiments – S27 collected April 2005, 63-500 μm size fraction, MW-2 groundwater collected April 2005, 300 g saturated with 100-150 mL, left 12.5°C in the dark for 4 d, repeated 6 times and in triplicate.

Figure 7. Concentrations of As in the eluant of a column packed with source area soil and eluted with simulated groundwater under saturated conditions. The column was run at 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). Experimental conditions: S27 collected July 2006, 0-250 μm size fraction, synthetic groundwater (44 μM NaCl, 75 μM CaSO₄, and 82 μM MgSO₄, buffered to pH 5.2 with 10 mM pyridine), pumped upward through column packed with 220 g of soil, 12.5°C in the dark.

Figure 8. Concentrations of solid-associated As as a function of dissolved As concentrations for 30 g/L suspensions of background sediments (core BSB-3, 0-125 μm size fraction) equilibrated with background groundwater (MW-2 collected July 2006) spiked with As(V). Solid-associated As was calculated as the difference between the total As concentration in the system (based on the As spike plus the ambient As content of the solid) and the measured dissolved As concentration. Symbols: ($\circ$) surficial aquifer sediment (4.0-4.3 m depth; negligible ambient As content), ($\bullet$) JBF sediment (16.0-16.2 m depth; ambient As content 9.6 mg/kg). Error bars correspond to standard deviations of triplicate analyses. Experimental conditions: 0.75 g in 25 mL, rotated end-over-end at 12.5°C in the dark for 36 h in triplicate.

Figure 9. Concentrations of solid-associated As as a function of dissolved As concentrations for 30 g/L suspensions of JBF sediments (core ASB-1, depth 14.0-14.9 m) equilibrated with background groundwater spiked with As(V). Solid-associated As was calculated from the difference between the total As concentration in the system (based on the As spike plus the ambient As content of the solid) and the measured dissolved As concentration. Symbols: (○) 0-63 μm fraction (ambient As content 24.1 mg/kg or 2.25 $\mu\text{g}/\text{m}^2$), (●) 63-125 μm fraction (ambient As content 4.7 mg/kg or 0.98 $\mu\text{g}/\text{m}^2$). Error bars correspond to standard deviations in triplicate analyses. Experimental conditions: 0.50 g in 16.67 mL, rotated end-over-end at 12.5°C in the dark for 36 h.