Final Cleanup Action Plan
USG Interiors Puyallup Site
Puyallup, Washington

Issued by:
Washington State Department of Ecology
Toxics Cleanup Program
Southwest Regional Office
Olympia, Washington

April 1, 2019

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Section 1

Introduction

This draft Cleanup Action Plan (CAP) has been prepared by CDM Smith Inc. (CDM Smith) for the USG Interiors (USG) property located at 925 River Road in Puyallup, Washington (Puyallup site). The site location is shown on **Figure 1**. A site plan is provided on **Figure 2**. This CAP was prepared to satisfy requirements of Agreed Order DE 5489 (current Order) between the Washington State Department of Ecology (Ecology) and USG under the Model Toxics Control Act (MTCA), Chapter 70.105D RCW. The current Order came into effect on June 17, 2008.

The CAP describes the Puyallup site, the nature and extent of contamination, the cleanup action alternatives considered, and the proposed cleanup action for soil, groundwater, and sediments with arsenic concentrations above the applicable MTCA cleanup levels. The CAP will be implemented pursuant to a Consent Decree or an Agreed Order between USG and Ecology.

Previous work conducted at the site to meet the requirements of Agreed Order No. DE 5489 include a Remedial Investigation (RI), the results of which are presented in a Remedial Investigation Report (CDM 2011); a Bench-Scale Treatability Study (CDM Smith 2012) and Supplemental Bench-Scale Treatability Testing (CDM Smith 2013b); and a Feasibility Study (FS), the results of which are presented in the Feasibility Study Report dated December 4, 2013 (CDM Smith 2013a).

1.1 Purpose

This CAP has been prepared in accordance with Washington Administrative Code (WAC) 173-340-380 to present the proposed cleanup action and specify cleanup standards and other requirements for the cleanup action. The cleanup action will meet the threshold requirements of WAC 173-340-360 to protect human health and the environment, comply with cleanup standards, comply with applicable state and federal laws, and provide for compliance monitoring. The cleanup action proposed in this CAP is summarized as follows:

- Solidifying and chemically stabilizing soil with arsenic concentrations exceeding 90 milligrams per kilogram (mg/kg) using vertical auger mixing to inject the reagent. Bench-scale testing performed previously indicates that the most effective solidification mix design is a formulation consisting of 13% cement, 2% bentonite, and an iron addition five times the amount of arsenic in the soil (on a molar basis).

- Treating arsenic-contaminated groundwater using *in-situ* application of ferrous iron and an oxidant. Ferrous iron will be introduced into groundwater upgradient of the arsenic plume via a trench. Ferrous iron will also be injected directly into the arsenic plume in and around the arsenic hot spot in groundwater. In addition, an oxidant will be injected into the arsenic plume in and around the arsenic hot spot. Laboratory and pilot testing will need to be conducted to select the oxidant and optimal dose for the Puyallup site, and verify that ferrous iron and oxidant injections will be effective under field conditions.

- Maintaining the oxidizing groundwater conditions at the site (and hence minimizing arsenic mobility) after soil solidification by constructing a stormwater infiltration gallery to enable infiltration of oxygenated water.
- Re-installing the monitoring well network for performance monitoring. Evaluating remedy effectiveness by performance monitoring. Additional injections of ferrous iron and the oxidant would be made based on performance monitoring data.
- Excavating contaminated sediment from the Puyallup River.

1.2 Cleanup Action Plan Organization

This CAP has been organized into the following sections:

- **Section 1 – Introduction:** This section provides the purpose and scope of the CAP.
- **Section 2 – Site Description and Background:** This section describes the Puyallup site and its history.
- **Section 3 – Remedial Investigation:** This section summarizes the results of the RI and describes the conceptual site model.
- **Section 4 – Cleanup Standards:** This section identifies the technical elements for the proposed cleanup action, including the applicable laws and regulations, contaminants of concern, media of concern, cleanup standards, and findings from the terrestrial ecological evaluation.
- **Section 5 - Evaluation and Selection of Cleanup Action Alternatives:** This section summarizes the evaluation of technically feasible cleanup action alternatives for the site.
- **Section 6 – Proposed Cleanup Action:** This section discusses the proposed cleanup action alternative and monitoring requirements.
- **Section 7 – Additional Requirements:** This section describes the documentation to be provided for the proposed cleanup action, including an Engineering Design Report, construction plans and specifications, and a Compliance Monitoring Plan.
- **Section 8 – References:** Section 8 lists the documents cited in this CAP.

Section 2

Site Description and Background

2.1 Location and Description

USG's Puyallup property consists of 1.58 acres located between River Road and the Puyallup River in Puyallup, Washington. The southern (paved) portion of the property was formerly occupied by several buildings, but is currently vacant. The northern portion of the property is unpaved. **Figure 2** shows the layout of the property and adjacent properties. The Inter-County River Improvement Right-of-Way (ICRI-ROW), administered by Pierce County Public Works and Utilities, runs between the property and the Puyallup River. A paved bike path is located on the ICRI-ROW and runs along the top of the south bank of the Puyallup River.

USG's property is bordered to the east and west by used car dealerships—Market Place Auto and Bonney Lake Used Cars, respectively. River Road borders USG's property to the south. The extent of the exploration stations shown on **Figure 2** is referred to as the "site" throughout this report, including portions of Bonney Lake Used Cars, the ICRI-ROW, and Market Place Auto in addition to all of USG's property.

2.2 Site History

The following description of property and site history is based on CDM Smith's interpretation of historical aerial photographs and information provided to Ecology by USG.

Exactly when commercial activity began at the property is not documented, but aerial photographs show business-related activities on the property by 1961. What appears to be a used car sales business occupied the southern portion of the property. The northern portion of the site at that time contained junk cars. Site use appears to be consistent throughout the remainder of the 1960s.

A February 1971 aerial photograph clearly shows fill being placed on the northern portion of the site. The source of this fill is unknown. Early to mid-1970s aerial photographs show that the northern portion of the property continued to be used as a junk car lot following the filling on the property that occurred circa 1971.

Aerial photographs taken in 1979 show a fence around most of the northern portion of the property; the area inside the fence was filled with junk cars. This fence arrangement is identical to that shown on an April 1982 topographic map of the property. An aerial photograph dated August 1982 shows the northern portion of the property still being used as a junk car lot, but there are noticeably fewer cars than seen in the 1979 aerial photograph.

Prior to 1971 and through the early 1970s, industrial waste from USG's Tacoma, Washington plant was used as fill at the site. Because exact dates of these activities are not documented, their association with fill operations observed in the February 1971 aerial photograph cannot be determined.

It is known that from about 1959 to 1973, the USG Tacoma plant used ASARCO slag as a raw material for mineral fiber production. The ASARCO smelter was located on Commencement Bay in Ruston and

Tacoma, Washington. It operated from 1890 to 1986 as a smelter of lead and copper ore. The copper ore contained high concentrations of arsenic, as did the slag. Baghouse dust and off-specification product from the USG Tacoma plant was reportedly used as fill at the Puyallup site. This fill had elevated arsenic concentrations.

In the early 1980s, USG became aware of the association between ASARCO slag and arsenic contamination. USG subsequently purchased the Puyallup property in October 1982 to facilitate its cleanup. That same year, USG voluntarily approached Ecology to negotiate an administrative process to govern removal of industrial waste fill from the site. USG conducted an assessment in 1983 that characterized site geology and groundwater conditions (Dames & Moore 1983).

Soil and groundwater cleanup standards had not been established in Washington State at this time. Accordingly, Agreed Order No. DE 84-506 established arsenic cleanup standards of 5 milligrams per liter (mg/L) by the EP Toxicity (leaching) method for soil and 0.5 mg/L for groundwater. Although detailed records have not been located, a March 1985 aerial photograph indicates a source removal action occurred in the spring of 1985. This photograph shows all of the junk cars had been removed and the unpaved (northern) portion of the site appears to have been graded. According to information submitted to Ecology by USG, 25,536 tons of industrial waste fill and underlying soil were removed from the site for off-site disposal. Of this total, approximately 3,500 tons of native soil was removed from the northwest corner of the property because verification samples collected immediately beneath the industrial waste fill did not achieve the soil cleanup standard. This area is termed the contaminant source area, and is located in the vicinity of the P3 (**Figure 2**) well cluster. An August 1985 aerial photograph shows that the site had undergone final grading after completion of the source removal action.

The 1984 Order also required USG to conduct post-cleanup groundwater monitoring. To this end, USG installed three clusters (P1, P2, and P3) of three monitoring wells each (P1-1, P1-2, P1-3, etc.) in May 1985 to assess the lateral and vertical extent of arsenic in groundwater. These monitoring wells are shown on **Figure 2**. Groundwater samples were collected from these wells on a monthly basis.

On April 22, 1987 Ecology issued Consent Order No. 86-S130, which required long-term groundwater sampling. The groundwater cleanup level listed in this Order was 500 micrograms per liter (µg/L). Groundwater sampling continued on a monthly basis for the P2 and P3 well clusters but was dropped for the P1 well cluster.

MTCA was enacted and went into effect in March 1989. MTCA governs state-led environmental cleanups in Washington State. In 1991, Ecology established MTCA 'Method A' arsenic cleanup levels of 20 mg/kg for soil and 5 µg/L for groundwater. These MTCA cleanup standards for arsenic did not come into force at the Puyallup site because it was under the cleanup levels established under Order No. 86-S130.

Long-term groundwater sampling performed by USG under Order 86-S130 continued until early 2006. In the last monitoring round conducted in April 2006, arsenic was detected at a concentration of 5,960 µg/L at groundwater monitoring well P3-1.

In 2006, Ecology determined that the MTCA Method A groundwater cleanup level would not be attained in a reasonable timeframe by natural attenuation and required that USG conduct a soil and groundwater assessment for arsenic. This assessment showed that arsenic in soil and groundwater exceeded MTCA Method A cleanup standards in the contaminant source area. On March 30, 2007, Ecology sent USG a letter naming USG as a potentially liable party for the release of arsenic at the site. This led to the issuance of the current Order in 2008.

Section 3

Remedial Investigation Summary

USG conducted an RI at the Puyallup site in 2009 through 2010. Results of the RI are presented in a CDM Smith report prepared for USG (CDM 2011) and summarized below.

3.1 Site Geology and Hydrogeology

3.1.1 Geology

The site is located on the south bank of the lower Puyallup River within the Puyallup valley. Soils in the Puyallup valley consist of alluvium derived from the Puyallup River, underlain by glacial deposits. The Puyallup River alluvial deposits are consistent with alluvial deposits found worldwide and consist of three major types: overbank flood deposits, slack water deposits, and bar accretion deposits. It is important to note that these depositional processes are currently active.

The specific site geology is summarized in geologic cross-section A **-** A’, which is identified on **Figure 2** and shown on **Figure 3**. Generalized stratigraphy consists of fill overlying alluvium associated with the Puyallup River.

The fill includes backfill material associated with the former remedial excavation and fill associated with early site development, likely prior to commercial use of the site. The fill extends to depths ranging from 2 to 16 feet below ground surface (bgs) and soil types include poorly graded sand with silt and gravel (SP-SM), poorly graded sand with gravel (SP), and poorly graded gravel (GP). Traces of man-made debris are present within the fill (paper, wood, plastic, metal, brick, and concrete fragments).

The fill is differentiated from alluvium by the presence of man-made debris and angular to subangular gravel. Minor quantities of recently deposited overbank flood deposits (poorly graded sand and silt) overlie fill in the northern portion of the site. This material was deposited during flood events that have occurred after the 1985 source removal action. As shown in the geologic cross-section on **Figure 3**, alluvium underlies the site to the total depth explored. The alluvium is subdivided into four units based on depositional environment, including:

- **Unit A** – Overbank and point bar deposits
- **Unit B** – Channel and point bar deposits
- **Unit C** – Slack water deposits
- **Unit D** – Overbank deposits

Each of these units is described in more detail below.

Unit A – Overbank and Point Bar Deposits

This unit extends from the ground surface, or bottom of fill, to an approximate depth of 40 feet bgs. Unit A includes interlayered, fine-grained, poorly graded sand (SP) and well-graded sand (SW) with minor clay (CL) interbeds up to 6 inches thick. The soils were deposited by the Puyallup River and are exposed in the banks and bed of the river.

Unit B – Channel and Point Bar Deposits

This unit consists of gravel (GP, GW, and GW-GM), which represents higher energy deposition in an active river channel. The unit is less than 5 feet thick and underlies Unit A at a depth of approximately 40 feet bgs.

Unit C – Slack Water Deposits

Unit C consists of a sequence of silty sand (SM) containing wood fragments and organic matter. The presence of increased silt and organic matter indicates deposition in a lower energy slack water environment. The unit is approximately 15 feet thick and extends to total depths ranging from 54 to 61 feet bgs.

Unit D – Overbank Deposits

Unit D consists of dense, fine-grained silty sand (SM) and poorly graded sand with silt (SP-SM). The soil contains minor sub-horizontal laminations. The fine-grained sand and higher silt content indicate deposition in a lower energy environment such as overbank deposits distal to an active river channel. Unit D underlies Unit C and the total depth is not known.

3.1.2 Hydrogeology

Groundwater occurs under unconfined conditions at the site. The sands and gravels of Units A and B form the primary aquifer at the site and the lower permeability soils of Units C and D may act as a local aquitard, limiting downward vertical flow. During RI drilling, groundwater was first encountered at depths ranging from 10 to 18 feet bgs.

A groundwater elevation contour map for the shallow aquifer, based on November 10, 2009 depth to groundwater measurements, is shown on **Figure 4**. The groundwater elevation contours indicate groundwater flows to the north. The horizontal hydraulic gradient ranges from 0.006 foot/foot in the south and central part of the site (between monitoring wells RRN and P3-1), flattening to approximately 0.004 foot/foot in the northern part of the site between well P3-1 and the bank of the Puyallup River. The hydraulic conductivity of the shallow aquifer (Unit A) ranges from 80 to 120 feet/day, based on an estimate using the Hazen (1911) method and the grain size distribution results for a representative soil sample collected from this aquifer.

The vertical hydraulic gradient was calculated at the P2-1 to P2-3, P3-1 to P3-3, MW4S to MW4D, and MW6S to MW6D well clusters. The vertical gradients were calculated by dividing the head differential between the shallow and deeper well by the vertical distance between screen midpoints. The results indicate an upward vertical hydraulic gradient of 0.005 foot/foot between wells MW4S and MW4D and 0.0006 foot/foot between MW6S and MW6D, indicating upward groundwater flow from the deeper portion of the aquifer (Unit B) toward the shallow portion of the aquifer near the discharge point at the Puyallup River. A slight downward vertical gradient in the uppermost portion of the aquifer (Unit A) was calculated at the P2-1 and P3-1 well clusters.

The average linear velocity of groundwater flow in the shallow aquifer is estimated to range from 1 to 2 feet/day based on the range of hydraulic conductivities and horizontal hydraulic gradients determined for the site. An effective porosity of 0.32 was assumed for the velocity measurement.

3.1.3 Surface Water

The Puyallup River extends 54 miles, flowing in a northwest direction from its glacial source on the southwestern slopes of Mt. Rainier and discharging into Commencement Bay adjacent to the City of Tacoma. The river and its tributaries drain an area of about 1,000 square miles in Pierce County and southern King County. The portion of the river adjacent to the site and near the city of Puyallup, approximately 8 miles upstream from Commencement Bay, is characterized by water flows that average 6,926 cubic feet per second (ft^3/s) and range from 597 to 40,700 ft^3/s; the median discharge is just under 3,000 ft^3/s (USGS 2008). Three dams built in the early to mid-1900s are located upstream of the site, and discharge at the reach of the river adjacent to the site is largely controlled by the operation of these dams.

The site falls within the lower Puyallup River valley and the 500-year Lower Puyallup floodplain as determined by the Federal Emergency Management Agency in 2007. Recently, Pierce County commissioned a flood protection investigation of the lower Puyallup River extending from its mouth to the Meridian Street Bridge in Puyallup and upstream of the site. Levees run the entire length of both banks of the river in this study area (Tetra Tech 2008). Despite the flood control levees located along the bank of the Puyallup River, occasional overbank flooding occurs during the winter months.

Sediment conditions of the lower Puyallup River were characterized as part of a study commissioned by Pierce County (Tetra Tech 2008). The study determined that a wide range of particle sizes are found in the Puyallup River. Coarser substrates (gravel and cobble) dominate the Puyallup River sediment upstream of its confluence with the White River and finer material (sands, silts, and clays) dominantly occur downstream of this confluence.

In the upper 3 miles of the study area, sediments collected from the river thalweg (the central, deepest part of the channel) are characterized as consisting of both poorly graded fine sand and poorly graded gravel (Tetra Tech 2008). Most of the estimates of suspended sediment load at the USGS City of Puyallup gauge range from 100 to 1,000 tons/day (Tetra Tech 2008). The area of the Puyallup River adjacent to the site is expected to have no or minimal sediment deposition (Tetra Tech 2008).

3.1.4 Groundwater/Surface Water Interaction

Under normal hydraulic conditions, the Puyallup River is a gaining stream, meaning groundwater from the site discharges to the river. This relationship is reversed during periods of overbank flooding (which occurs occasionally in the winter), but this condition is transitory.

3.2 Nature and Extent of Contamination

3.2.1 Distribution of Arsenic in Soil

The distribution of residual arsenic in soil was investigated during the 2006 subsurface assessment and the RI conducted in 2009 through 2010. **Figure 5** shows the average of the extent of arsenic in soil at concentrations exceeding the MTCA Method A cleanup level of 20 mg/kg from the ground surface to 12 feet bgs. Isocontour maps of arsenic in soil at various depths were prepared for the RI to show both the lateral and vertical extent of arsenic at the site.

Arsenic concentrations are generally low—typically less than 20 mg/kg—across the site at ground surface and in the vicinity of the P3 well cluster in the shallow subsurface (up to 4 feet bgs or 32 to 28 feet mean sea level [MSL]). This likely represents low arsenic concentrations in fill imported and placed over a broad area after the 1985 remedial action, and recent (post-1985) deposition from overbank flooding. However, arsenic was detected at concentrations exceeding the MTCA Method A cleanup level of 20 mg/kg in surface soil around boring location A-6. Concentrations of arsenic exceeding the MTCA Method A cleanup level also occur to the south and west of the P3 well cluster in the shallow subsurface (i.e., 4 to 10 feet bgs) in areas assumed to be on the fringe of the 1985 remedial excavation.

Arsenic isocontours change dramatically approximately 10 feet bgs (in the 24 to 20 feet MSL elevation interval) in the intermittently saturated zone where the highest arsenic concentrations are near the P3 well cluster. These data indicate that soil excavation in 1985 was focused on the northwest corner of the property and that it reached approximately 8 to 10 feet below the current grade at its deepest.

Elevated arsenic concentrations in soil shift to the north of the P3 well cluster below approximately 12 to 14 feet bgs (20 feet MSL), likely representing transport of dissolved arsenic by groundwater and subsequent adsorption or precipitation of this arsenic. Also note that the soil sample with the highest arsenic concentration detected at the Puyallup site (2,900 mg/kg at D3 approximately 12 feet bgs) is below the water table.

3.2.2 Distribution of Arsenic in Groundwater

The distribution of dissolved total arsenic in groundwater at the site is shown on **Figure 6**. The highest arsenic concentrations were detected in the area focused around the P3 well cluster. A maximum dissolved arsenic concentration of 6,100 μg/L was detected in monitoring well P3-1, the shallowest well in the P3 well cluster.

Arsenic concentrations attenuate by nearly an order of magnitude between P3-1 and MW-6S (a distance of 135 feet), adjacent to the Puyallup River. Arsenic concentrations also attenuate with depth. This is illustrated in the P3 well cluster where arsenic was detected at 6,100 μg/L in shallow well P3-1, at 420 μg/L in mid-level well P3-2, and at 2 μg/L in P3-3, the deepest well in the P3 cluster. The vertical distance between the P3-1 and P3-3 screened intervals is approximately 10 feet.

3.2.3 Distribution of Arsenic in Sediment

A bathymetric survey of the Puyallup River and topographic survey of the adjacent bank were completed in 2009. Elevation contours are shown in **Figure 2**. These surveys were performed to define the geometry of the zone where site groundwater discharges to the Puyallup River and assist in selecting sediment sample locations.

Nine sediment samples (SED1through SED9) were collected from the river bank or river bottom of the Puyallup River as part of the RI. Sediment sample locations are shown on **Figure 2**. Arsenic concentrations in two of the nine sediment samples (SED3 and SED5) exceeded the Sediment Management Standards (WAC Chapter 173-204) freshwater sediment cleanup screening level of 120 mg/kg. The sediment cleanup screening level is the level established for minor adverse effects to the benthic community. Arsenic concentrations in three of the nine sediment samples (SED3, SED4, and SED5) exceeded the Sediment Management Standards freshwater sediment cleanup objective of 14 mg/kg, which is the no adverse effects level for the benthic community. These three samples are located along the river bank.

3.3 Conceptual Site Model

A conceptual site model (CSM) for the Puyallup site was developed during the RI. A conceptual site model is a representation of an environmental system and the physical and chemical processes that control the transport and fate of contaminants through environmental media to environmental receptors and their most likely exposure modes. The CSM for the Puyallup site is described below.

Industrial waste fill that served as the original source of arsenic at the site was removed in 1985, along with some of the impacted native soil in the contaminant source area. However, RI soil data indicate that not all of the arsenic-impacted soil in the vadose zone was removed in 1985, and this impacted soil serves as an ongoing source of groundwater contamination at the site, driven by precipitation infiltrating through this arsenic-impacted soil.

Elevated arsenic concentrations occur in soil from ground surface and approximately 34 feet bgs (0 feet MSL). The base elevation vadose zone (i.e., top of the water table) varies seasonally. For purposes of this CAP, the base of the vadose zone in the contaminant source area during the dry season is at 20 feet MSL (approximately 12 to 14 feet bgs). Elevated arsenic concentrations in soil in the saturated zone (i.e., below elevation 20 feet MSL) extend to the north of the contaminant source area. Arsenic contamination in soil within the saturated zone is interpreted to have leached out of the overlying material, transported downgradient by groundwater flow, and then adsorbed to soil or precipitated out of solution. This is evidenced by a “plume-like” distribution of elevated arsenic concentrations in soil hydraulically downgradient of the contaminant source area.

The transport and fate of arsenic at the Puyallup site was developed from an understanding of the environmental history of the site, data collected during the RI, arsenic geochemistry, bench-scale testing, and geochemical modeling performed using site-specific data. The results of geochemical modeling are presented in the RI (CDM 2011), while the bench-scale study results are presented in a supplemental bench-scale treatability report (CDM Smith 2013b).

Our understanding of arsenic transport and fate at the site are summarized below:

- Arsenic in the contaminant source area (P3-1, P3-2, MW2) is found predominantly in the oxidized arsenate (As V) form.
- Elsewhere in the plume, arsenic exists predominantly in the reduced arsenite (As III) form. Over time, arsenite is predicted to oxidize to the less mobile arsenate form.
- Iron and arsenic concentrations in groundwater at the site are likely controlled geochemically by ferric oxyhydroxides, the mineral scorodite, and green rust phases. This interpretation is based on electron microprobe analyses and site-specific geochemical modeling performed for the RI and supplemental bench-scale treatability study.
- Redox conditions at the site are not in equilibrium with arsenic, dissolved oxygen, or total organic carbon (TOC) due to the presence of a redox gradient.
- Arsenic transport in groundwater is significantly slower than the groundwater velocity, resulting in long travel times for arsenic to migrate downgradient from the contaminant source area. This is a result of adsorption of arsenic to the surfaces of iron-bearing minerals and co-precipitation with iron oxyhydroxides, which retards the transport of arsenic relative to groundwater.
- Arsenic is elevated in Puyallup River sediment downgradient of the contaminant source. This indicates that dissolved arsenic is transported to the river by groundwater flow. Dissolved

arsenic then precipitates onto sediment upon coming in contact with the oxygenated surface water.

Section 4

Cleanup Standards

This section describes applicable laws and regulations, remedial goals and objectives, constituents and media of concern, and cleanup standards for the cleanup action, including definition of cleanup levels and points of compliance. This section also summarizes the terrestrial ecological evaluation.

4.1 Applicable Laws and Regulations

Applicable laws and regulations provide the framework for the cleanup action. WAC 173-340-360(2) and 173-340-710(1)(a) require that cleanup actions conducted under MTCA comply with applicable federal and state laws. Applicable laws are defined as those requirements that are legally applicable, as well as those that Ecology determines to be both relevant and appropriate.

The available administrative or legal mechanisms for conducting the remedial action include either modifying the current Agreed Order or entering into a consent decree. A consent decree is a formal legal agreement filed in court. Remedial actions conducted under a consent decree with Ecology and the Attorney General's office must comply with the substantive requirements of the applicable or relevant and appropriate requirements (ARARs), but are exempt from their procedural requirements, such as permitting and approval requirements (WAC 173-340-710[9]). This exemption applies to certain state and local permitting requirements, including the Washington State Water Pollution Control Act, the Solid Waste Management Act, the Hazardous Waste Management Act, the Clean Air Act, the State Fisheries Code, the Shoreline Management Act, and local laws requiring permitting.

The applicable laws and regulations for the cleanup action will likely include the following:

Federal ARARs

- The Clean Water Act (33 USC 1251 et seq.)
- National Toxics Rule (40 CFR 131.36 et seq.)
- Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (42 USC 9601 et seq. and 40 CFR 300)
- Resources Conservation and Recovery Act (40 CFR Part 261 through 265, 268, 270, and 271)
- Endangered Species Act (16 USC § 1531 et seq.)
- Native American Graves Protection and Repatriation Act (25 USC 3001 through 3113; 43 CFR Part 10)
- Archaeological Resources Protection Act (16 USC 470aa et seq.; 43 CFR Part 7)
- National Historic Preservation Act (16 USC 470 et seq.; 36 CFR Parts 60, 63, and 800)

State ARARs

- MTCA (Revised Code of Washington [RCW] 70.105D)

- MTCA Cleanup Regulations (WAC 173-340)
- Sediment Management Standards (WAC 173-204)
- Washington State Environmental Policy Act (RCW 43.21)
- Water Quality Standards for Washington Surface Waters (Chapter 173-201A WAC)
- Washington State Shoreline Management Act (RCW 90.58, Chapter 173-18 WAC, Chapter 173-22 WAC, and Chapter 173-27 WAC)
- Washington Underground Injection Control Program (Chapter 173-218 WAC)
- Washington State Hydraulics Projects Approval (RCW 77.55; Chapter 220-110 WAC)
- Washington Dangerous Waste Regulations (Chapter 173-303 WAC)
- Washington's Indian Graves and Records Law (RCW 27.44); Archaeological Site Assessment Requirements (RCW 27.44 and 27.53)
- State of Washington Worker Safety Regulations

4.2 Remedial Goals and Objectives

The overall goals for the proposed remedy at this site are to:

- Protect human health and the environment.
- Comply with applicable regulations.
- Satisfy all provisions of the current Order and receive written notification from Ecology that USG has completed the remedial activity required by the Order.

The following remedial action objectives (RAOs) have been developed to meet these overall goals:

Remedial Action Objective #1 – Remediate Soil Exceeding Cleanup Levels. Arsenic exceeds MTCA cleanup levels over a wide area. The objective of this remedial action is to prevent exposure or remediate soil to be protective of human health and environmental receptors.

Remedial Action Objective #2 – Achieve MTCA Method A Cleanup Standards for Arsenic in Groundwater at the Standard Point of Compliance. Remediate groundwater to achieve MTCA Method A cleanup standards for arsenic in groundwater across the entire site. This RAO will be used in conjunction with RAO #3.

Remedial Action Objective #3 – Mitigate Arsenic in Groundwater to be Protective of Surface Water or Sediment at a Conditional Point of Compliance. Set a conditional point of compliance for groundwater in pore water adjacent to the Puyallup River or at groundwater monitoring wells adjacent to the river. This point of compliance would be protective of Puyallup River surface water and sediment. A conditional point of compliance would be established if achieving RAO #2 is technically impracticable or disproportionately costly.

Remedial Action Objective #4 – Remediate Sediment Exceeding Cleanup Levels. Sediment at the bank of the Puyallup River exceeds cleanup levels for arsenic. The objective of this remedial action is to remove impacted sediment to protect ecological receptors.

4.3 Media of Concern

Soil, groundwater, and sediment are the media of concern for the cleanup action. Elevated concentrations of arsenic occur in the northern portion of USG's property and extend west onto the Bonney Lake Used Cars property and north onto the ICRI-ROW. The highest arsenic concentrations in groundwater were detected in the area focused around the P3 well cluster. The results of the RI indicate that dissolved arsenic in shallow groundwater at the site is discharging to the Puyallup River and adsorbing onto sediment or co-precipitating with iron onto sediment at the groundwater/surface water interface.

4.4 Cleanup Standards Established for the Site

As defined in WAC 173-340-700, cleanup standards for the site include establishing cleanup levels and the points of compliance at which those cleanup levels will be attained. The cleanup standards for the site have been established in accordance with WAC 173-340-700 through 173-340-760, are protective of human health and the environment, and comply with the ARARs defined for the site.

4.4.1 Cleanup Levels

Cleanup levels are the concentrations of the contaminants of concern that will be met for the media of concern at the points of compliance defined for the site to meet MTCA requirements. The contaminant of concern at the site is arsenic. The soil, groundwater, and sediment cleanup levels for arsenic are as follows:

Arsenic Cleanup Level

Media	Basis	Cleanup Level
Soil	MTCA Method A	20 mg/kg
Groundwater	MTCA Method A	5 µg/L
Sediment	WAC 173-204	14 mg/kg(a)

(a) Freshwater sediment cleanup screening levels and sediment cleanup objectives for protection of the benthic community are established in the Sediment Management Standards (WAC 173-204). The freshwater sediment cleanup screening level for arsenic is 120 mg/kg, which is the concentration that minor adverse effects are expected to the benthic community. The freshwater sediment cleanup objective is 14 mg/kg, which is the concentration that no adverse effects are expected to the benthic community.

4.4.2 Points of Compliance

WAC 173-340-200 defines the points of compliance as the locations where cleanup levels (established in accordance with WAC 173-340-720 through 173-340-760) will be attained to meet MTCA requirements If the cleanup levels for groundwater cannot be met within a reasonable restoration time frame, conditional points of compliance can be defined in accordance with WAC 173-340-720(8)(c) and an institutional control that precludes the use of groundwater in the shallow water-bearing zone as a potable water source would be implemented at the site. Once the cleanup levels have been maintained at the defined points of compliance, the site is no longer considered to be a threat to human health or the environment. The points of compliance for the cleanup action for soil, groundwater, and sediment are provided in the following subsections.

Soil

The point of compliance for soil is defined in WAC 173-340-740(6)(b) as being throughout the site for protection of groundwater and from the ground surface to a depth of 15 feet for protection of human health based on direct contact exposure. Where hazardous substances remain on-site as part of the cleanup action, institutional controls will be required.

Groundwater

The point of compliance for groundwater is both vertically and horizontally throughout the aquifer.

Sediment

The point of compliance for sediment in the Puyallup River is within the biologically active zone in the upper 10 centimeters (approximately upper 4 inches) of sediment.

4.5 Terrestrial Ecological Evaluation

A simplified terrestrial ecological evaluation (TEE) was conducted during the RI to assess the potential risk of exposure to wildlife from arsenic in soil. The simplified TEE exposure analysis concluded that there is a risk of exposure to terrestrial wildlife. However, the site is relatively disturbed and there is significantly less than 10 acres of native vegetation within the property boundaries and within 500 feet of the site. While the site is adjacent to a narrow band of public land at the top of the river bank, the area includes a paved public walking path and contains limited habitat values.

The simplified TEE concluded that pursuant to WAC 173-340-7492, the contaminant concentrations provided in Table 749-2 may be used as cleanup levels for the cleanup process based on the risk of exposure to terrestrial wildlife. As soils at the site alternate between saturated, anaerobic conditions and unsaturated, aerobic conditions, the value for arsenic III should be used. The arsenic III cleanup level as provided in Table 749-2 for the protection of terrestrial wildlife is 20 mg/kg.

The arsenic soil cleanup level selected for the site in Section 4.4.1 - Cleanup Levels is the MTCA Method A cleanup level of 20 mg/kg for the protection of human health. The MTCA Method A cleanup level is more conservative than the terrestrial wildlife cleanup value as it constitutes total arsenic (and not just arsenic III), and is protective of both human health and terrestrial wildlife that may use the site.

Section 5

Evaluation and Selection of Cleanup Alternatives

The Feasibility Study Report (CDM Smith 2013a) contains a detailed screening and evaluation of technologies to address arsenic contamination at the site. Ecology determined that the screening of technologies was adequate to develop specific cleanup alternatives for the site. The alternatives evaluated for the site included the following:

- Alternative 1: Solidification/Stabilization of Vadose Zone Soil Containing Greater than 20 mg/kg Arsenic, Groundwater Treatment with Permeable Reactive Barrier (PRB) in a "Funnel and Gate" Configuration, Performance Monitoring, Sediment Removal
- Alternative 2: Solidification/Stabilization of Vadose Zone Soil Containing Arsenic at Elevated Concentrations (the alternative was split into three sub-alternatives to evaluate three different arsenic concentrations in soil as listed below), Institutional Controls, Injection of Ferrous Iron into Groundwater using an Upgradient Trench and Direct Push Technology (DPT) Borings, *In-Situ* Chemical Oxidation (ISCO) by DPT Borings and Injection Wells, Performance Monitoring, Sediment Removal
    - Alternative 2a – Solidification/stabilization of soil greater than 90 mg/kg arsenic
    - Alternative 2b – Solidification/stabilization of soil greater than 50 mg/kg arsenic
    - Alternative 2c – Solidification/stabilization of soil greater than 20 mg/kg arsenic
- Alternative 3: Excavation of Soil Exceeding 20 mg/kg Arsenic and Off-Site Disposal, Sediment Removal, Extraction of Groundwater During Excavation, Pre-Treatment of Groundwater and Disposal to a Publically Owned Treatment Works (POTW), Monitored Natural Attenuation (MNA)

The cleanup action alternatives were screened against the MTCA threshold criteria for selection of cleanup actions (WAC 173-340-360), which include protection of human health and the environment, compliance with cleanup standards, compliance with applicable state and federal laws, and provision for compliance monitoring. The evaluation of cleanup action alternatives also considered future development plans for the site and the potential adverse impact on the Puyallup River.

5.1 Technical Basis for Soil and Groundwater Treatments

5.1.1 Technical Basis for Determining the Extent of Treatment Area for Soil Solidification

Remedial action Alternatives 1 and 2 use solidification/stabilization to treat arsenic impacted soil in the vadose zone. This subsection provides the technical basis for how the treatment area for soil solidification was developed.

Arsenic in soil has a heterogeneous spatial distribution with depth at the Puyallup site as shown in the 2-foot elevation interval contour maps developed for the RI Report (CDM 2011) and provided in Appendix B of the FS (CDM Smith 2013a). Soil solidification is typically performed with auger mixing of soil, where mixing is conducted while injection of a cement-based reagent and stabilization agent is also occurring. The auger is typically raised and lowered two to three times during the injection to provide adequate mixing. Two features of soil solidification by auger mixing become evident:

- Arsenic tends to be transported and homogenized over the vertical extent of the treatment zone due to the mixing action of the auger as it is raised and lowered.
- Soil solidification by auger mixing is a mass-production operation. Thus, it is not practical to target individual depth intervals for treatment.

The geospatial analysis performed during the RI consisted of variogram analysis followed by block kriging. This produced a series of soil arsenic concentration maps at 2-foot elevation intervals. In addition to the contour maps, this analysis calculated an average arsenic concentration for each 20-foot by 20-foot by 2-foot block of soil**.** Note that the 20-foot length and 20-foot width are nominal dimensions used for purposes of discussion. The actual dimensions determined by the kriging algorithm are 19.72 feet by 19.81feet. These actual dimensions are used for volume calculations.

For purposes of this analysis, the thickness of the vadose zone is approximately 12 feet (in the unpaved northern portion of the site), corresponding to 32-foot to 20-foot MSL elevation intervals. While these intervals will vary seasonally with the depth of the water table, this assumption was used to provide an estimate. Thus, the mean arsenic concentration in the vadose zone for each 20-foot by 20-foot block was calculated by finding the average concentration of the 6 corresponding 2-foot intervals.

The resulting calculations are presented in Appendix C of the FS Report (CDM Smith 2013a). Three scenarios were analyzed: A) treating all soil with average arsenic concentrations greater than 90 mg/kg, B) treating all soil with average arsenic concentrations of 50 mg/kg, and C) treating all soil with average arsenic concentrations greater than 20 mg/kg. The calculations indicate that Scenario A will treat 70 percent of the arsenic mass in vadose zone soil, Scenario B will treat 82 percent of the arsenic mass in vadose zone soil, and Scenario C will treat 100 percent of the arsenic mass in vadose zone soil.

5.1.2 Technical Basis for the Selection of In-Situ Chemical Oxidation and Ferrous Iron to Remediate Arsenic in Groundwater

Remedial action Alternative 2 relies on *in-situ* application of ferrous iron and an oxidant to remediate arsenic in groundwater. This section provides the technical basis for the *in-situ* use of ferrous iron and ISCO. ISCO would be performed in much the same way as for treatment of organic compounds using oxidants such as:

- Potassium or sodium permanganate ($KMnO_4$ and $NaMnO_4$, respectively)
- Sodium persulfate (NaS_2O_8)
- Hydrogen peroxide (H_2O_2)
- Ozone (O_3)

Chemical oxidation would provide several benefits, including:

1. Oxidation of arsenic in groundwater from arsenite (As III) to the less mobile arsenate form (As V)

2. Oxidation of ferrous iron in groundwater to ferric iron and precipitation of iron oxyhydroxides and co-precipitation of arsenic

Sampling and bench-scale studies conducted for the Puyallup site indicate that iron is a limiting reagent in the precipitation of iron oxyhydroxides and co-precipitation of arsenic at this site (i.e., concentrations of dissolved iron are too low). The study (CDM Smith 2013b) indicated that iron would need to be added to groundwater to drive this reaction at the Puyallup site.

The use of ISCO and ferrous iron to remediate dissolved arsenic in groundwater is well established in the scientific literature. While no two remediation sites are identical, the studies listed below and provided in **Appendix A** are relevant for the Puyallup site:

- *In Situ Treatment of Arsenic Contaminated Groundwater* (Matthess 1981) is an early study that provides a description of a site in Germany where potassium permanganate was used to treat arsenic contaminated groundwater. Potassium permanganate was injected into 17 wells over a six-month period. The study used a lower concentration of the oxidant to minimize the clogging effect caused by the precipitation of iron hydroxides. Arsenic concentrations lowered from an average concentration of 13,600 µg/L to 60 µg/L after the injections.

- *Subterranean Removal of Arsenic from Groundwater* (Rott and Friedle 1998) presents the results of three field studies in which oxygenated water was added to groundwater containing arsenic at concentrations ranging from 15 to 38 µg/L using recirculation systems (injection wells coupled with pumping wells). Arsenic concentrations below the standard of 10 µg/L were able to be achieved at all three sites following several injection/withdrawal cycles.

- *Modeling In Situ Iron Removal from Ground Water* (Appelo et al. 1999) discusses clogging of drinking water wells by iron precipitates. The study indicates that clogging has not been reported as an issue with in-situ iron removal (and associated arsenic removal) using oxygenated water (slow reaction rate) as the precipitation of iron appears to take place at some distance from the well where the groundwater iron concentration has not yet been diminished.

- *In Situ Arsenic Removal in an Alkaline Clastic Aquifer* (Welch et al. 2008) demonstrated that dissolved arsenic in groundwater can be removed by injecting oxygenated water and iron into an aquifer where iron concentrations are low (few tens of µg/L) to form iron oxides along with injecting hydrogen chloride to lower the pH in the alkaline aquifer to approximately 5.3 to 6.4 to promote arsenic adsorption/co-precipitation on the iron oxides. From 0.15 to 6.4 mg/L of ferrous iron were added to oxygenated water and injected into groundwater containing dissolved arsenic up to 36 µg/L. Excellent arsenic removal was obtained when using iron concentrations from 3 to 5 mg/L and an injection/pumping recirculation system, resulting in arsenic concentrations lowering to 1 to 6 µg/L in the treated water.

- *Subsurface Iron and Arsenic Removal for Shallow Tube Well Drinking Water Supply in Rural Bangladesh* (van Halem et al. 2010) presents the results of a study conducted at a community-scale test facility to remove iron and arsenic from groundwater used as a drinking water source. Aerated water was periodically injected into the aquifer through a tube well using a hand pump causing the formation of ferric iron hydroxides and adsorption of ferrous iron and adsorption/co-precipitation of arsenic. The study found that subsurface arsenic removal is controlled by the amount of oxidized iron available per injection/adsorption cycle, and arsenic removal can be enhanced by increasing the oxidation zone.

In-situ application of ferrous iron and an oxidant would enhance the attenuation process that is currently taking place by accelerating the oxidation rate of iron and arsenic. Currently, oxygen within the shallow groundwater flowing into the site is believed to be oxidizing the limited available iron to form an iron/arsenic oxyhydroxide co-precipitate. An oxidant such as permanganate not only accelerates the oxidation of ferrous iron, but the rate of oxidation of arsenic is much faster for permanganate than for dissolved oxygen in groundwater.

ISCO with the addition of ferrous iron has the potential to rapidly remove arsenic from groundwater *in-situ*. However, this is not viewed as a stand-alone method to treat arsenic in groundwater. Remedial action Alternatives 1 and 2 include stabilization/solidification to remediate soil with elevated arsenic concentrations and minimize the potential for this arsenic to leach into groundwater.

5.2 Alternative 1

5.2.1 Solidification/Stabilization of Vadose Zone Soil Containing Greater than 20 mg/kg Arsenic

Under this alternative, soil with arsenic concentrations exceeding 20 mg/kg would be treated by solidification/stabilization and vertical auger mixing. The proposed treatment area is shown on **Figure 7**. Bench-scale testing performed previously (CDM Smith 2013b showed that the most effective solidification/stabilization mix design was a formulation consisting of 13% cement, 2% bentonite, and an iron addition five times the amount of arsenic in the soil (on a molar basis).

The treatment zone at Puyallup is relatively shallow. This will allow use of a large-diameter auger (diameters ranging from 3 feet to 12 feet) to uniformly mix the soil while injecting the solidification reagent. Vertical auger mixing is typically applied in an overlapping "brick" pattern that provides full horizontal and vertical coverage of the proposed treatment area. Soil solidification is planned for the fall, when groundwater levels are lowest, to allow solidification of contaminated soil that is in seasonal contact with the water table. Monitoring wells within the treatment area would be abandoned prior to mobilizing the solidification equipment. Alternative 1 would treat approximately 33,500 cubic yards of soil.

5.2.2 Groundwater Treatment with a PRB in a "Funnel and Gate" Configuration

Groundwater would be treated using a funnel (slurry wall) and gate (PRB) approach. The conceptual layout of the funnel and gate system is shown on **Figure 7**. The effectiveness of this treatment would be determined by performance groundwater monitoring. It was assumed that the slurry wall would extend down to the aquitard, an estimated depth of 45 feet. The total length of the two sides of the funnel is 640 feet.

The PRB would be constructed of zero-valent iron (ZVI) and assumed to have a top depth of 10 feet bgs and a base of 45 feet bgs. It is assumed the PRB would be replaced every 10 years or twice during the duration of the planned remediation.

5.2.3 Performance Monitoring

The effectiveness of the PRB in treating the arsenic plume would be assessed by performance groundwater monitoring. It is assumed that groundwater performance monitoring would be semi-annual for the first 5 years and annual afterward for a total of 30 years.

5.2.4 Sediment Removal

Sediment cleanup would be implemented when soil and groundwater cleanup actions have demonstrated that there is no risk of recontamination of sediment from groundwater. The proposed extent of the sediment remediation area is shown on **Figure 7**. The Puyallup River sediment cleanup would take place during an in-water work period. The proposed sediment cleanup area includes all sampling locations where arsenic concentrations exceeded the sediment cleanup objective (no adverse effects level) of 14 mg/kg. A sediment sampling round would need to be performed prior to cleanup to provide current data. A site-specific arsenic cleanup level may be developed using a human health and environmental risk assessment as described in WAC 173-304.

Sediment cleanup is expected to be relatively simple from a construction standpoint, with an excavator digging sediment from the river bank and loading it into trucks. Turbidity resulting from the excavation would be managed using silt curtains.

5.3 Alternative 2

5.3.1 Solidification/Stabilization of Vadose Zone Soil Containing Arsenic

Alternative 2 uses solidification to treat three different average arsenic concentrations in soil as sub-alternatives. Alternative 2a treats soil with arsenic concentrations exceeding approximately 90 mg/kg; Alternative 2b treats soil with arsenic concentrations exceeding approximately 50 mg/kg; and Alternative 2c treats soil with arsenic concentrations exceeding 20 mg/kg (the same as Remedial Action Alternative 1). Soil would be treated by solidification/stabilization and vertical auger mixing. The treatment areas are shown on **Figures 8a**, **8b**, and **8c**. As described earlier, bench-scale testing (CDM Smith2013b) showed that the most effective solidification mix design was a formulation consisting of 13% cement, 2% bentonite, and an iron addition five times the amount of arsenic in the soil (on a molar basis).

As discussed for Alternative 1, the treatment zone at Puyallup is relatively shallow, allowing use of a large-diameter auger (diameters ranging from 3 feet to 12 feet) to uniformly mix the soil while injecting the solidification/stabilization reagent. Vertical auger mixing is typically applied in an overlapping "brick" pattern that provides full horizontal and vertical coverage of the proposed treatment area. Soil solidification is planned for the late fall, when groundwater levels are lowest, to allow solidification of contaminated soil that is in seasonal contact with the water table. Monitoring wells within the treatment area would be abandoned prior to mobilizing the solidification equipment.

The following subsections describe the remedial action sub-alternatives. These sub-alternatives differ primarily in the amount (volume and areal extent) of soil solidified. As shown on **Figures 8a**, **8b**, and **8c**, some other features of the remedial action sub-alternatives (for example, the location of the ferrous iron injection trench) are adjusted to be outside the solidified soil area.

Proposed Soil Solidification Area – Alternative 2a

As shown on **Figure 8a**, Alternative 2a would treat approximately 11,460 cubic yards of soil. Treating this area would solidify approximately 70% of the arsenic in vadose zone soil that is above the cleanup level. This metric was selected because it treats the soil in the contaminant source area and the surrounding soil. Soil above the cleanup level and outside of the treatment area shown on **Figure 8a** can be addressed in several ways:

- Shallow arsenic soil hot spots (such as encountered in boring A-6) can be excavated and transported to the treatment area for solidification.
- Institutional controls can be implemented to limit potential human contact with the soil exceeding the cleanup level.
- Potential impacts to groundwater from arsenic leaching out of vadose zone soil from peripheral areas can be addressed by *in-situ* treatment using ferrous iron and oxidants as described below.
- Areas outside the solidification area shown on **Figure 8a** can be solidified later (greater than 20 mg/kg and less than 90 mg/kg arsenic) if an analysis of performance monitoring data indicates that this will result in attainment of the groundwater cleanup standard.

Proposed Soil Solidification Area – Alternative 2b

As shown on **Figure 8b**, Alternative 2b would treat approximately 16,500 cubic yards of soil. Treating this area would solidify approximately 82% of the arsenic in vadose zone soil that is above the cleanup level. This metric was selected to provide an intermediate solidification scenario between 90 mg/kg and 20 mg/kg arsenic. Methods to address soil above the cleanup level in the area surrounding the treatment area shown on **Figure 8b** are the same as described above for Alternative 2a.

Proposed Soil Solidification Area – Alternative 2c

As shown on **Figure 8c**, Alternative 2c would treat approximately 33,500 cubic yards of soil. Treating this area would solidify all of the arsenic in vadose zone soil that is above the cleanup level.

Qualitative Analysis of Alternative 2 Sub-Alternatives

The Alternative A sub-alternatives present a somewhat unique balancing of risks in remediating arsenic in soil and groundwater. Clearly, the residual arsenic hot-spot in soil centered at the P3 well cluster needs to be remediated to address the co-located arsenic hot-spot in groundwater. All of the remedial Alternative 2 sub-alternatives treat the arsenic soil hot-spot and the surrounding soil by solidification. In addition, Alternative 2 (all sub-alternatives) treats arsenic in groundwater (both in the hot-spot and in the surrounding area) by injecting ferrous iron and an oxidant.

On the other hand, the oxidizing groundwater conditions at the site (caused by infiltrating precipitation) are currently attenuating dissolved arsenic in groundwater by precipitation of iron-arsenic oxyhydroxides. The risk of a more laterally extensive soil solidification sub-alternative is solidifying too much soil over too great an area, causing less precipitation to infiltrate near the heart of the plume and making groundwater conditions more reducing. More reducing groundwater conditions will tend to increase the mobility of arsenic in groundwater.

When comparing the solidification areal extent of the sub-alternatives, sub-alternative 2c encompasses approximately 3 times the surface area as sub-alternative 2a (compare **Figures 8a** and **8c**). Clearly, if the area shown on **Figure 8c** is solidified, the existing, favorable patterns of precipitation infiltration will be drastically altered, potentially making groundwater conditions more reducing. In addition, the solidification area shown on **Figure 8c** will be difficult to construct from a practicality standpoint.

When comparing sub-alternatives 2a and 2b, sub-alternative 2b encompasses approximately 50% more surface area than sub-alternative 2a. However, the increased mass of arsenic solidified (82% for sub-alternative 2b versus 70% for sub-alternative 2a) is relatively minor. This reflects the arsenic distribution in soil at the site, where most of the arsenic in soil (on a total mass basis) is concentrated in the source area. Arsenic in soil outside of the source area is widely disseminated. The proposed groundwater treatment approach, described below, is designed to address groundwater impacts resulting from widely disseminated arsenic in the vadose zone.

5.3.2 Groundwater Treatment

Groundwater for all three sub-alternatives would be treated using *in-situ* application of ferrous iron and an oxidant. As shown on **Figures 8a**, **8b**, and **8c**, the conceptual approach includes a trench where ferrous iron can be continuously introduced into the groundwater upgradient of the plume. Also shown are injection points where ferrous iron can be injected directly into the arsenic plume. A greater density of ferrous iron points is shown in and around the arsenic hot spot in groundwater centered at the P3 monitoring well cluster. Ferrous iron would be injected using a DPT drill rig.

Geochemical modeling indicates that, in addition to ferrous iron, an oxidant will need to be introduced into groundwater to oxidize the arsenic and drive the iron-arsenic oxyhydroxide co-precipitation reactions. **Figures 8a**, **8b**, and **8c** show a conceptual layout of ISCO injection points or wells. Selection of the oxidant and optimal dose would be made by laboratory and pilot-scale testing.

For this remedy to be effective over the long-term it will be necessary to maintain the redox gradient where groundwater comes in contact with oxygenated infiltration water. This causes the precipitation of iron-arsenic oxyhydroxides, which remove dissolved arsenic from groundwater. The conceptual design includes a stormwater infiltration gallery (shown on **Figures 8a**, **8b**, and **8c**) to maintain these existing groundwater geochemical conditions after solidification.

5.3.3 Performance Monitoring

The effectiveness of this remedy would be assessed by performance monitoring. An adaptive management approach, based on performance monitoring data, would be used to determine the scope of future ferrous iron and oxidant applications. It was assumed that there will be annual applications for 4 years after the initial application, and bi-annual applications totaling two rounds after that. It was also assumed that the performance monitoring would be performed on a quarterly basis for 4 years, semi-annual for 6 years, and annually for an additional 20 years, for 30 years total.

5.3.4 Sediment Cleanup

Cleanup of Puyallup River sediment will be the same as described in Alternative 1.

5.4 Alternative 3

5.4.1 Excavation of Soil Exceeding 20 mg/kg Arsenic and Off-Site Disposal, and Sediment Removal

Under this alternative, soil exceeding the 20 mg/kg arsenic soil cleanup level would be excavated and disposed of off-site. Due to the proximity of the Puyallup River, the excavation would be performed in two phases as shown on **Figure 9**. The excavation is planned to extend an average of 3 feet below the water table.

It is assumed that 82,000 cubic yards of soil would need to be excavated for Alternative 3. Upon excavation, soil would be tested for waste profiling purposes. It was assumed that approximately 28,150 cubic yards of soil would be disposed of in a solid (nonhazardous) waste landfill. This soil would be trucked to a transfer station in Tacoma for haulage by rail to the Rabanco Landfill in Roosevelt, Washington or the Columbia Ridge Landfill in Arlington, Oregon.

As shown on **Figure 9**, the two excavation phases would require approximately 1,310 linear feet of sheet pile shoring to allow excavation at depth. Puyallup River sediment exceeding the cleanup levels would be remediated as part of the second phase of excavation.

Soil meeting the cleanup standards would be considered as suitable for use as backfill. Quarry spalls would be used to backfill areas where the excavation extends below the water table. Stockpiled and imported soil would be used to backfill the excavation above the water table.

5.4.2 Extraction and Treatment of Groundwater During Excavation

Excavation near or below the water table would require dewatering. Groundwater generated during these dewatering operations would be pre-treated in a wastewater treatment plant installed on-site. Pre-treated wastewater would be discharged to a POTW.

5.4.3 Monitored Natural Attenuation

Following restoration, the monitoring well network would be re-installed. It was assumed an MNA program would be implemented on a semi-annual basis for the first 5 years and an annual basis afterward for a total of 30 years.

5.5 Comparative Evaluation of the Remedial Action Alternatives

This subsection comparatively evaluates the remedial action alternatives with regard to the evaluation criteria listed in WAC 173-340-360 (3)(f). **Table 1** summarizes the scores given to each alternative for each criterion and **Table 2** summarizes the rationale for the numeric ranking assigned to each criterion.

Protectiveness: All three remedial action alternatives would improve the overall protectiveness. Arsenic-contaminated soil exceeding the Method A cleanup standard would be treated by a combination of solidification/stabilization, excavation and off-site disposal, and institutional controls. All remedial alternatives address impacts from groundwater to Puyallup River sediment and surface water, providing protectiveness to human and environmental receptors.

Remedial action Alternatives 1 and 2 would treat arsenic-contaminated soil in the vadose zone by solidification/stabilization. The difference between these alternatives is the extent of soil treated. Remedial action Alternative 1 would treat all soil above the MTCA Method A cleanup level, for an estimated total of approximately 33,500 cubic yards.

Solidification/stabilization for remedial action Alternative 2a is focused on the contaminant source area and would treat all soil above 90 mg/kg, for an estimated total of approximately 11,460 cubic yards. The peripheral area (with soil concentrations greater than 20 mg/kg and less than 90 mg/kg) for remedial action Alternative 2 would be addressed with institutional controls and performance groundwater monitoring. The smaller solidification footprint in remedial action Alternative 2a is compatible with its *in-situ* groundwater remediation approach, which relies on maintaining the current oxidation-reduction gradient in groundwater that is causing arsenic to co-precipitate with iron in the form of oxyhydroxides.

Implementation of a barrier wall and PRB as a 'funnel and gate' configuration in remedial action Alternative 1 presents technical uncertainty and risk. Barrier walls and PRBs function best when they are keyed into an aquitard. At the Puyallup site, the aquitard is approximately 45 feet deep, and while within practical construction limits, would pose some challenge because of its depth.

Experience shows that groundwater tends to flow under a barrier's walls, and groundwater leaks (lateral flow) occur in the barrier wall and in the area where the barrier wall and PRB join. The funnel also increases groundwater velocity through the PRB, which can decrease residence time required for treatment. Additionally, groundwater with high arsenic concentrations can consume a very small portion of the PRB and create a hole for treating the arsenic in groundwater. Leaks and holes are typically difficult to detect and isolate by groundwater monitoring. Accordingly, Alternative 1 is ranked as uncertain for protectiveness.

Remedial action Alternative 3 would remove all arsenic-contaminated soil from the site, but would require significant effort, including: 1) excavating and stockpiling clean soil to access contaminated soil, and 2) excavating and disposing of arsenic-contaminated soil beneath the water table that poses little risk to Puyallup River sediment and surface water (if current geochemical conditions can be maintained). An evaluation of site geochemistry shows that arsenic exceeding the MTCA Method A cleanup level in soil beneath the water table has for the most part precipitated out of solution. Excavating and disposing of this soil off-site will do little to improve the overall protectiveness.

Permanence: Remedial action Alternatives 1 and 2 use solidification to address arsenic-contaminated soil in the vadose zone. Research and bench-scale testing (CDM Smith 2013b) indicate that the solidification mix-design proposed for this project will immobilize arsenic by both chemical stabilization and solidification. While cement-based solidification of nonorganic wastes is generally viewed as a permanent remedy, performance monitoring would be necessary to verify that solidification is acting as a permanent remedy to greatly reduce leaching of arsenic.

Geochemical modeling indicates that oxidizing groundwater conditions at the site are permanently removing dissolved arsenic from groundwater by precipitation into iron-arsenic oxyhydroxides. Adding ferrous iron and oxidants to groundwater will speed and enhance this naturally occurring process. Oxidizing groundwater conditions will ensure that iron-arsenic oxyhydroxides remain insoluble. Engineering measures will need to be taken during final site grading to ensure that oxidizing groundwater conditions that allow precipitation to infiltrate are maintained. This issue is also addressed in the discussion of effectiveness over the long-term.

Remedial action Alternative 3 gets a very favorable rating for permanence because it includes excavation and off-site disposal of all soil and sediment exceeding MTCA cleanup standards.

Cost: The cost for each remedial action alternative was qualitatively evaluated in the Feasibility Study and is summarized below:

Evaluation Criteria	FS Cost Estimate Range	Remedial Action Alternative
Very Favorable	$100,000 to $2,000,000	None
Favorable	$2,000,000 to $4,000,000	2
Somewhat Favorable	$4,000,000 to $8,000,000	None
Unfavorable	$8,000,000 to $16,000,000	1
Very Unfavorable	Greater than $16,000,000	3

Note that these estimated costs include capital and the net present value of long-term operations, maintenance, and monitoring costs.

Effectiveness over the Long-Term: An evaluation of remedial action Alternative 1 found uncertainty over its long-term effectiveness. As discussed under the protectiveness criteria, groundwater contaminated with arsenic could bypass the PRB by flowing through leaks in the barrier wall or flow under the barrier wall or PRB. In addition, holes can develop in sections of the PRB that are in contact with portions of the plume with high arsenic concentrations. In any case, it is assumed that the PRB will need to be replaced after 10 years.

Remedial action Alternative 2 relies on introducing ferrous iron and ISCO to cause precipitation of iron-arsenic oxyhydroxides, thus immobilizing dissolved arsenic in groundwater. Long-term effectiveness and permanence are closely related for this alternative. The long-term effectiveness of Alternative 2 depends on maintaining the current oxidizing groundwater conditions in the core remediation area. The conceptual design for remedial action Alternative 2 incorporates a stormwater infiltration gallery to maintain the current oxidizing groundwater conditions. The FS gives a score of 3 to remedial action Alternative 2 because maintaining this current geochemical process will rely on long-term performance monitoring to verify its effectiveness after the site is modified by solidification.

Remedial action Alternative 3 is very favorable for effectiveness over the long-term for the same rationale discussed for the permanence criteria.

Management of Short-Term Risks: Remedial action Alternative 1 is rated as uncertain for management of short-term risks. The footprint of the solidification is quite large and extends onto adjoining businesses. Constructing a slurry wall and PRB would require careful management to avoid impacting the Puyallup River with excavation spoils or slurry. The PRB could also result in ferrous iron bleed into the Puyallup River and cause downstream staining.

Remedial action Alternative 2 is favorable for managing short-term risks. *In-situ* treatment of soil and groundwater minimizes the chance of human exposure to arsenic during remediation.

Remedial action Alternative 3 is unfavorable for short-term risk management. This alternative calls for extensive excavation beneath the water table, which is inherently risky, especially with respect to caving. The conceptual design specifies temporary shoring along River Road and the Puyallup River. However, if either of these shoring walls were to fail during construction, the results would be catastrophic.

Technical and Administrative Implementability: Remedial action Alternatives 1 and 2 received a somewhat favorable or uncertain ranking for this criterion. The *in-situ* groundwater treatment methods (slurry wall and PRB for Alternative 1 and ferrous iron and oxidant injections for Alternative 2) are implementable from a technical standpoint. However, determining the effectiveness of these measures will require careful analysis of performance monitoring data. Access agreements with the adjoining property owners will need to be obtained prior to conducting work.

Remedial action Alternative 3 received an unfavorable ranking for technical and administrative implementability. Excavation and off-site disposal envisioned in the conceptual design would be large, complex, and adversely impact the existing commercial operations. Finding space to stockpile the large quantity of clean soil for backfill would be difficult. Conducting the second phase of excavation out to the Puyallup River would be technically difficult to implement because of the shoring required.

Consideration of Public Concerns: Remedial action Alternatives 1 and 2 received a somewhat favorable or uncertain ranking for consideration of public concerns. Construction activities would have some impact to the bike path adjoining the Puyallup River. Concerns from the general public about the Puyallup site are unknown at this time.

Remedial action Alternative 3 received an unfavorable ranking, primarily for the deep excavations next to River Road and the Puyallup River. The bike path adjacent to the Puyallup River would need to be closed for a significant period of time to accommodate construction.

Section 6

Proposed Cleanup Action

Alternative 2a was selected as the proposed cleanup action for the site. Following is a description of the proposed cleanup, implementation, and cleanup action monitoring. The proposed cleanup action meets the threshold criteria of MTCA (WAC 173-340-360) as discussed in Section 5, Evaluation and Selection of Cleanup Alternatives.

6.1 Cleanup Action Description

Cleanup action alternative 2a consists of the following activities:

- Assessing soil oxidant demand and select the most effective oxidant.
- Conducting a pilot test to verify that ferrous iron and oxidant injections will be effective under field conditions, including verification monitoring.
- Constructing the ferrous iron introduction trench and implementing the full-scale *in-situ* application of ferrous iron and oxidant via DPT borings, wells, and an introduction trench.
- Abandoning monitoring wells located in the soil solidification zone.
- Solidifying vadose zone soil by injecting a cement-bentonite-iron solidification reagent during vertical auger mixing.
- Constructing the stormwater infiltration gallery.
- Re-installing the monitoring well network and conducting performance monitoring.
- Injecting additional doses of ferrous iron and oxidant based on performance monitoring results.
- Implementing institutional controls such as land use restrictions.
- Constructing curtains around the planned sediment cleanup area in the Puyallup River to contain turbidity and then excavating impacted sediment for off-site disposal. Restoring the river channel/bank.

6.2 Implementation of Cleanup Action

Following is a detailed discussion of the proposed methods to implement the cleanup action.

6.2.1 Remediate Arsenic in Groundwater

The conceptual approach to remediate arsenic in groundwater is by *in-situ* application of ferrous iron and chemical oxidant via DPT borings, wells, and an introduction trench. The first step to implement this remedy is expected to be a laboratory testing to assess soil oxidant demand and the most effective oxidant to use at the site. This would be followed by a pilot test conducted to verify that ferrous iron and oxidant injections will be effective under field conditions. Full-scale application, such as shown on **Figure 8a**, would then be implemented using a DPT drill rig. Included in this initial phase would be construction and operation of the ferrous iron introduction trench. The next phase of remediation would be soil solidification as described in Section 6.2.2 below.

The stormwater infiltration gallery would be constructed after soil solidification is completed. The stormwater infiltration gallery would maintain the redox gradient downgradient of the contaminant source area and promote precipitation and long-term stability of iron-arsenic oxyhydroxides. The monitoring well network would be re-installed and performance monitoring would commence. Additional injections of ferrous iron and the oxidant would be made based on performance monitoring data.

Ferrous iron would be applied in two ways: 1) continuously introduced into the upgradient trench, and 2) through DPT borings. The oxidant would be applied downgradient of the iron injection locations. The conceptual approach envisions constructing ISCO injection wells where a slow-release oxidant in a solid form can be placed in the injection well and easily replaced when consumed (such as a solid oxidant within a “sock” that can be lowered into a well).

Remedy effectiveness would need to be verified by performance monitoring. An analysis of performance monitoring data would determine the course of *in-situ* groundwater treatment. This proposed remedy will be inherently flexible because it will follow an adaptive management approach with the scope of subsequent *in-situ* groundwater treatment based on performance monitoring. Part of the adaptive management approach will include development of a performance monitoring plan that will contain provisions to perform an assessment should results indicate the remedy is not functioning as intended. The assessment will determine the cause of inadequate performance, followed by an evaluation of potential correction actions. For example, the duration of ferrous iron and/or oxidant injections could be extended to treat groundwater.

6.2.2 Soil Solidification

Soil solidification would be accomplished by vertical auger. The cement-bentonite-iron solidification reagent would be injected during auger mixing. Monitoring wells in the solidification area would be abandoned prior to construction.

Schedule is a key consideration for implementing soil solidification. Soil solidification would be scheduled for late fall when the water table is its lowest. This would enable the solidified soil ‘monolith’ to extend into the water table when the water table is higher.

The proposed *in-situ* groundwater remediation approach combined with performance monitoring is compatible with soil solidification because its effectiveness can be evaluated by performance monitoring.

6.2.3 Remediate Sediment in the Puyallup River

Puyallup River sediment would be cleaned up after treatment of arsenic in soil and groundwater has commenced. The remedial approach is conceptually straightforward and includes: 1) constructing curtains to contain the turbidity that would be generated during sediment removal, 2) excavating sediment above arsenic cleanup levels and disposing of it off-site, and 3) restoring the river bank. Work conducted in the Puyallup River would need to account for the fish work window. The sediment remediation effort would also need to address any Puyallup Tribe concerns.

6.3 Compliance Monitoring

The cleanup action will be monitored in accordance with the requirements of WAC 173-340-410, and include protection, performance, and confirmational monitoring. The monitoring requirements for the cleanup action are discussed in the following subsections. Specific requirements for monitoring the cleanup action will be provided in a Compliance Monitoring Plan (described in Section 7).

6.3.1 Protection Monitoring

Protection monitoring of soil, sediment, groundwater, and surface water quality would be conducted during the cleanup action to confirm that human health and the environment are protected. The frequency, scope, and duration of monitoring and sampling will be detailed in the Compliance Monitoring Plan. Monitoring will be conducted to ensure workers are protected during the cleanup action.

6.3.2 Performance Monitoring

Groundwater monitoring and sampling and analysis would be conducted to verify the effectiveness of solidification of arsenic in soil, and *in-situ* ferrous iron and oxidant treatment of groundwater. Groundwater monitoring would also occur to assess arsenic concentrations over time and evaluate geochemical parameters to ensure oxidizing conditions are maintained. The frequency, scope, and duration of the monitoring and sampling and analysis will be detailed in the Compliance Monitoring Plan.

6.3.3 Confirmational Monitoring

Following completion of the remedial action, confirmation monitoring and sampling and analysis of groundwater and Puyallup River sediment would be performed to evaluate the effectiveness of the cleanup action and assess when the cleanup levels have been met at the defined points of compliance. The frequency, scope, and duration of the monitoring and sampling and analysis will be detailed in the Compliance Monitoring Plan.

6.4 Special Requirements for Containment Remedies

The remedy for the site contains, rather than removes, arsenic. MTCA (WAC 193-340-380 [a][ix]) requires that “the type, level, and amount of hazardous substances remaining on site and the measures that will be taken to prevent the migration of those substances” be specified.

Information about the concentration of contaminants at the site is summarized in the RI Report (CDM 2011). The hot spot of arsenic in vadose zone soil would be contained by solidification. Ferrous iron and oxidant will be injected into the subsurface to promote the precipitation of arsenic from groundwater and immobilize it. The overall mass of arsenic at the site is not expected to be significantly reduced by the cleanup action.

The selected remedial action is a containment remedy and includes institutional controls. Institutional controls that would be applied at the site include land use controls to protect the integrity of the remedy's various features (e.g., stormwater infiltration gallery) and groundwater use restrictions. An environmental covenant would be instituted on the affected properties. The environmental covenant would be filed with Pierce County.

Section 7

Additional Requirements

This section discusses the documentation to be provided for the cleanup action, including an Engineering Design Report, construction plans and specifications, and a Compliance Monitoring Plan.

7.1 Engineering Design Report

An Engineering Design Report will include sufficient information to develop and review construction plans and specifications and document engineering concepts and criteria used to design the cleanup action. The information required under WAC 173-340-400(4)(a)(i) through 173-340-400(4)(a)(xx) will be included in the Engineering Design Report.

The Engineering Design Report will include a Sampling and Analysis Plan for conducting an additional subsurface investigation to collect samples for laboratory analysis to determine oxidant demand. The Engineering and Design Report will also include a Pilot Study Work Plan that will describe the testing to be conducted to determine the most effective oxidant for groundwater treatment. The findings from the pilot study will be appended to the Engineering Design Report.

7.2 Construction Plans and Specifications

The Construction Plans and Specifications will detail the cleanup action to be performed. As required by WAC 173-340-400(4)(b), the documents will include the following information, as applicable:

- A description of the work to be performed and a summary of the engineering design criteria from the Engineering Design Report
- A site location map and a map of existing conditions
- A copy of applicable permit applications and approvals
- Detailed plans, procedures, and specifications necessary for the cleanup action
- Specific quality control tests to be performed to document the construction, including specifications for testing or reference to specific testing methods, frequency of testing, acceptable results, and other documentation methods
- Provisions to ensure that the health and safety requirements of WAC 173-340-810 are met

All aspects of construction will be performed and documented in accordance with WAC 173-340-400(6). These aspects include approval of all of the plans listed above prior to commencement of work, oversight of construction by a Professional Engineer licensed in the State of Washington, and submittal of a Construction Completion Report that documents all aspects of the cleanup and includes an opinion of the engineer as to whether the cleanup was conducted in substantial compliance with the CAP, the Engineering Design Report, and the construction plans and specifications.

7.3 Compliance Monitoring Plan

The Compliance Monitoring Plan, prepared in accordance with WAC 173-340-410, will describe monitoring to be performed during the cleanup action. It will also include a Sampling and Analysis Plan prepared in accordance with WAC 173-340-820 that will specify the procedures to be followed to ensure that sample collection, handling, and analysis will result in data of sufficient quality to plan and evaluate the cleanup action at the site. The Compliance Monitoring Plan will include the purpose and objective of data collection, rationale for the sampling approach, and responsibilities for sampling and analysis activities. The Compliance Monitoring Plan will describe specifications for sample identifiers; type, number, and location of the samples to be collected; analyses to be performed; documentation of samples; sample containers, collection, and handling; and sampling schedule.

7.4 Permits

The cleanup action at the USG Puyallup site would be conducted under either a Consent Decree or an Agreed Order with Ecology; therefore, the cleanup action is exempt from the procedural requirements of certain laws and all local permits (WAC 173-340-710[9][a]) but must comply with the substantive requirements of these laws and permits. The exemption from procedural requirements applies to:

- Washington Clean Air Act (RCW 70.94)
- Solid Waste Management Act (RCW 70.95)
- Hazardous Waste Management Act (RCW 70.105)
- Construction Projects in State Waters (RCW 75.20)
- Water Pollution Control Act (RCW 90.48); the Shoreline Management Act (RCW 90.58)
- Any laws requiring or authorizing local government permits or approvals

The exemption is not applicable if Ecology determines that the exemption would result in the loss of approval from a federal agency that may be necessary for the state to administer any federal law. The cleanup action for the site is expected to fully comply with all ARARs as described in Section 4.1.

Section 8

References

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Tables

Table 1
Evaluation of Remedial Action Alternatives and Disproportionate Cost Analysis
Feasibility Study - USG Puyallup Site
Puyallup, Washington

Alternative	Description	Disproportionate Cost Analysis Criteria	Protectiveness		Cost		Permanence		Long-term Effectiveness		Management of Short-Term Risks		Technical and Administrative Implementability		Consideration of Public Concerns		Sum	Overall Recommendation
	Weighting Factor		**0.2**		**0.2**		**0.15**		**0.15**		**0.1**		**0.1**		**0.1**		**1**	
			Rank	**Value**	**Rank**	**Value**	**Rank**	**Value**	**Rank**	**Value**	**Rank**	**Value**	**Rank**	**Value**	**Rank**	**Value**		
1	Solidification/Stabilization of Vadose Zone Soil Greater than 20 mg/kg Arsenic, Groundwater Treatment with PRB is 'Funnel and Gate' Configuration, Sediment Removal, Performance Monitoring		**3**	**0.6**	**2**	**0.4**	**4**	**0.6**	**3**	**0.45**	**3**	**0.3**	**3**	**0.3**	**3**	**0.3**	**3.0**	No
2	Solidification/Stabilization of Vadose Zone Soil Greater than 90 mg/kg Arsenic, Institutional Controls, Injection of Ferrous Iron to Groundwater with an Up-Gradient Trench and DPT Borings, ISCO by DPT Borings by DPT Borings and Wells, Performance Monitoring		**4**	**0.8**	**4**	**0.8**	**4**	**0.6**	**3**	**0.45**	**4**	**0.4**	**3**	**0.3**	**3**	**0.3**	**3.7**	**Yes**
3	Excavation of Soil Exceeding 20 mg/kg Arsenic and Off-Site Disposal, Extraction of Groundwater During Excavation, Pre-Treatment of Groundwater and Disposal to the POTW, Sediment Removal, MNA		**5**	**1**	**1**	**0.2**	**5**	**0.75**	**5**	**0.75**	**2**	**0.2**	**2**	**0.2**	**2**	**0.2**	**3.3**	No

Disproportionate Cost Analysis Ranking Criteria

5	Very Favorable, Ideal
4	Favorable, Good
3	Somewhat Favorable or Uncertain
2	Unfavorable
1	Very Unfavorable

Table 2
Disproportionate Cost Analysis
Feasibility Study - USG Puyallup Site
Puyallup, Washington

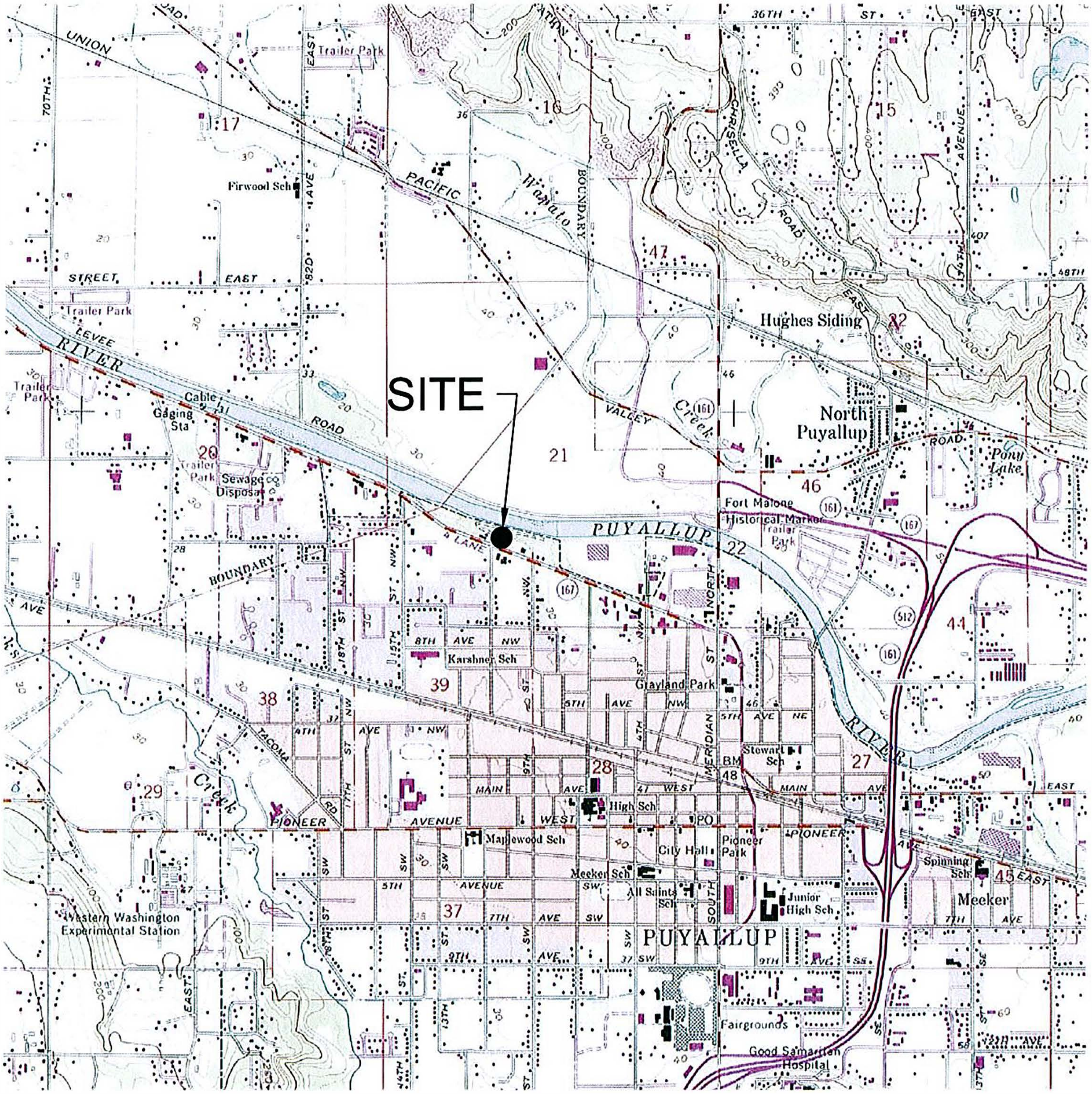
	Alternative Number					
	Alternative 1		**Alternative 2**		**Alternative 3**	
Alternative Information	**Description**	**Score**	**Description**	**Score**	**Description**	**Score**
Description	Solidification/Stabilization of Vadose Zone Soil Greater than 20 mg/kg Arsenic, Groundwater Treatment with PRB in a 'Funnel and Gate' Configuration, Sediment Removal, Performance Monitoring		Solidification/Stabilization of Vadose Zone Soil Greater than 90 mg/kg Arsenic, Institutional Controls, Injection of Ferrous Iron to Groundwater with an Upgradient Trench and DPT Borings, ISCO by DPT Borings by DPT Borings and Wells, Performance Monitoring		Excavation of Soil Exceeding 20 mg/kg Arsenic and Off-Site Disposal, Extraction of Groundwater During Excavation, Pre-Treatment of Groundwater and Disposal to the POTW, Sediment Removal, MNA	
Amount of Soil Treated	33,500 cubic yards		11,460 cubic yards		--	
Amount of Soil Removed	--		--		28,150 cubic yards	
Overall Alternative Ranking	3.0		3.7		3.3	
Evaluation Criteria						
Protectiveness - Weight 20%	This alternative will achieve overall protection. Arsenic-contaminated soil in the vadose zone would be treated by solidification/stabilization. However, use of barrier wall and PRB in a "funnel and gate" configuration presents technical uncertainty as it will be impractical to key into an aquitard based on aquitard depth and leaks/holes will be difficult to detect and isolate.	3	This alternative will achieve overall protection. Risk that "hot spot" removal may not be sufficient to reduce overall site mean contaminant concentration below the MTCA Method A cleanup level. The smaller solidification footprint is compatible with the in situ groundwater remediation approach, which relies on maintaining the current oxidation-reduction gradient in groundwater that is causing arsenic to co-precipitate with iron.	4	This alternative will achieve overall protection as all soil exceeding 20 mg/kg arsenic would be excavated and disposed of off-site.	5
Cost - Weight 20%	$9,460,000	2	$3,270,000	4	$28,900,000	1
Permanence - Weight 15%	Arsenic will be immobilized by solidifying and chemically stabilizing contaminated soil in the vadose zone.	4	Soil containing arsenic at concentrations exceeding 90 mg/kg will be immobilized by solidification and chemical stabilization. The smaller footprint of soil to be treated is compatible with the in situ groundwater remediation approach, which relies on maintaining the current oxidation-reduction gradient in groundwater that is causing arsenic to attenuate by co-precipitation with iron.	4	Alternative reduces the volume of impacted material located at the site by completely removing contaminated soil to the greatest degree technically feasible. This alternative does not reduce the toxicity or volume of the hazardous substance as the contaminated material is simply transferred to a landfill.	5
Long-Term Effectiveness - Weight 15%	The long-term effectiveness is uncertain based on the use of a barrier wall and PRB in a "funnel and gate" configuration, which presents technical uncertainty as it will be impractical to key into an aquitard based on aquitard depth and leaks/holes will be difficult to detect and isolate.	3	Relies on introducing ferrous iron and ISCO to cause precipitation of iron-arsenic oxyhydroxides, thus immobilizing dissolved arsenic in groundwater. Long-term effectiveness depends on maintaining the current oxidizing groundwater conditions in the core remediation area. The conceptual design incorporates a stormwater infiltration gallery to maintain the current oxidizing groundwater conditions.	3	Alternative removes and disposes of contaminated soil off-site.	5
Short-Term Risk Management - Weight 10%	The footprint of the solidification is quite large and extends onto adjoining businesses. Constructing a slurry wall and PRB would require careful management to avoid impacting the Puyallup River with excavation spoils or slurry. The PRB could also result in ferrous iron bleed into the Puyallup River and cause downstream staining.	3	Favorable for managing short-term risk. In-situ treatment of soil and groundwater minimizes the chance of human exposure to arsenic during remediation, and the treatment footprint is smaller than Alternative 1.	4	Creates the most disturbance of impacted soil and the highest short-term risks. This alternative calls for extensive excavation beneath the water table, which is inherently risky, especially with respect to caving. Temporary shoring is specified along River Road and the Puyallup River. However, the impact would be significant if either of these shoring walls were to fail during construction.	2
Implementability - Weight 10%	Implementable; solidification and the slurry wall and PRB are implementable from a technical standpoint. However, determining the effectiveness of these measures will require careful analysis of performance monitoring data. Access agreements with the adjoining property owners will need to be obtained prior to conducting work.	3	Implementable; solidification and the ferrous iron and oxidant injections are implementable from a technical standpoint. However, determining the effectiveness of these measures will require careful analysis of performance monitoring data. Access agreements with the adjoining property owners will need to be obtained prior to conducting work.	3	Difficult to implement; the excavation would be large, complex, and adversely impact the existing commercial operations. Finding space to stockpile the large quantity of clean soil for backfill would be difficult. Conducting the second phase of excavation out to the Puyallup River would be technically difficult to implement because of the shoring required.	2
Consideration of Public Concerns - Weight 10%	Construction activities would have some impact to the bike path adjoining the Puyallup River. Concerns from the general public about the Puyallup site are unknown at this time.	3	Construction activities would have some impact to the bike path adjoining the Puyallup River. Concerns from the general public about the Puyallup site are unknown at this time.	3	Deep excavations would occur next to River Road and the Puyallup River. Traffic impacts expected caused by trucks hauling contaminated soil offsite for disposal and bringing backfill to site. The bike path adjacent to the Puyallup River would need to be closed for a significant period of time to accommodate construction.	2

Notes:
DPT - direct push technology
ISCO - in situ chemical oxidation
mg/kg - milligram per kilogram
MNA - monitored natural attenuation
POTW - publicly owned treatment works
PRB - Permeable Reactive Barrier

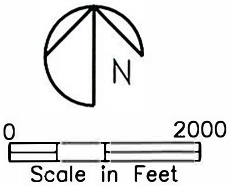
Criteria Ranking

5	Very Favorable, Ideal
4	Favorable, Good
3	Somewhat Favorable or Uncertain
2	Unfavorable
1	Very Unfavorable

Figures



Source: USGS Puyallup, Wash. 7.5' Quadrangle, 1981



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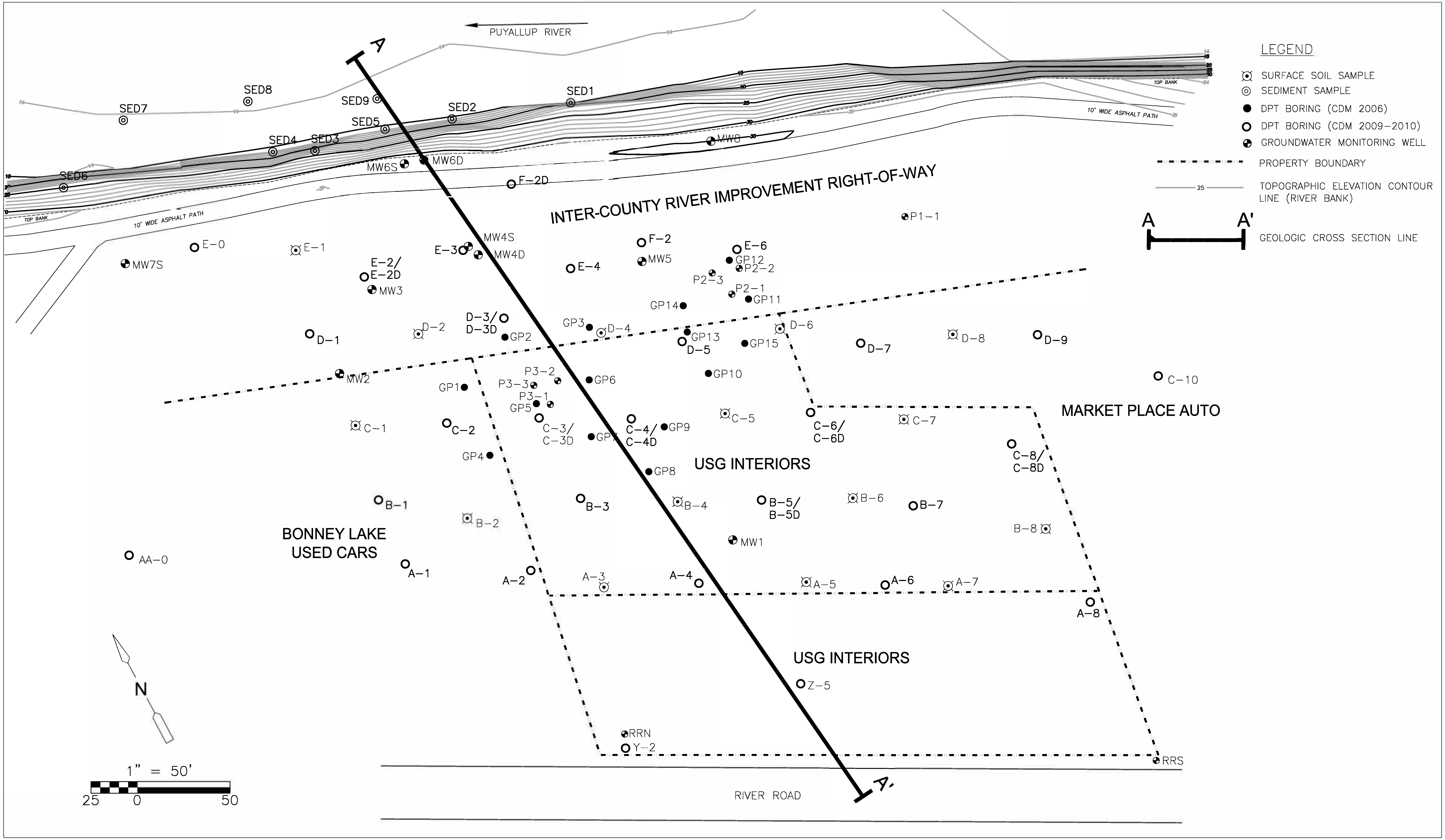
USG INTERIORS/REMEDIAL INVESTIGATION
PUYALLUP, WASHINGTON

Figure No. 1
Vicinity Map



USG INTERIORS/FEASIBILITY STUDY
PUYALLUP, WASHINGTON

Figure No. 2
Site Map and Sample Locations

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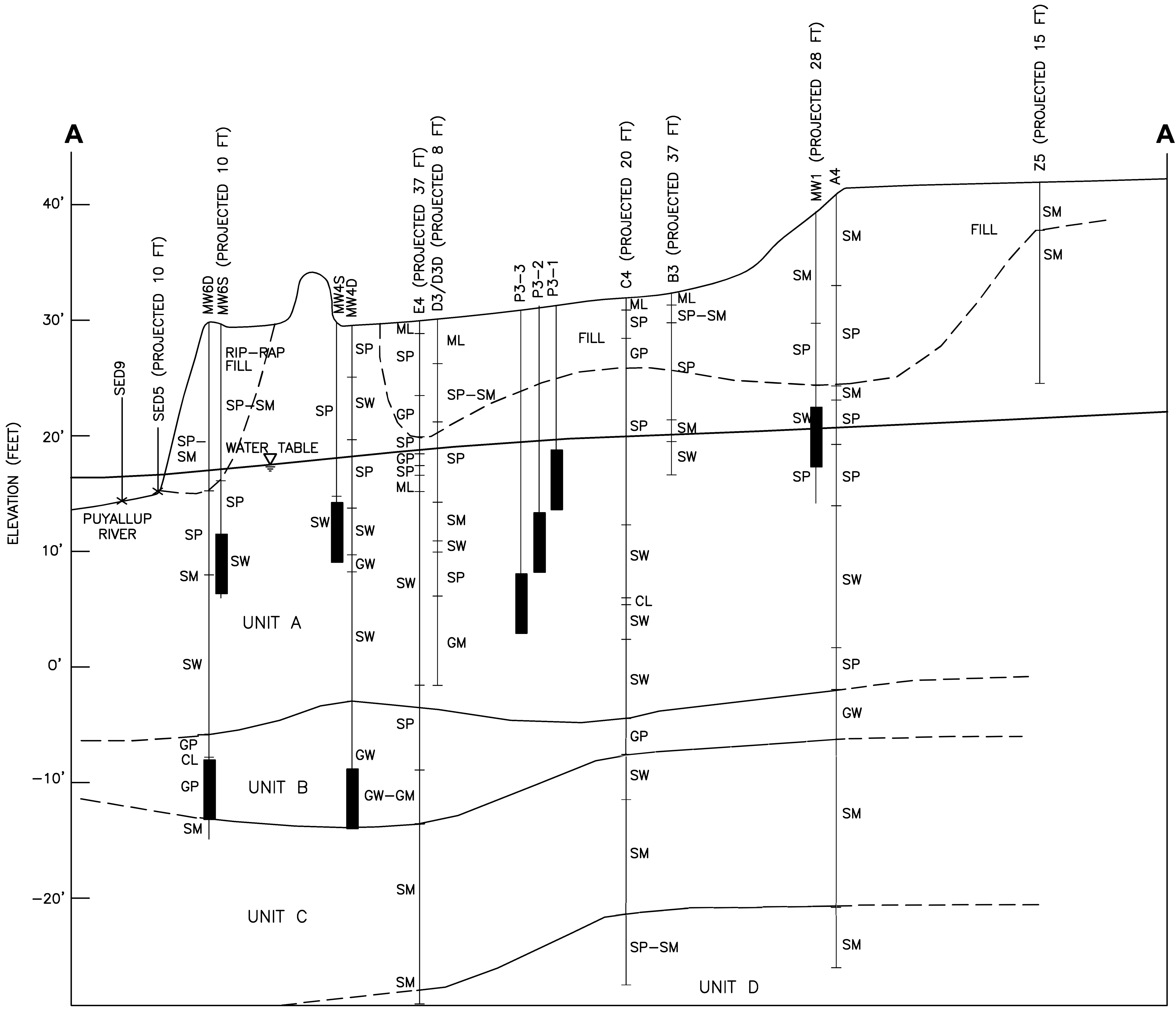

GENERALIZED HYDROGEOLOGIC UNITS

UNIT A – OVERBANK AND POINT BAR DEPOSITS HAVING MODERATE TO HIGH HYDRAULIC CONDUCTIVITY. INCLUDES POORLY GRADED SAND, FINE TO MEDIUM GRAINED AND WELL GRADED SAND, FINE TO COARSE GRAINED WITH TRACE TO SOME FINE TO MEDIUM GRAVEL.

UNIT B – CHANNEL AND POINT BAR DEPOSITS HAVING HIGH HYDRAULIC CONDUCTIVITY. INCLUDES WELL GRADED AND POORLY GRADED GRAVEL, WELL GRADED GRAVEL WITH SILT, AND POORLY GRADED SAND WITH GRAVEL.

UNIT C – SLACKWATER DEPOSITS HAVING LOW TO MODERATE HYDRAULIC CONDUCTIVITY. INCLUDES SILTY SAND, FINE TO MEDIUM GRAINED WITH TRACE GRAVEL AND WOOD FRAGMENTS.

UNIT D – OVERBANK DEPOSITS HAVING LOW HYDRAULIC CONDUCTIVITY. INCLUDES SILTY SAND AND POORLY GRADED SAND WITH SILT, DENSE, FINE GRAINED SAND, LAMINATED.

LEGEND

GEOLOGIC CONTACT, DASHED WHERE INFERRED

▽ WATER TABLE BASED ON DEPTH TO GROUNDWATER DURING DRILLING IN AUGUST AND OCTOBER 2010

MONITORING WELL

SW UNIFIED SOIL CLASSIFICATION SYSTEM (USCS) SOIL TYPE

1" = 50'

25 0 50

HORIZONTAL

VERTICAL EXAGGERATION 2X

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Figure No. 3

Geologic Cross Section A–A'

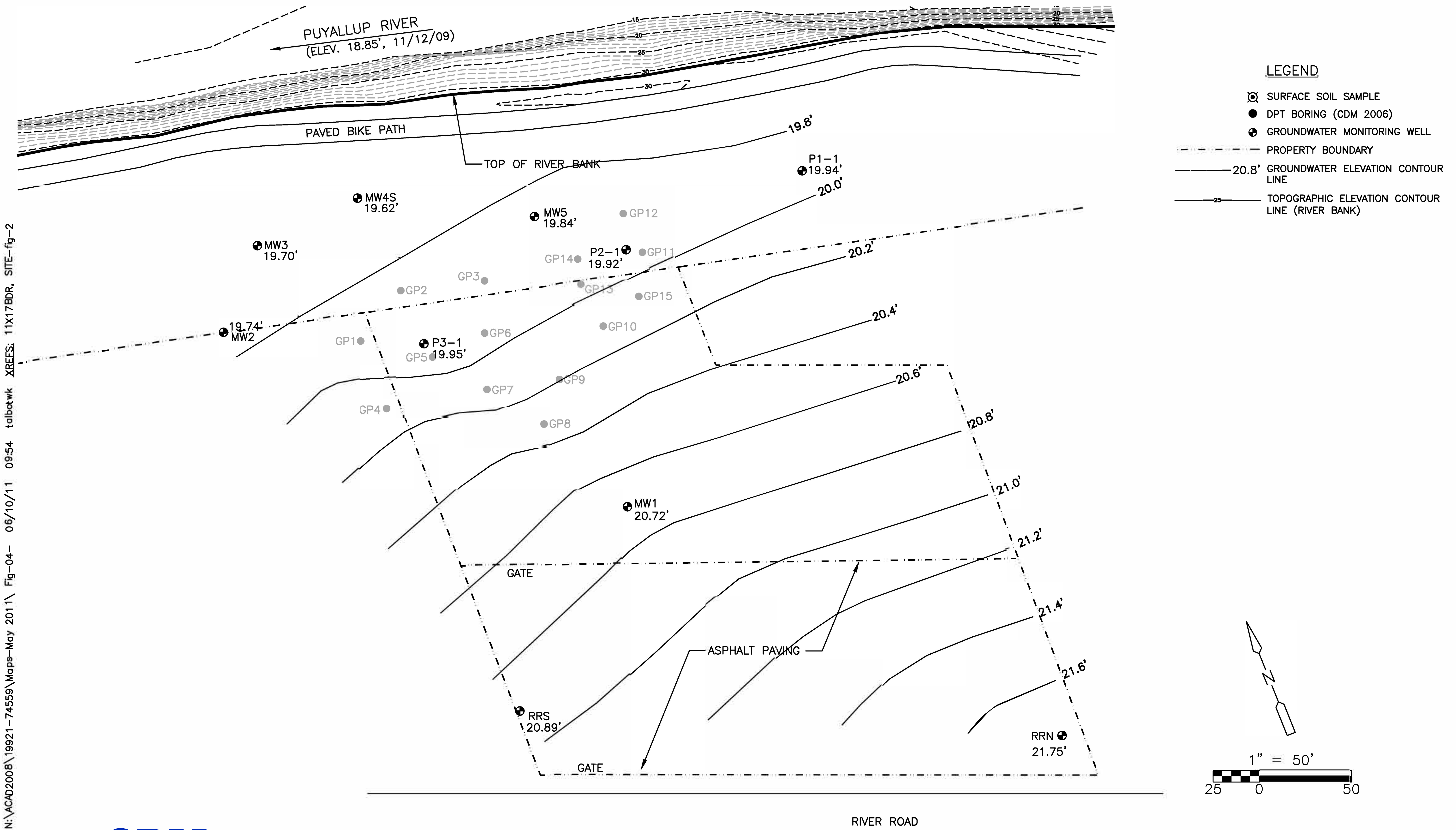

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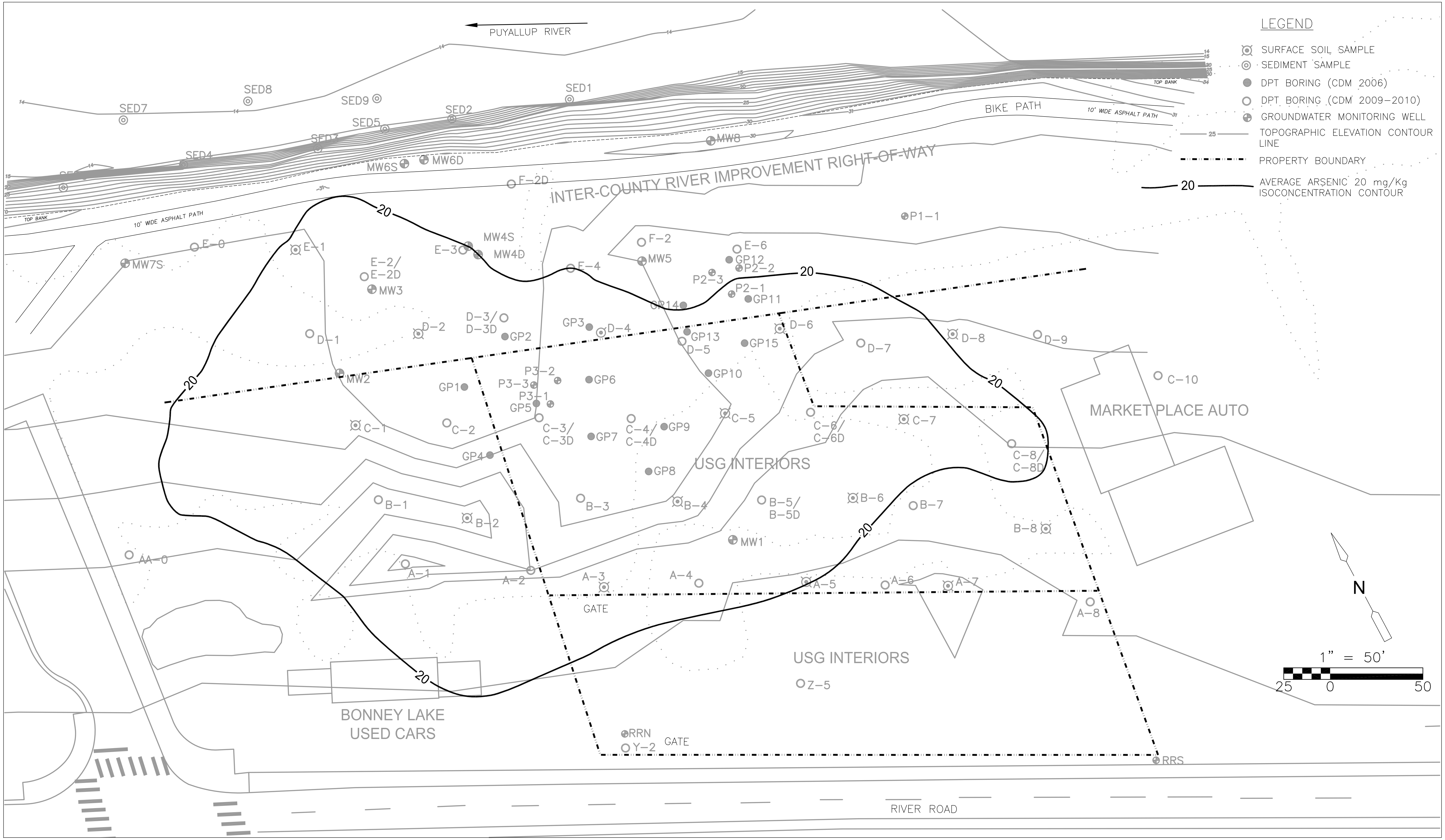
Figure No. 4
Groundwater Elevation Contours
Shallow Aquifer
November 10, 2009



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PUYALLUP, WASHINGTON

Figure No. 5
Extent of Arsenic in Soil

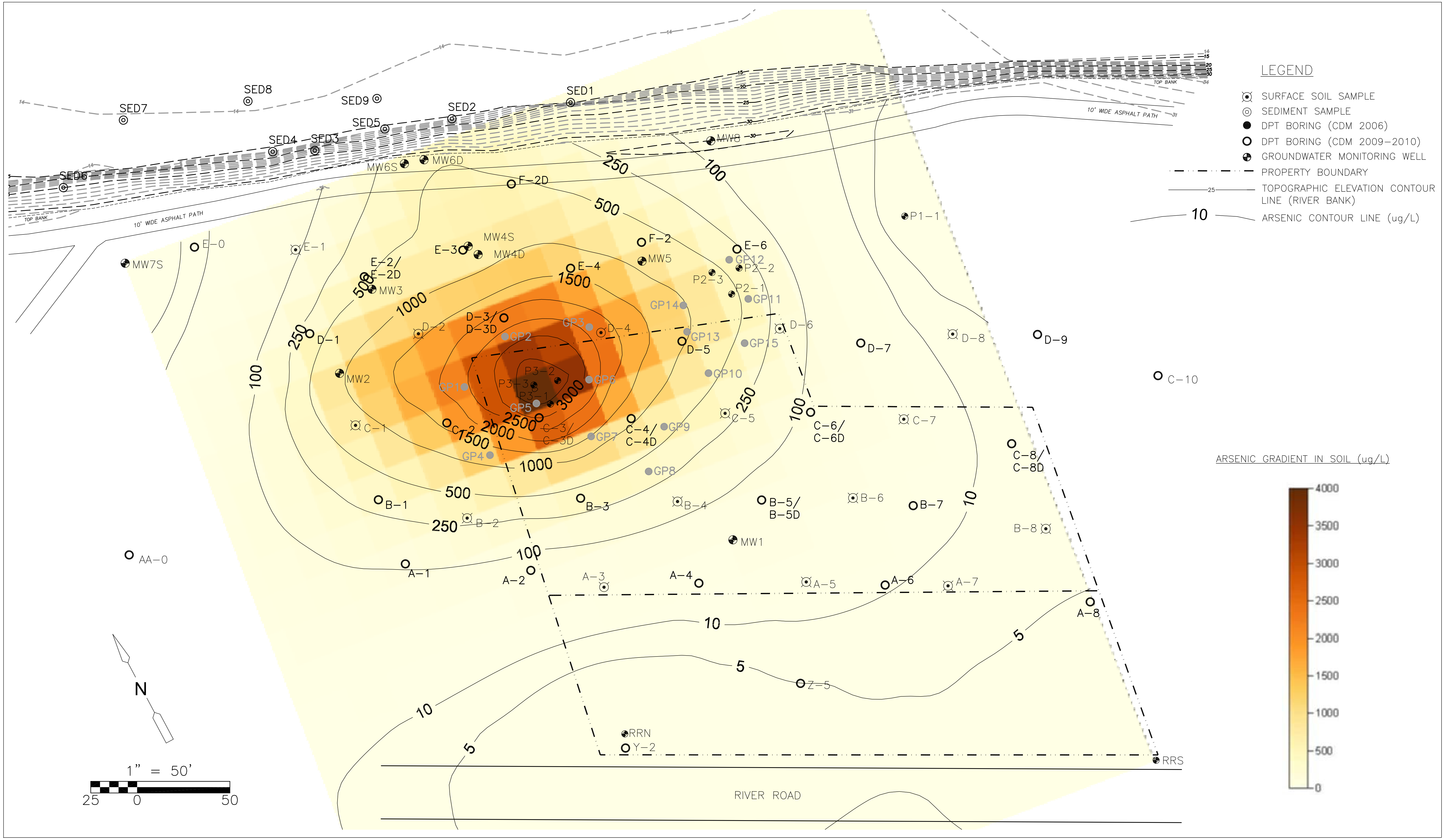

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Figure No. 6
Site Map
Dissolved Arsenic in Groundwater

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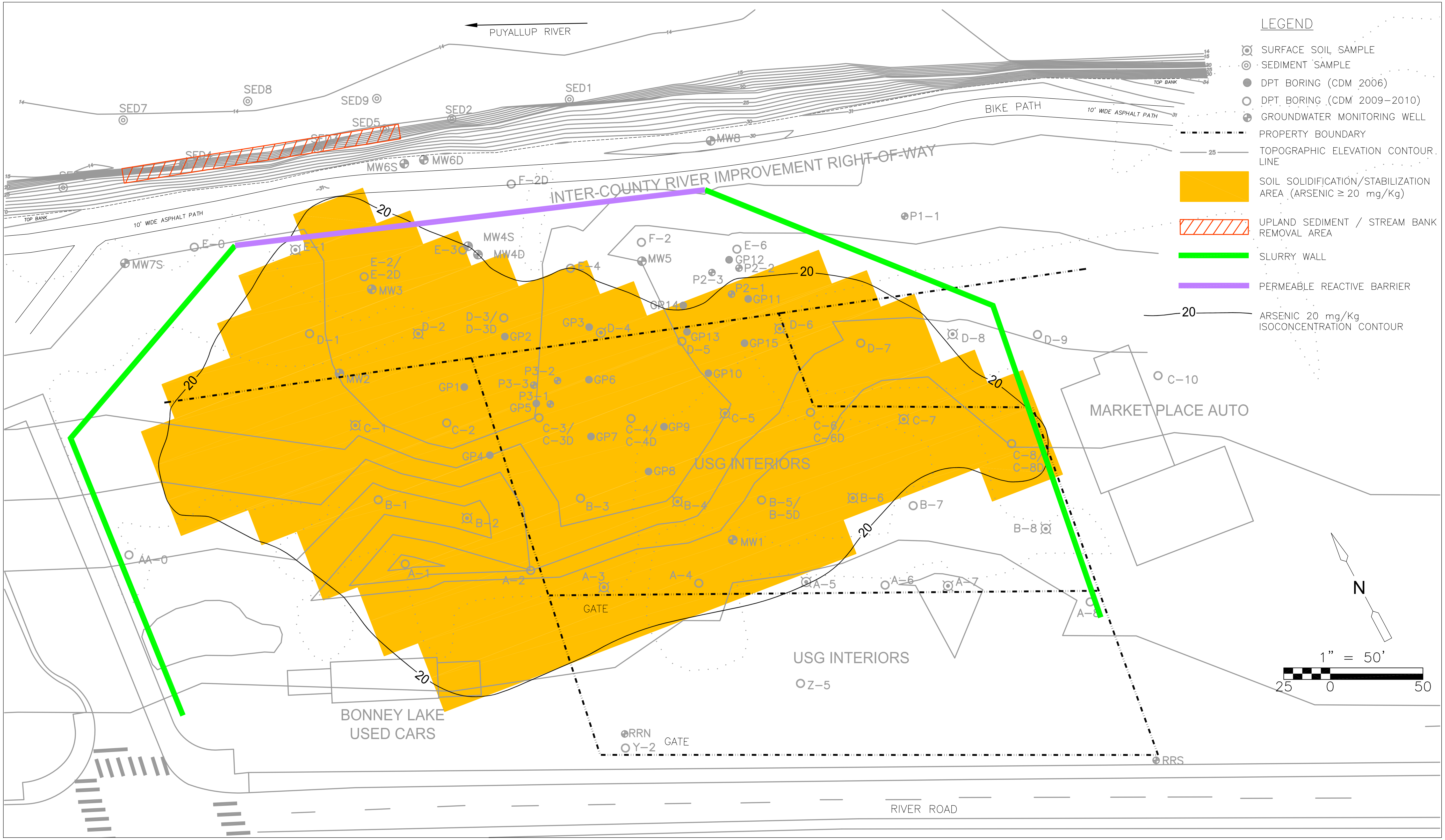

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Figure No. 7
Remedial Action Alternative No. 1

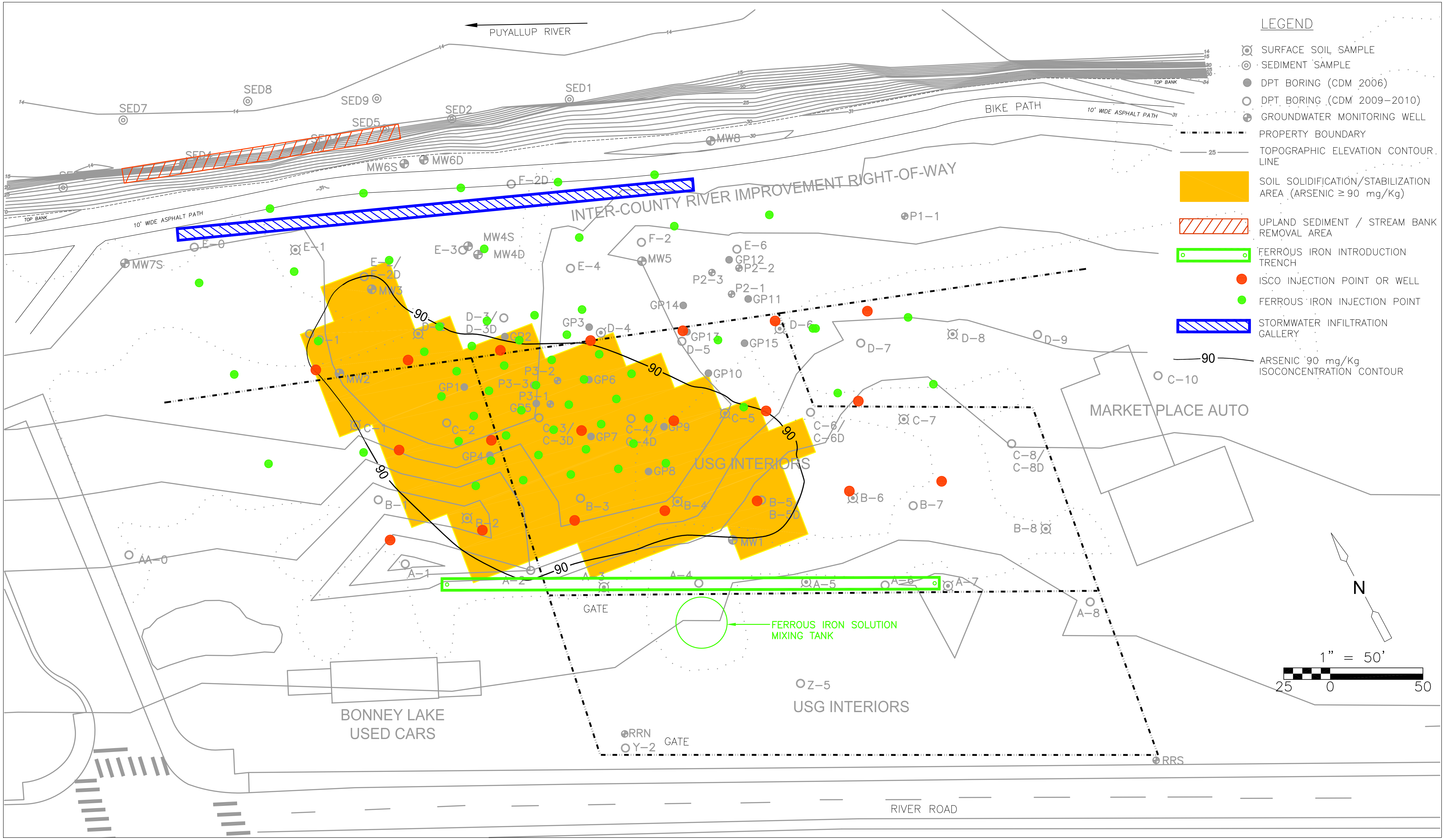

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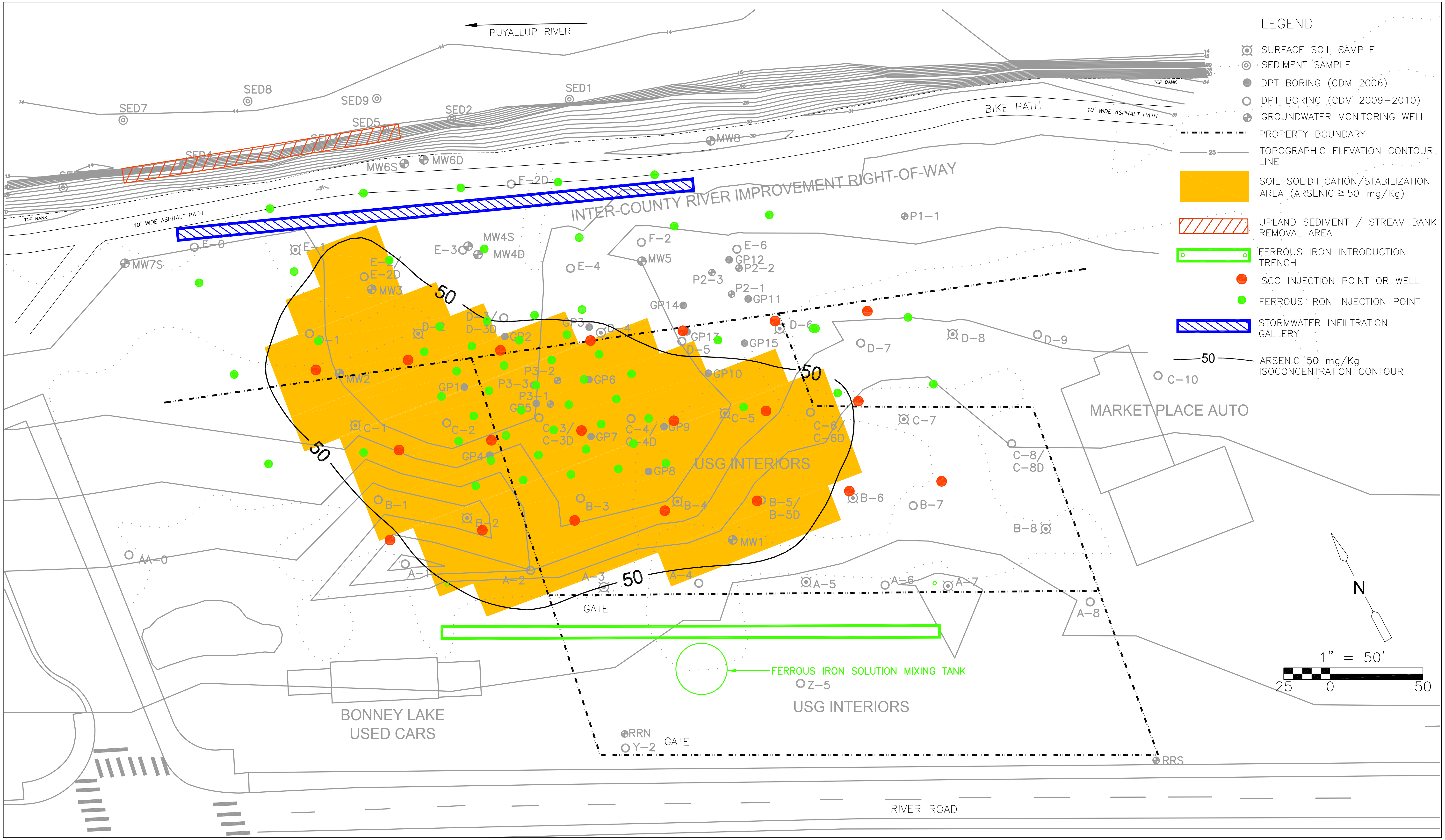
Figure No. 8A
Remedial Action Alternative No. 2A



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USG INTERIORS
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Figure No. 8B
Remedial Action Alternative No. 2B

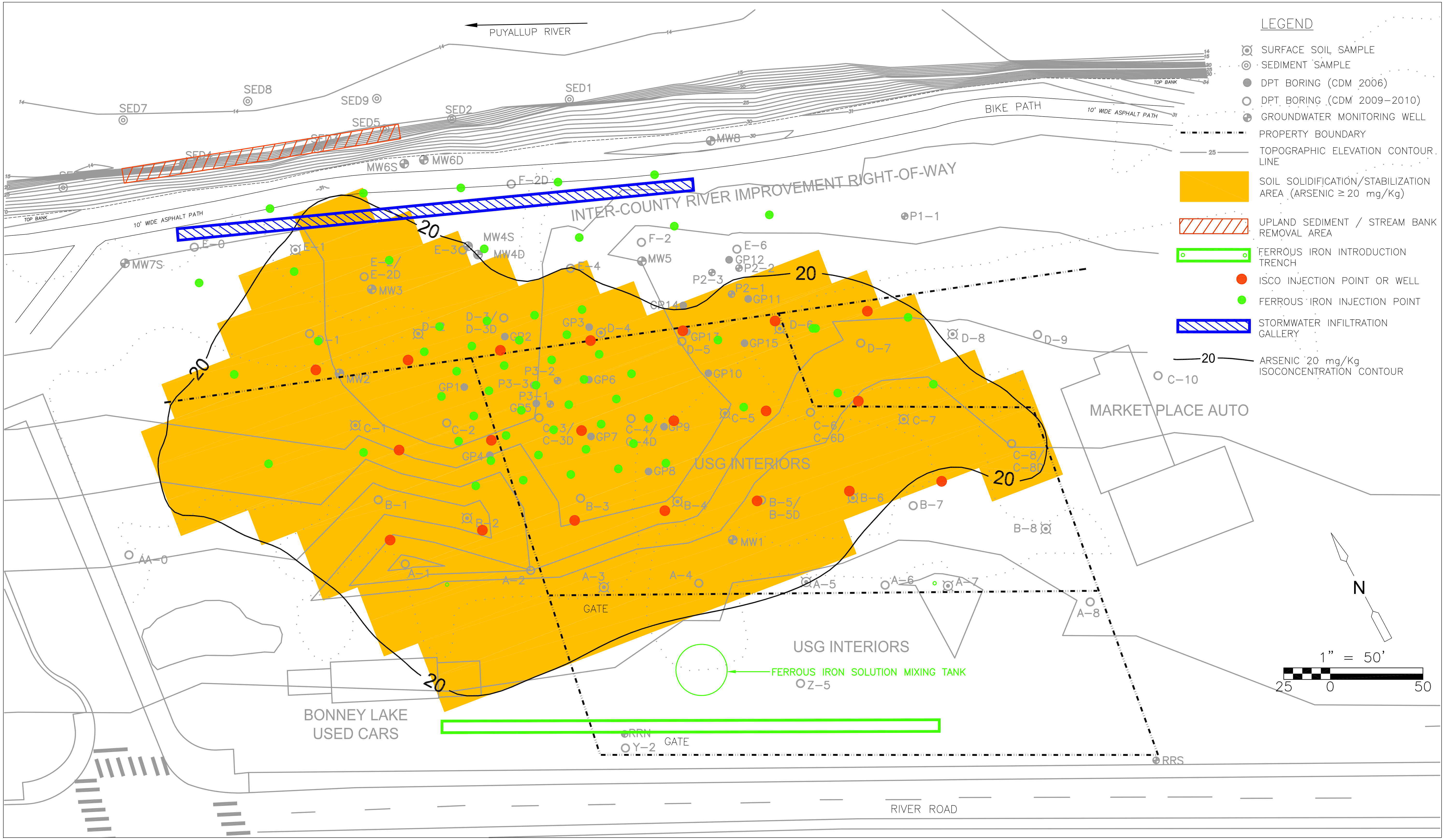

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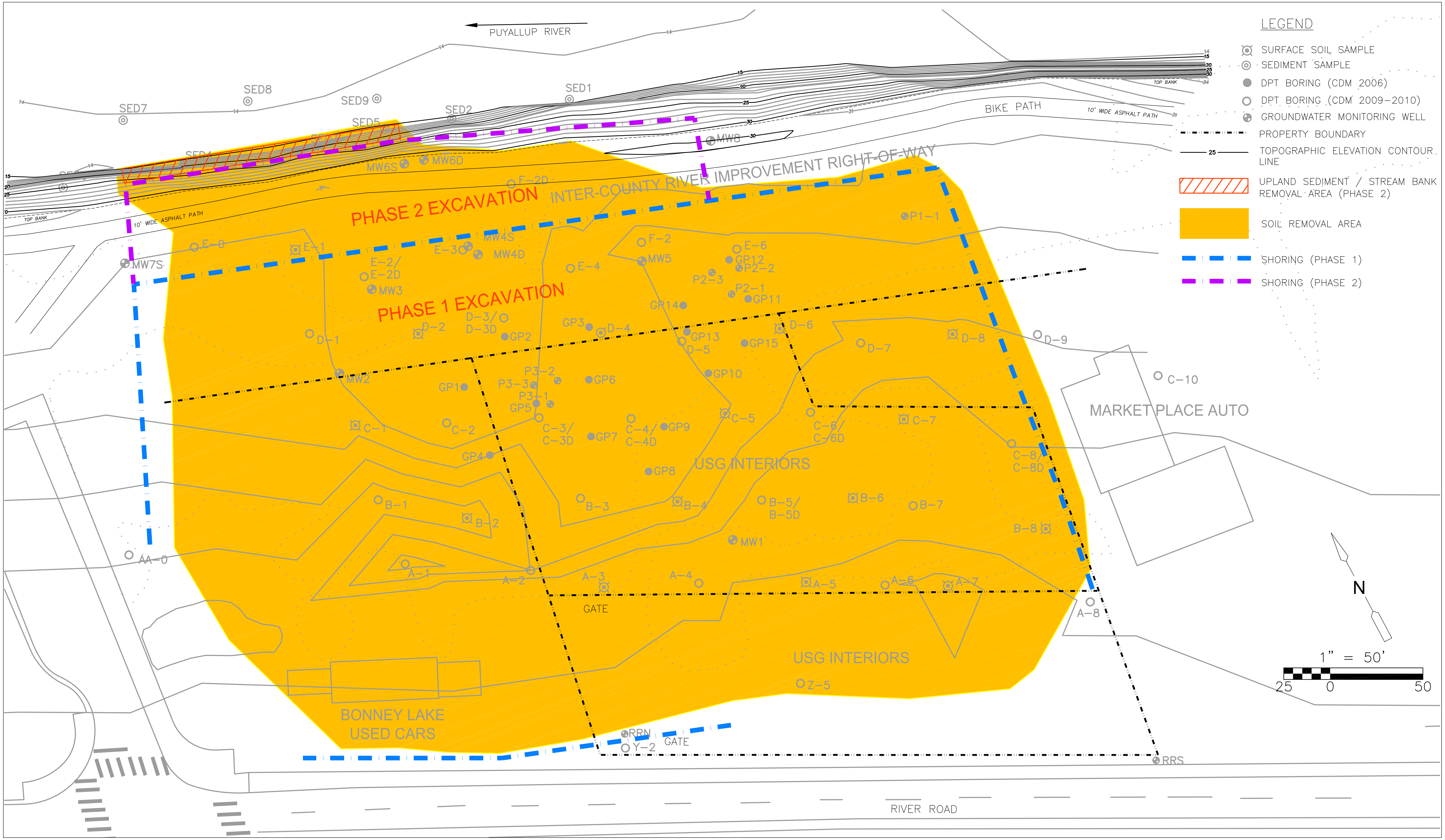
Figure No. 8C
Remedial Action Alternative No. 2C



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USG INTERIORS
PUYALLUP, WASHINGTON

Figure No. 9
Remedial Action Alternative No. 3

Appendix A

Reference Papers on Treatment of Arsenic Using *In Situ* Chemical Oxidation

Environ. Sci. Technol. **2002**, *36,* 3096−3103

Surface Complexation of Ferrous Iron and Carbonate on Ferrihydrite and the Mobilization of Arsenic

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Surface complexation models are commonly used to predict the mobility of trace metals in aquifers. For arsenic in groundwater, surface complexation models cannot be used because the database is incomplete. Both carbonate and ferrous iron are often present at a high concentration in groundwater and will influence the sorption of arsenic, but the surface complexation constants are absent in the database of Dzombak and Morel. This paper presents the surface complexation constants for carbonate and ferrous iron on ferrihydrite as derived for the double-layer model. For ferrous iron the constants were obtained from published data supplemented by new experiments to determine the sorption on the strong sites of ferrihydrite. For carbonate the constants were derived from experiments by Zachara et al., who employed relatively low concentrations of carbonate. The double-layer model, optimized for low concentrations, was tested against sorption experiments of carbonate on goethite at higher concentration by Villalobos and Leckie, and reasonable agreement was found. Sorption was also estimated using linear free energy relations (LFER), and results compared well with our derived constants. Model calculations confirm that sorption of particularly carbonate at common soil and groundwater concentrations reduces the sorption capacity of arsenic on ferrihydrite significantly. The displacing effect of carbonate on sorbed arsenate and arsenite has been overlooked in many studies. It may be an important cause for the high concentrations of arsenic in groundwater in Bangladesh. Sediments containing high amounts of sorbed arsenic are deposited in surface water with low carbonate concentrations. Subsequently the sediments become exposed to groundwater with a high dissolved carbonate content, and arsenic is mobilized by displacement from the sediment surface.

Introduction

The widespread, high As concentration in Bangladesh groundwaters threatens the lives of millions of people. Currently, three theories have been advanced to explain the high As concentrations in Bangladesh groundwater as the result of hydrogeochemical reactions. One theory relates the high As concentration to reduction and dissolution of iron oxyhydroxides to which As was naturally bound during the deposition of sediment in the delta (*1*, *2*). Another theory considers reduction of sorbed As in the aquifer and desorption of less strongly bound arsenite as the major factor (*3*). The third theory invokes the oxidation of arsenic-containing pyrite, formed in the sediments during an earlier reductive step in which sulfate was reduced and arsenic was scavenged.

However, all of these theories do have some inconsistencies. The pyrite oxidation theory calls upon an extensive groundwater drawdown to enable the increased passage of oxygen via gaseous diffusion to pyritic sediment. However, a general drawdown is unlikely in the regularly flooded lowlands of Bangladesh. Nickson et al. (*1*) noted contradictions in their iron reduction theory, namely, a lack of correlation of Fe and As concentrations in groundwater and an Fe^{2+}/HCO_3^- ratio that is much too small. Also, if iron oxyhydroxide is the sole electron acceptor for oxidation of organic matter, the pH would become much higher than observed, even if siderite ($FeCO_3$) would precipitate. The other reduction theory comprises desorption of arsenite but does not explain why in many groundwater samples with a high As concentration, arsenate is still the major species (special study areas of the British Geological Survey, *4*).

Displacement of arsenic by dissolved carbonate is in this paper proposed as an alternative mechanism for the genesis of high arsenic groundwater. To calculate the speciation of trace metals among oxides in contact with river water, soil water, and groundwater (*5*−*11*) and in water treatment (*11*, *12*), surface speciation models are commonly employed. The standard choice incorporated in geochemical models (*13*, *14*) is Dzombak and Morel's (D&M) database (*15*) for metal and anion sorption on ferrihydrite (hydrous ferric oxide, Hfo). Unfortunately, the database does not comprise constants for Fe^{2+} and HCO_3^-. These species often have a high concentration in Bangladesh groundwater and may influence the sorption of arsenic on the sediment.

Sorption of carbonate is well-known to be strong (*16*) and to shift the point of zero charge (PZC), the zeta potential, and the proton buffering capacity of oxides (*17*−*22*). It also affects the sorption of chromate (*23*, *24*) and forms ternary surface complexes with U and Pb (*25*−*27*). Surprisingly, carbonate was found to enhance sorption of sulfate and selenate anions at small concentrations (*28*). Zachara et al. (*23*) have measured carbonate adsorption on ferrihydrite and modeled the data with the triple-layer model (*29*). The total carbon concentration in their experiments was 4.6 μM, which is much smaller than is found in natural waters and, consequently, constants derived from these laboratory data may not be applicable in a model for the natural environment. Van Geen et al. (*24*) and Villalobos and Leckie (*30, 31*) have recently published data on CO_2 sorption on goethite that span a larger concentration range. They modeled the data with the triple-layer model (*29*) and the double-layer model (*15*, *32*).

Sorption constants for Fe^{2+} on ferrihydrite can be estimated to lie in the range of those for Cd^{2+} and Zn^{2+} (*11*). The concentration of Fe^{2+} in anaerobic groundwater may be 1000 times (or more) higher than of these heavy metals, and Fe^{2+} will then dominate the majority of the strong sorption sites. Sorption edges of Fe^{2+} on various iron oxides have also been reported (*33*−*35*) and were fitted with the constant capacitance model by Liger et al. (*35*).

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TABLE 1. Surface Complexation Constants for the Ferrihydrite Double-Layer Model Optimized in This Study[a]

		Carbonate	
$Hfo\_wOH + CO_3^{2-} + H^+$	=	$Hfo\_wOCO_2^- + H_2O$	$\log K = 12.78 \pm 0.48$
$Hfo\_wOH + CO_3^{2-} + 2H^+$	=	$Hfo\_wOCO_2H + H_2O$	$\log K = 20.37 \pm 0.20$
		Fe^{2+}	
$Hfo\_wOH + Fe^{2+}$	=	$Hfo\_wOFe^+ + H^+$	$\log K = -2.98 \pm 0.30$
$Hfo\_wOH + Fe^{2+} + H_2O$	=	$Hfo\_wOFeOH + 2H^+$	$\log K = -11.55 \pm 0.23$
$Hfo\_sOH + Fe^{2+}$	=	$Hfo\_sOFe^+ + H^+$	$\log K = -0.95 \pm 0.5$

[a] Uncertainty interval indicates the approximate 95% confidence limits.

Here, the D&M compatible sorption constants for Fe^{2+} and CO_3^{2-} are determined to extend the applicability of the D&M database. The CO_2 sorption experiments with goethite (*24, 30*) are investigated as a means for validating the proposed extrapolations from the experiments of Zachara et al. Sorption envelopes, calculated with data-optimized and estimated constants, are compared. Example calculations illustrate the important effects of these species on the sorption of Cd, Pb, and As. The relationship between HCO_3^- and As concentrations in groundwater (*1, 36, 37*) is reinvestigated in light of the displacing action of (bi-)carbonate ions for sorbed As on iron oxyhydroxide. An increasing carbonate concentration can significantly enhance As desorption and probably does contribute markedly to observed high As concentrations in Bangladesh groundwater.

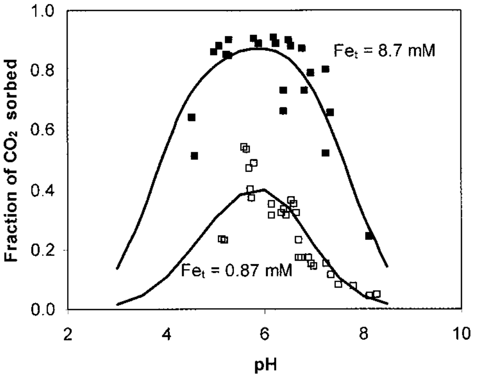

FIGURE 1. Sorption of CO_2 on ferrihydrite in 0.1 N $NaNO_3$. Data points are from Zachara et al. (*23*), lines are from optimized ferrihydrite double-layer model with standard sorption site density, and pK_a values are for ferrihydrite.

Computations

Model fits were optimized with the least squares, nonlinear parameter estimation program PEST (*38*) in combination with PHREEQC-2 (*14*) as illustrated in the Supporting Information. The basic data for the modeling were obtained from tables as published or by digitizing graphs.

Sorption of CO_3^{2-}. Zachara et al. (*23*) measured carbonate adsorption in ferrihydrite suspensions spiked with ^{14}C-labeled $NaHCO_3$ at a concentration of 4.6 μM total carbon, over a pH range of 5.5−9.0. For the model here, the properties of ferrihydrite were defined according to the values proposed by D&M (surface area = 600 m^2/g, pK_{a1} = 7.29, pK_{a2} = 8.93, 0.87 mM Fe = 78 mg of ferrihydrite/L with 0.174 mM sites, for anions only the weak sites are active).

Two complexes were included in the optimization, the uncharged complex Hfo_wOCO_2H and the singly charged complex $Hfo\_wOCO_2^-$, which result from surface-OH ligand-exchange by bicarbonate and carbonate ions, respectively:

$$Hfo\_wOH + CO_3^{2-} + H^+ = Hfo\_wOCO_2^- + H_2O \quad (1)$$

and

$$Hfo\_wOH + CO_3^{2-} + 2H^+ = Hfo\_wOCO_2H + H_2O \quad (2)$$

The combination of these complexes provided a better fit than provided by the uncharged complexes $(SOH_2{-}HCO_3)^0$ and $(SOH{-}H_2CO_3)^0$ (*23*), which are indiscernible in the double-layer model. The optimized constants are listed in Table 1, and the fit is shown in Figure 1. The confidence limits in Table 1 provide only an indication of parameter uncertainty, as they rely on a linearity assumption that may not extend as far in parameter space as the confidence limits themselves. Nevertheless, the smaller 95% confidence interval for the uncharged complex indicates that it is more important for explaining the data. The fit shown in Figure 1 is similar to the one obtained with the triple-layer model (*23*).

The applicability of the derived constants for higher concentrations of total carbon can be tested on experiments with goethite (*24, 30*). Sorption of carbonate species on different iron oxides (goethite and hematite) has been found to be comparable on a *per site* basis (*24*), and also Manceau (*39*) proposes that sorption of oxyanions occurs on structurally similar sites on goethite and ferrihydrite. Van Geen et al. (*24*) measured CO_2 sorption on goethite as a function of pH in an ingenious reaction vessel with tubing for transferring small amounts of headspace gas to a gas chromatograph. Villalobos and Leckie (*30*) repeated the experiments of Van Geen et al., and their experimental data for 63 μM total carbonate are compared in Figure 2a with the ferrihydrite model predictions (constants from Table 1), both expressed as surface coverage in micromoles of carbonate per square meter. The ionic stength effect and the peak values are matched, but the calculated sorption envelopes are shifted by 1 pH unit. The pH shift could be related to the different PZC values of ferrihydrite (PZC = 8.11) and goethite (PZC = 9.1), and the constants were reoptimized, using pK_{a1} = 8.1 and pK_{a2} = 10.1. However, the description remained inadequate. The fit also did not improve when pK_a values were included as variables in the optimization, indicating that the speciation model for carbonate was incorrect.

The triple-layer model fit of the same data greatly improved when Hiemstra and Van Riemsdijk's (*40*) concept of charge distribution was applied (*31*), namely, when the charge of the carbonate complex was distributed over the oxygens at different distances from the surface instead of being condensed in a point charge. Sorption in the triple-layer model is conceived to occur in three layers or planes with different potentials. The 0 plane is located at the surface oxygens of the oxide, and protons and inner-sphere complexes bind there (*32, 41*). The β plane is where the ions from background electrolytes form outer-sphere complexes and where two oxygens of a monodentate bound $\equiv OCO_2^-$ group reside (*31, 40, 42*). Villalobos and Leckie (*31*) attributed almost all of the charge of the $\equiv OCO_2^-$ complex to the β plane instead of the 0 plane. The capacitances of the 0 and β planes were 1.1 and 0.2 F/m^2, respectively (with NaCl as electrolyte, *31*), and the major effect of the charge distribution is that allocating the negative charge of $\equiv OCO_2^-$ to the β plane

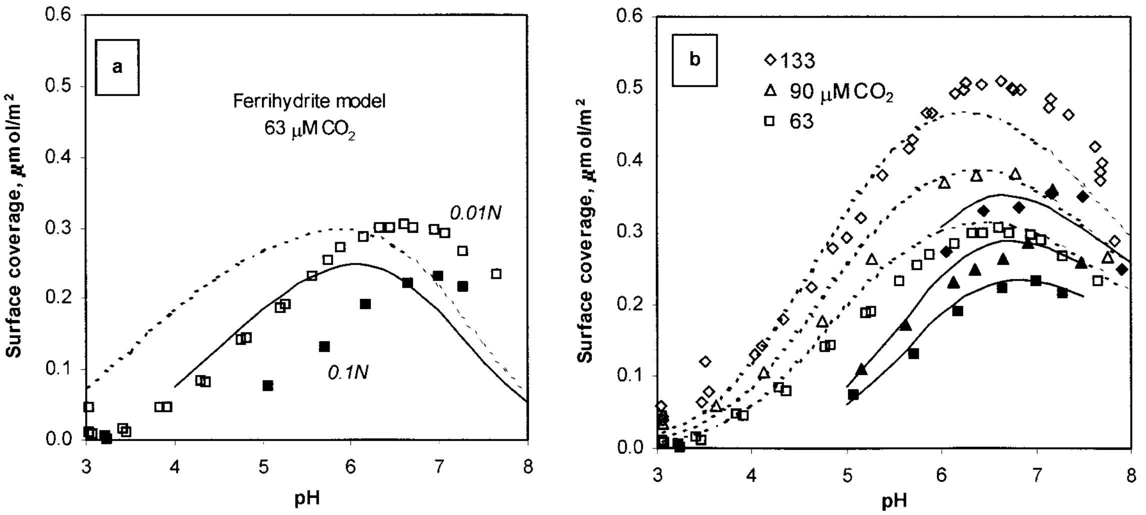

FIGURE 2. Sorption of CO_2 on 2 g of goethite/L in 0.01 N (open symbols, dotted lines) and 0.1 N (solid symbols, full lines) NaCl: (a) ferrihydrite model; (b) optimized goethite double-layer model with doubly charged carbonate complex. Data points are from Villalobos and Leckie (*30*).

TABLE 2. Surface Complexation Constants for Carbonate Sorption in the Goethite Double-Layer Model[a]

closed system, 2 g of goethite/L, 70 m^2/g, $pK_{a1} = 8.1$, $pK_{a2} = 10.1$

$Go\_wOH + CO_3^{2-}$	$= Go\_wOHCO_3^{2-}$	$\log K = 4.78 \pm 0.14$
$Go\_wOH + CO_3^{2-} + 2H^+$	$= Go\_wOCO_2H + H_2O$	$\log K = 20.30 \pm 0.53$

[a] Data from Villalobos and Leckie (*30*). Uncertainty interval indicates the approximate 95% confidence limits.

decreases the potential at the surface 5 times more than attribution of the charge to the 0 plane would do. The resulting lower potential will enhance proton adsorption, and the charge distribution model is helpful for fine-tuning the pH dependence of the sorption envelope.

In the double-layer model, a charge redistribution is not possible because all of the complexing species are placed at the surface. However, the *effect* of charge distribution in the electrostatic model can be simulated by increasing the negative charge on the sorbed carbonate complex, as this will also decrease the surface potential. Thus, in the goethite double-layer model a doubly charged complex was introduced:

$$Go\_wOH + CO_3^{2-} = Go\_wOHOCO_2^{2-} \qquad (3)$$

Go_w represents the sorption site in the goethite double-layer model. This doubly charged complex provided a much better fit than the single-charge surface complex, as is shown in Figure 2b (constants in Table 2). The 95% confidence intervals indicate that the doubly charged complex is the most important. Apparently, the speciations of carbonate on goethite and ferrihydrite are different, a conclusion that was drawn also from the different infrared spectra (*21*). Nevertheless, the performance of the double-layer model in the open system measurements of Villalobos and Leckie (*30*) where total CO_2 concentrations increase to 6 mM may provide a clue to the validity of the model predictions for such high concentrations. Results for the highest CO_2 pressure are presented in Figure 3. The model overestimates sorption by a maximum of 0.3 log unit for pH <5 but improves somewhat at higher pH. For pH >8, and at atmospheric CO_2 pressure, the model was found to underestimate sorption. Villalobos and Leckie invoked sorption of the $NaHCO_3$ complex to explain the observed increase, but this complex has no significant contribution in the double-layer model. Apparently, the double-layer model is less well equipped for modeling CO_2 sorption over a large concentration range than the triple-layer model, and sorption at total carbonate concentrations of natural waters may be incorrect by a factor of ~2 ($=10^{0.3}$).

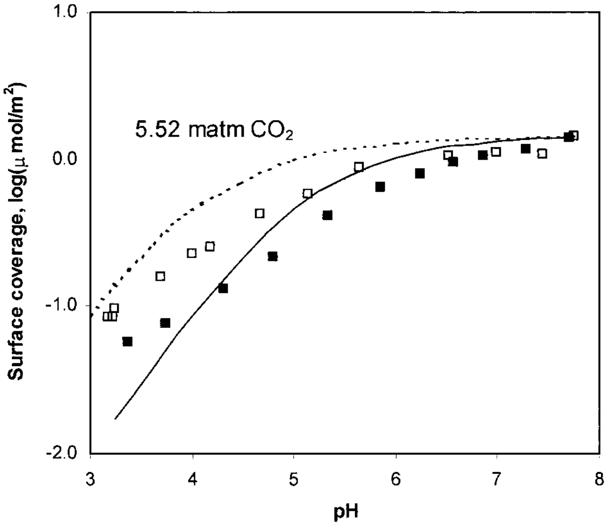

FIGURE 3. Sorption of CO_2 at $P_{CO_2} = 5.52$ matm on 14.7 g of goethite/L in 0.01 N (open symbols, dotted line) and 0.1 N (solid symbols, full line) NaCl. Data points are from Villalobos and Leckie (*30*), and lines are from goethite double-layer model optimized on closed system data (Figure 2b).

Sorption of Fe^{2+}. Liger et al. (*35*) determined sorption of Fe^{2+} on ferrihydrite as a function of pH. They used 0.21 g of ferrihydrite/L with a surface area of 244 m^2/g and a site density of 2.27/nm^2, which gives 0.193 mM sorption sites. The ferrihydrite had $pK_{a1} = 7.70$ and $pK_{a2} = 9.05$ (recalculated from conditional constants for $I = 0.1$ mol/L). The total concentration of Fe^{2+} was 0.16 mM in 0.1 M $NaNO_3$. The

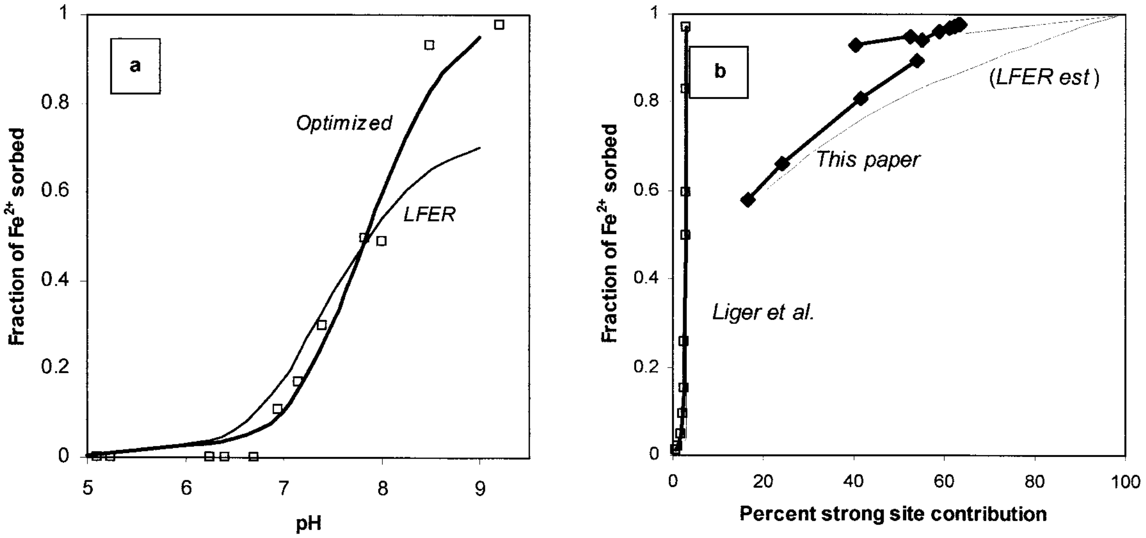

FIGURE 4. Sorption edge of 0.16 mM Fe^{2+} on ferrihydrite in 0.1 N $NaNO_3$, with experimental data from Liger et al. (*35*) (a) and contribution of strong sites on these and new experiments at pH 7.0 with increased concentration of ferrihydrite (b). The full, thick line is for the optimized model, and the thin line is for the model with surface complexation constants estimated with linear free energy relations.

TABLE 3. Results of Experiments at High Hfo/Fe^{2+} Ratio in 0.1 M $NaNO_3$[a]

pH	mM FeOOH	mM Fe^{2+} total	mM Fe^{2+} aqueous
7.10	86.7	0.0074	0.0000
7.10	86.6	0.0120	0.0000
7.08	85.8	0.0397	0.0003
7.05	84.9	0.0678	0.0015
7.01	83.3	0.1240	0.0042
6.94	80.7	0.2155	0.0128
7.01	78.0	0.3059	0.0162
7.01	68.3	0.5880	0.0495
7.19	14.6	0.0267	0.0029
7.08	14.6	0.0885	0.0165
6.97	14.5	0.2430	0.0814
6.92	14.4	0.3980	0.1680

[a] Ferrous iron was added as ferro-sulfate salt. Column labeled "aqueous" gives solute Fe^{2+} after adsorption.

data were modeled (*35*) with the constant capacity model, with two complexes

$$\mathrm{Hfo\_OH} + \mathrm{Fe}^{2+} = \mathrm{Hfo\_OFe}^{+} + \mathrm{H}^{+} \quad (4)$$

and

$$\mathrm{Hfo\_OH} + \mathrm{Fe}^{2+} + \mathrm{H_2O} = \mathrm{Hfo\_OFeOH} + 2\mathrm{H}^{+} \quad (5)$$

for one type of site. The data were fitted to the D&M database with 0.188 mM weak sites and 4.71 μM strong sites, on 0.143 g of ferrihydrite with a surface area of 600 m^2/g. The unidentate, monohydroxy neutral species was included for the weak sites only, in agreement with other species in ref *15*. Initially, the association constant for the strong sites was fixed to $\log K = 0.7$, estimated using LFER (discussed next). However, its value proved to be unimportant in modeling the experimental data of Liger because the contribution of the strong sites to the sorbed concentrations was relatively small. Additional experiments were done at pH 7.0 following the procedures of Liger, but with about 20 or 100 times higher concentration of ferrihydrite and lower concentrations of Fe^{2+} (Table 3). The data did allow for optimization of the surface complexation constant for the strong sites. The concentration of surface sites on the newly prepared ferrihydrite appeared to be different from that of Liger et al. and was included in the optimization, with the ratio of the weak and the strong sites fixed to give 97.5% weak and 2.5% strong sites. The optimized numbers of weak and strong sites for these experiments were 0.21 and 5.4×10^{-3} mol/mol of ferrihydrite, respectively. The data fit is shown by the thick lines in Figure 4, and the constants are noted in Table 1.

Discussion

Estimating Species and Constants with LFER. Dzombak and Morel (*15*) have suggested linear free energy relations (LFER) among surface complexation constants and aqueous hydroxy complexes. The values for Fe^{2+} can be estimated to be for weak and strong sites, respectively

$$\mathrm{Hfo\_wOH} + \mathrm{Fe}^{2+} = \mathrm{Hfo\_wOFe}^{+} + \mathrm{H}^{+}; \quad \log K = -2.5 \quad (6)$$

and

$$\mathrm{Hfo\_sOH} + \mathrm{Fe}^{2+} = \mathrm{Hfo\_sOFe}^{+} + \mathrm{H}^{+}; \quad \log K = 0.7 \quad (7)$$

by interpolation, using the data for Zn^{2+} and Cd^{2+}. The neutral monohydroxy species of eq 5 is not considered by D&M for transition metals. Slightly different *K* values are obtained with the formulas derived for the complete dataset in ref *15*. However, the hydrolysis constant for Fe^{2+} lies between those for Zn^{2+} and Cd^{2+}, and the *K* values based on these ions do provide a quite good estimate for Fe^{2+} sorption when the pH is <8, as is shown in Figure 4a. For pH values >8, the estimated sorption edge levels off because the D&M model does not consider sorption of the hydroxy complex for transition metal ions. Nevertheless, the remarkably good estimate, obtained by LFER with species that are not redox-sensitive, indicates that the sorption edge of Fe^{2+} shown in Figure 4a is due to sorption only and is not influenced by oxidation (*34*). This was further confirmed by desorbing Fe^{2+} at pH 3.0 in the experiments with 14.5 mM ferrihydrite (Table 3).

The strong sites have only a small contribution to the sorption edge in the experiments of Liger et al., and the log *K* for the strong sites was found to be immaterial, as is shown in Figure 4b where the thin line from the LFER estimate coincides with the thick line from the optimized model. In our experiments, the contribution of the strong sites varies from 17 to 63% of the fraction of Fe^{2+} sorbed. From these data, the surface complexation constant for the strong sites

TABLE 4. Effect of Including Carbonate and/or Ferrous Iron Sorption on Dimensionless Distribution Coefficients (K_d) for Heavy Metals among Ferrihydrite and Water

surface coverage (%)		$K_d(-)$			
carbonate	Fe^{2+}	As(III)	As(V)	Cd	Pb
0	0 (no complexes)	22	422	1.0	427
79	0 (carbonate complex)	5	23	0.7	303
0	9 (Fe^{2+} complex)	20	446	0.8	314
78	3 (carbonate + Fe^{2+} complexes)	5	27	0.5	246
61	0 (carbonate complex, low K)[a]	8	86	0.8	372

Water Composition

pH	pe	Ca^{2+}	Fe^{2+}	HCO_3^-	As(III)	As(V)	Cd^{2+}	Pb^{2+}
7.0	−0.21	100	5	315	5×10^{-3}	5×10^{-3}	10^{-3}	10^{-3} mg/L

Ferrihydrite

89 mg/L, weak sites 0.2 mM, strong sites 0.005 mM, surface area 600 m^2/g

[a] log K for carbonate complexes at low end of 95% confidence limit.

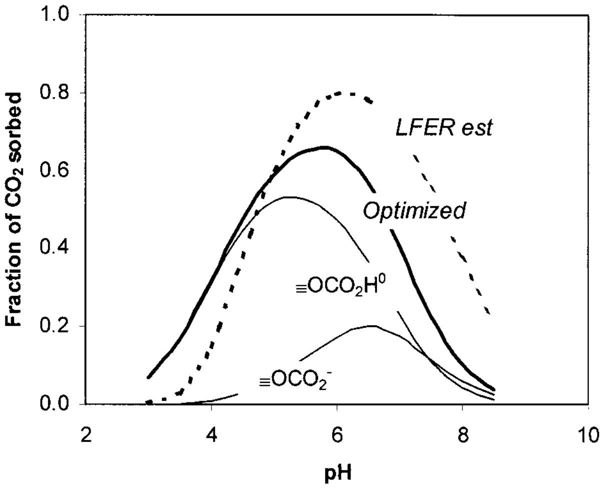

FIGURE 5. Sorption of carbonate species on 0.15 g of ferrihydrite/L in 0.1 N $NaNO_3$ (cf. Figure 1). Full lines are for the ferrihydrite double-layer model, and the dotted line is for the Hfo_wOCO_2^- species with a complexation constant estimated using LFER.

was optimized to log $K = -0.95$, which is much smaller than the LFER estimate.

For anions, D&M suggest a LFER of the surface complexation constant with the second dissociation constant of the acid anion. The estimated constant for the carbonate complex Hfo_wOCO_2^- (reaction 1) is log K = 13.86. The optimized value is log K = 12.78. However, in the optimization, it was necessary to use also an uncharged complex (reaction 2), which D&M reserve for trivalent anions only. The uncharged complex is needed for modeling carbonate sorption at pH <4.5, and it is the dominant complex in the optimized model (Figure 5). With only the single-charge complex, sorbed concentrations are too small at low pH and, conversely, too high at pH 6, where sorption is maximal. However, the overall trend of the sorbed fraction is well followed with the LFER estimated complex (Figure 5).

The binding strengths of the neutral complex are nearly the same for goethite and ferrihydrite in the double-layer model (cf. Tables 1 and 2), and given the nearly identical intrinsic K values for chromate and phosphate in the double-layer models for ferrihydrite and goethite (*43*), one could hope that the double-layer model would have the same intrinsic constants for oxyanions sorbed to any iron oxyhydroxide. However, the doubly charged complex invoked for goethite did not improve the double-layer model for ferrihydrite. The doubly charged complex has the form of an outer-sphere complex (without ligand exchange with the surface hydoxyl), whereas, generally, the oxyanion complexes on goethite are considered to be inner-sphere for carbonate (*21*, *31*) and for As (*42*, *44*, *45*). Contrary to the physical interpretation of charge distribution for carbonate complexation in the triple-layer model, the doubly charged complex in the double-layer model is an artifact that is nevertheless effective for shifting the carbonate sorption maximum to the observed pH because the surface potential is decreased and the proton is removed from the reaction equation (compare reactions 1 and 3).

Effects of Sorption of CO_3^{2-} and Fe^{2+} on Oxyanion and Heavy Metal Adsorption. Van Geen et al. (*24*) and Villalobos and Leckie (*30*, *31*) concluded that carbonate species will cover a large part of the sorption sites of goethite at the CO_2 pressures which are encountered in soil water and groundwater. Anions are supposed to sorb only to the weak sites of ferrihydrite in the D&M database, and carbonate is thus especially important for limiting sorption of oxyanions such as selenate (*28*) and arsenite and arsenate; the effects of ternary complexes of carbonate and metals (*25*, *26*) are here neglected. The importance of Fe^{2+} for modeling sorption of trace metals in anaerobic groundwater is due to the relatively high concentration of Fe^{2+} that will flood the strong sites and thus limit the sorption capacity for other metals. Moreover, sorbed Fe^{2+} catalyzes reduction reactions (*34*, *46*), and it strongly reduces the desorption of other sorbed metals (*34*), but this may be caused by oxidation and occlusion in the precipitate.

An example calculation for a Ca−HCO_3 water type with 5 mg of Fe^{2+}/L and heavy metals at trace concentrations will clarify the effects (Table 4). The sorbed concentrations on 1 mmol of ferrihydrite/L (equivalent to 0.2 and 5×10^{-3} mM weak and strong sites, respectively) were calculated in equilibrium with the groundwater composition given in Table 4, with and without Fe^{2+} and/or carbonate sorption. The dimensionless distribution coefficient K_d (ratio of sorbed and solute concentrations in moles per liter) shows dramatic variation. Including sorption of carbonate reduces the sorption of As(V) almost 20-fold and also reduces the sorption of Cd^{2+} and Pb^{2+} by about one-third because 70% of the weak sites are occupied by carbonate at a groundwater concentration of 315 mg of HCO_3^-/L. Including sorption of Fe^{2+} also reduces the sorption of Cd^{2+} and Pb^{2+} by about one-third. It enhances the sorption of arsenate anions because the surface potential increases. When both Fe(II) and carbonate surface complexes are included, little arsenic and little cadmium may sorb on ferrihydrite. Finally, bringing the constants for carbonate to the lower limit of the estimated

TABLE 5. Model Concentrations of As in Groundwater in Bangladesh, with and without Carbonate Surface Complexes on Ferrihydrite

			μg of As/L	
	Alk, mg of HCO_3^-/L	mg of Fe^{2+}/L	without complex	with complex
A = river water	260	0	1	1
B[a] = (A) + CO_2(g) + calcite + 0.32 mM HFO	471	0	3	150
C[a] = (B) + 0.282 mM C(0)	474	3	35	187

A = River Water Composition

pH	pe	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	As
8.39	12.24	19.3	4	14.1	55.7	9.6	260	4.4	10^{-3} mg/L

[a] B and C are groundwater compositions with reactions (explained in text) imposed on infiltrating river water (A).

95% confidence interval reduces surface coverage by carbonate to 61%. Especially the sorption of arsenate increases again, because surface complexes of arsenate are negatively charged and thus more affected by a negative surface than arsenite, which is sorbed as a neutral species.

The notable effect of HCO_3^- that is concluded here may appear to disagree with experiments of Fuller et al. (*47*) and Meng et al. (*48*), who found a minor effect of HCO_3^- on coprecipitation of As in iron oxyhydroxide. However, the concentration of HCO_3^- in the experiments of Meng et al. (*48*) was obtained from laboratory air and was <0.01 mmol/L, which is 500 times smaller than in the example of Table 3. Fuller et al. (*47*) started with artificial streamwater with 3 mM total inorganic carbon (TIC) but purged it with air at pH 8.0, which should lower the TIC to <0.6 mM. Again, this is an order of magnitude less than is commonly found in groundwater. The small effects on As sorption noted by Wilkie and Hering (*49*) when adding 1 mM $NaHCO_3$ can be predicted well by the model, except for arsenite at pH 6, when desorption is predicted but no effect was observed. Also in this case, it is uncertain whether the actual CO_2 species distribution and concentrations had changed during the pH adjustment in the experiment.

Implications for As Concentrations in Bangladesh and West Bengal Groundwaters. High arsenic concentrations in groundwater are commonly correlated with high HCO_3^- concentrations (*1*, *36*, *37*). The increased HCO_3^- concentrations are usually associated with reducing conditions, under which arsenic takes the form of arsenite, which is less strongly sorbed than arsenate at pH 7 and for concentrations <1 μM As (*49*). Also, iron oxyhydroxide may be reduced and dissolved, which diminishes the sorption capacity of the aquifer (*1*, *37*). However, recent experiments by Kim et al. (*50*) have shown that HCO_3^- by itself is effective in increasing the As concentration in dissolution experiments with pyrite containing rock, under both aerobic and anaerobic conditions. Kim et al. suggested that aqueous $As-HCO_3$ complexes form, which solubilize As. The displacing effect of HCO_3^- for As sorbed to iron oxyhydroxides, which is implied in the present paper, has not been considered so far.

The displacing effect of HCO_3^- may offer an explanation for high As concentrations in Bangladesh groundwater, given that the pH values and alkalinities of river water and groundwater are much different. The river water has a low CO_2 pressure of $10^{-3.0}$ atm and a high pH. The groundwater has a very high alkalinity of 474 mg of HCO_3^-/L (average of the groundwater analyses, *4*), which is related to the high CO_2 pressure of $10^{-1.09}$ atm on average, which develops in the soil at the high temperatures of the area. We can calculate the contribution of the various processes by first equilibrating river water with ferrihydrite. Subsequently, we imagine that river water infiltrates in a levee and gains a high CO_2 pressure of $10^{-1.09}$ atm while equilibrating with calcite and also with the river water-equilibrated ferrihydrite. In a third step, the water encounters organic carbon, which reduces dissolved oxygen and ferrihydrite to give a concentration of 3 mg of Fe^{2+}/L, the average concentration in the groundwater. The reduction of ferrihydrite will liberate the complexed ions in proportion. The river water composition from the BGS database (*4*) was used with 1 μg of As/L and equilibrated initially with 0.32 mmol of ferrihydrite/L. The concentration of ferrihydrite was selected to yield the observed average As concentration in the study areas of the BGS. The D&M surface complexation constants were used for As(III) and As(V), and the surface complexation capacity was coupled to the amount of ferrihydrite in PHREEQC-2 (*14*).

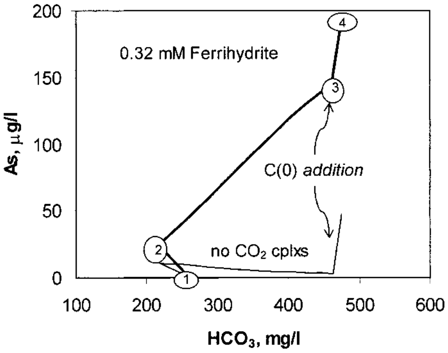

FIGURE 6. Modeled As concentration in Bangladesh groundwater as a function of the HCO_3 concentration with and without surface complexation of carbonate. The numbers on the curve are for (1) river water, (2) river water equilibrated with calcite, (3) after the CO_2 pressure had been increased, and (4) after C(0) had been added, which reduces ferrihydrite and releases As by decreasing the complexation capacity.

The calculations indicate that for the imposed conditions, bicarbonate displaces 147 ppb of As (cf. Table 5). In the river bank, where groundwater is still aerobic, the As concentration is calculated to be 150 ppb, compared with only 3 ppb for the case without carbonate surface complexes (composition B). Decrease of the complexation capacity due to reduction and dissolution of ferrihydrite adds another 37 ppb of As, to give 187 ppb of As (composition C). The latter is close to the average observed As concentration in groundwater (188 ppb in ref *4*). Thus, the high alkalinity, which is primarily a result of a high CO_2 pressure in the soil zone, acts as the major driving force for high As concentrations in these groundwaters, and reduction of arsenic and iron oxyhydroxides and concomitantly of the sorption capacity is not even necessary as was believed until now (*1*−*3*).

The effect of increasing HCO_3^- on the As concentration in Bangladesh groundwaters is graphed in Figure 6. Again, 0.3 mM ferrihydrite was equilibrated with the river water containing 1 μg of As/L. CO_2 was added stepwise while equilibrium was maintained with calcite and ferrihydrite. In the first step, As is released because the pH decreases due to precipitation of calcite (the river water is supersaturated with respect to calcite); this decrease of pH augments sorption of carbonate, which in turn imparts the surface with a negative charge and repels the arsenate anions. In the second step, CO_2 is added, calcite dissolves, and Figure 6 shows the gradual increase of the As concentration when alkalinity increases and As is displaced from ferrihydrite. In the third step C(0) was added to reduce ferrihydrite to give the average Fe^{2+} concentration of 3 mg/L in groundwater, and the As concentration leaps because sorption capacity is lost. On the other hand, the neglect of carbonate complexation decreases the As concentration in water with alkalinity, because sorption of As(V) is enhanced as pH decreases. The small initial increase of the As concentration in step 1 is now related to the redistribution of surface complexes of Mg^{2+} and H^+, which, even though the pH decreases, lowers the surface potential at the ferrihydrite surface. In this case, the As concentration in groundwater increases only when ferrihydrite is reduced in the last step.

It should be noted that carbonate is not the only uniquely determining factor for high As concentrations in Bangladesh groundwater. The first and most important cause is that much arsenic is transported into the area as evidenced by the high As concentrations in river water. The BGS database gives a value of 29 ppb of As, and Kinniburgh (*54*) has found concentrations of 2−10 ppb at other locations and times in the area. Accordingly, the amount of As sorbed to ferrihydrite in the river sediments is high, and much As is available in the aquifers built from these sediments. Phosphate is undoubtedly active in displacing arsenic from the iron oxyhydroxides (*51*, *52*). Including a phosphate concentration of 0.1 mg of PO_4^{3-}/L in river water and increasing it to only 0.13 mg/L in groundwater has the same effect on model results as increasing the CO_2 pressure. Silicate and sulfate may also act as desorbers of As from ferrihydrite (*49*, *53*), but the silicate concentrations are nearly equal in surface waters and groundwaters in the area, and the sulfate concentrations are quite variable. However, the silicate in river water (and also phosphate) may limit the amount of As that is sorbed on riverine iron oxyhydroxide. Furthermore, the concentration of 0.32 mM ferrihydrite was adopted in the calculations to yield approximately the observed arsenic concentration in groundwater. In the sediments, the iron and arsenic concentrations are much higher (*1*, *54*), meaning that only a part of the arsenic is reacting while the major part is fixed, probably in the structure of the iron oxides (*1*, *47*).

Despite these cautions, and although experiments with ferrihydrite and higher total carbonate concentrations are desirable to ascertain the effects of wider concentration variations, an important conclusion is that carbonate complexation must be incorporated in Dzombak and Morel's double-layer model when it is appled to simulate the behavior of trace metals in natural waters. The same conclusion holds for ferrous iron.

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Supporting Information Available

PHREEQC-2 input file for modeling Van Geen et al.'s (*24*) experiments on carbonate sorption on goethite. This material is available free of charge via the Internet at http://pubs.acs.org.

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Arsenic Exposure and Health Effects

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Arsenic Exposure and Health Effects
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Subterranean Removal of Arsenic from Groundwater

U. Rott, M. Friedle

ABSTRACT

In some regions of the world arsenic, as also iron and manganese, is a natural component of the aquifer. In contrast to iron and manganese, which are not very toxic for human beings, arsenic has a high toxicity so that the arsenic contamination of pumped groundwater is affecting the health of millions of people. Much of the total arsenic consists of As(III) which is more toxic than As(V). The maximum admissible concentration for arsenic according to the German guideline for drinking water had been 0.04 mg/L As until 1990. Since then the limit has been 0.01 mg/L As (Rott and Meyerhoff, 1996). In Pabna e.g., a northern district of Bangladesh, a very high arsenic contamination of 14 mg/L was found in the pumped groundwater. In this paper the results of three field studies of large scale plants for *in situ* treatment of groundwater with elevated concentrations of iron, manganese and arsenic are presented. The parameters arsenic and iron, measured in the pumped groundwater, fell below the guideline limits of 0.01 mg/L As and 0.2 mg/L Fe respectively, within the first few treatment cycles. On the other hand, the period of ripening of the manganese removal normally lasts several weeks or months. The reason for the delayed start of the demanganization is the dependence on bacteria which must first adapt to the changed environment. As the duration of treatment continues, the concentration of Mn can fall below the guideline value of 0.05 mg/L. *In situ* treatment of groundwater can be a cost-efficient and reliable alternative for conventional above-ground water treatment. Because of the use of the aquifer as a natural reactor no filter sludge is produced and no above-ground buildings are necessary. In the case of new building or extension of an existing treatment plant, *in situ* processing should always be taken into account.

Keywords: arsenic, iron, manganese, ammonia, water treatment, ground-water supply, *in situ* treatment, groundwater, mobilisation

INTRODUCTION

In connection with the planning of the water supply for three communities in Germany, different variants for the treatment of groundwater with elevated contents of iron, manganese and arsenic are discussed. Field experiments have been conducted from 1994 to the present. The main aim of the experiments that have been carried out by the Institute of Sanitary Engineering, Water Quality and Solid Waste Management of the University of Stuttgart were to prove the transferability of the practical experience with subterranean removal of iron and manganese from groundwater to a similar elimination of arsenic (Rott and Meyerhoff, 1996).

After a short description of the application of *in situ* treatment and the general structure of a treatment plant, the results of field experiments for removal of arsenic under the specific conditions, concerning the raw water quality and the character of the wells and the aquifer, are presented.

METHODOLOGY

By the subterranean removal of iron, manganese and arsenic, the oxidation and filtration processes of conventional above-ground water treatment plants are transferred into the aquifer. Therefore the underground is used as a natural bio-chemical reactor. In this technology, a part of the pumped groundwater is recirculated back into the aquifer carrying an oxidising agent, generally atmospheric oxygen. A simple approach to introduce oxygen into the water is the application of a water jet air pump (Rott and Friedle, 1998).

After the pump, a degasification container is used to purge out the excessive gas. As an alternative, technical oxygen can be used as oxidising agent. Because of the high concentration of technical oxygen, chemical reactions are accelerated compared to air-oxygen.

The oxygen-enriched water is reinfiltrated into the aquifer, using the filter pipes of the production wells. The ratio of the delivered volume and the recharged water volume is called the "efficiency coefficient". This coefficient usually reaches values between 2 and 12, depending on the aquifer- and raw water conditions. The basic configuration of an *in situ* treatment plant is shown in Figure 1.

Figure 2 shows the structure of an *in situ* treatment plant near Paderborn, in the north of Germany. The drinking water supply has a total capacity of about 3.75 Mio. m³/a. The treatment plant consists of four horizontal filter wells with different aquifer characters. The structure of a horizontal filter well is given in Figure 3. In this case horizontal filter wells are used because of the greater yielding capacity of this kind of well. Because of the great distance to the other wells and the enrichment station of more than 4 km, well IV is equipped with its own oxygenation station.

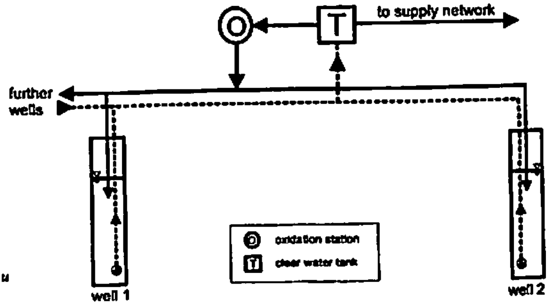
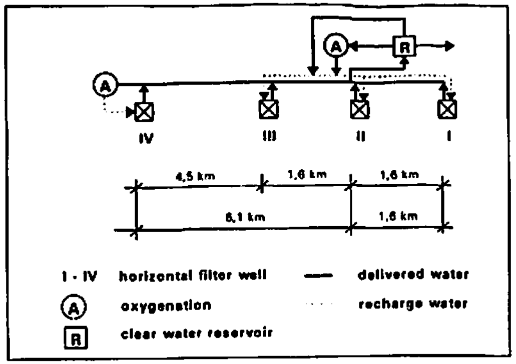


Fig. 1. Basic configuration of an *in situ* treatment plant.

Fig. 2. Scheme of *in situ* plant near Paderborn.



This plant shows that applying *in situ* treatment of groundwater can lower the concentrations of iron, manganese, ammonia, nitrite, nitrate, sulphurhydrogen and organic substances far beyond the drinking water standards. A drinking water supply is thus possible directly from the aquifer without any further above-ground treatment.

Because of the input of oxygen, the redox potential of the water is increased. A number of different physical, chemical and biological processes in the surrounding area of the well screen section, the so-called oxidation-zone, start or are intensified. The alternate operation of the wells for delivering groundwater and infiltration of oxygen-rich water induces alternating oxidation- and adsorption-periods on the surface of the solid material in the aquifer.

During the groundwater delivering period (discharge) Fe(II), Mn(II) and As(III) are adsorbed to the surface of soil grains which are partially coated by previously deposited oxidation products and bacteria. In the following recharge period the bivalent ions are oxidised to relatively insoluble ferric hydroxides and manganese oxides by the oxygen transported with the infiltration water into the pores of the aquifer.

The oxidation processes are accelerated by autocatalytic effects of the oxidation products and by autotrophic micro-organisms utilising energy from the oxidation process. Additionally, dissolved iron and manganese are adsorbed on the bacteria sheaths by the bio-film.

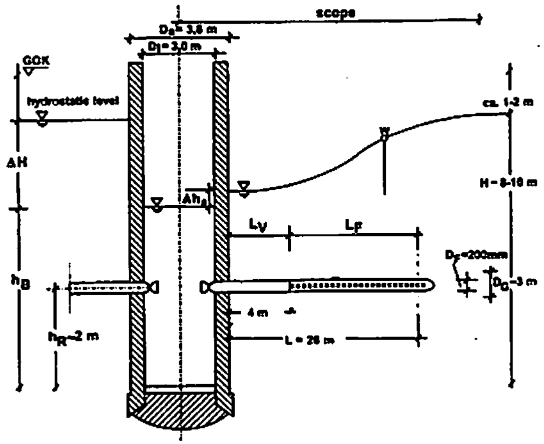


Fig. 3. Structure of a horizontal filter well.

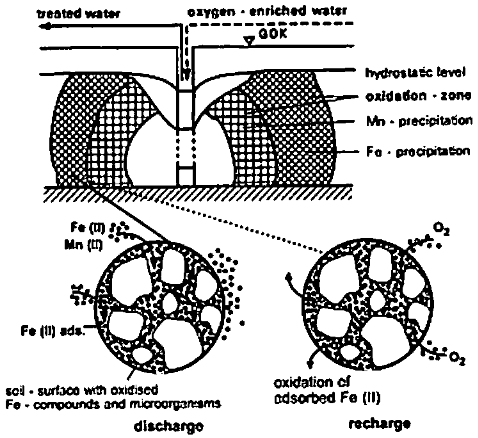


Fig. 4. Scheme of the oxidation zone.

Arsenic(III) requires first an oxidation to Arsenic(V) before it can be precipitated by iron or adsorbed to iron-hydroxide and manganese-oxide, which are known as remarkable adsorbers for arsenic ions. Furthermore, other ions such as cadmium, copper, zinc and other micro-pollutants can be removed (Gulledge and O'Conner, 1973; Pierce and Moore, 1982).

Some specific bacteria are also able to oxidise ammonia in a two step process, the so-called nitrification. This process is very important for the *in situ* treatment, because of the high oxygen-consumption of more than 3.55 mg O_2/mg NH_4^+. Figure 4 shows the oxidation zone and the preparation process of the groundwater.

Because of the different oxidation-reduction potential, the removal of iron and manganese can only take place in spatial isolated regions of the aquifer. An increase of the redox potential from 40 to 160 mV reduces the solubility of iron in water from 10 mg/L to 0.1 mg/L. On the other hand, the stability-range of manganese-oxides starts with a higher pH-value compared to a lower pH-value for iron(III)-hydroxides. This means that the oxidation of manganese requires a higher redox-potential and a higher pH-value, respectively, than the iron oxidation.

The Eh-pH-Diagram for selected chemical combinations which are often part of the aquifer is shown in Figure 5 (Rott and Friedle, 1998).

A great advantage of *in situ* treatment is the retention of the oxidation products of iron, manganese and arsenic. While in above-ground treatment plants voluminous, arsenic-containing sludge is produced, which requires an ecologically compatible and cost-efficient disposal, the oxidation products remain in the aquifer because of subterranean groundwater treatment.

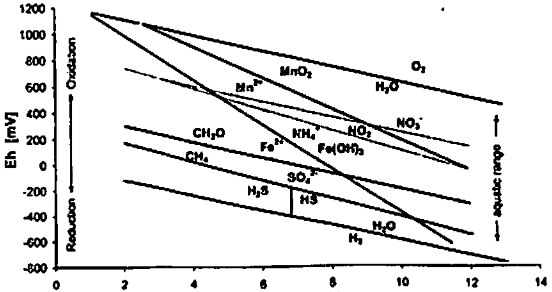


Fig. 5. Eh-pH-Diagram for aquatic systems.

TABLE 1

Raw water quality

Parameter	Raw water (A)	Raw water (B)	Raw water (C)	Guideline limit
Iron: Fe (mg/L)	0.94	1.97	0.94	0.20
Manganese: Mn (mg/L)	0.20	0.35	0.15	0.05
Arsenic (III): As(III) (mg/L)	-	0.024	-	-
Arsenic, total: As (mg/L)	0.015	0.038	0.015	0.010

Although the oxidation products are deposited in the aquifer, a blockage of the underground system does not occur. The first reason is the proportionality of the volume of the oxidation-zone to the volume of the infiltrated water. This means, that the oxidation zone increases with a decreasing pore volume. The second reason is the deposit of the oxidation products in so-called "dead-end-pores" and the aging of the voluminous hydrous hydroxides to less voluminous oxides and oxide hydrates. Last but not least, the reduction of chemical iron combinations decreases because of the application of *in situ* treatment.

RESULTS

The initial parameters of the raw water quality found in the three case studies are shown in Table 1. In all three cases the raw water was almost free of oxygen.

Treatment Results of Plant A

The processing aim of the field experiment was a permanent falling short of the parameters iron, manganese and arsenic below the valid guideline limits. The limiting values for drinking water are 0.2 mg/L Fe, 0.05 mg/L Mn and 0.01 mg/L As.

The scheme of Plant A is shown in Figure 6. In this case of application, groundwater from well 1 is enriched with air oxygen and infiltrated into well 2.

Well 2 has a depth of ca. 115 m and consists of four filter pipes with a common length of about 50 m. The aquifer at the well location is fissured. In spite of these bad ancillary conditions, very good treatment results could be achieved. The treatment results of the experiment are given in Figure 7. As the illustration shows, the removal of iron, manganese and arsenic began within the first few treatment cycles. One cycle consists of a recharge and

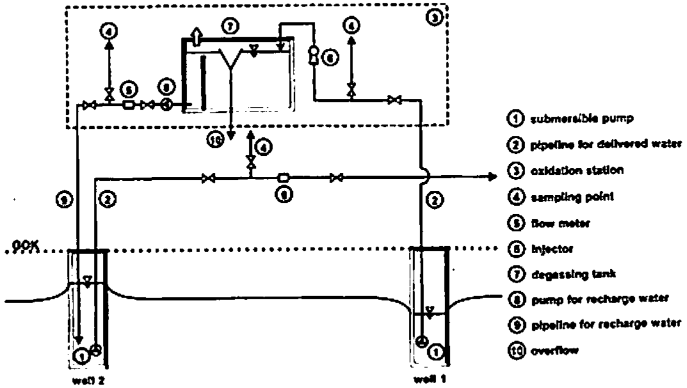


Fig. 6. Scheme of Plant A.

delivery period and two short pauses of ca. 30 minutes between the two phases. The iron concentration fell below the limit value of 0.2 mg/L after three days of treatment, while the arsenic concentration of the delivered groundwater had already decreased below the guideline limit of 0.01 mg/L As after the first infiltration of oxygen-enriched water.

The results of the arsenic elimination are in a close relation to the removal of iron, because iron(II) and iron(III) is known as an excellent floccing agent for arsenic. The increased iron concentrations between a total delivery volume of ca. 22,000 and 24,000 m³ are explicable with an entry of ferrous particles which are detached from the filter pipe of the well when the submersible pump was activated.

Contrary to expectations, the removal of manganese also started within the first treatment cycle and reached ca. 50% of the raw water concentration at the end of the field experiment. It can be assumed that the treatment results improve with a further application of *in situ* treatment.

To investigate a potential remobilization of the deposited arsenic oxidation products precipitated in the aquifer as ferric arsenate ($FeAsO_4$) or As(V) adsorbed to ferric and manganese-hydroxides, the experiment at plant A was terminated with a kind of "crash test", which means a continuous delivery was realised for four weeks without any infiltration of oxygen-rich water. The discharge time of about one month can also be expressed in the form of the efficiency coefficient of 23 as in Figure 8 (Rott and Friedle, 1998).

Whereas the manganese concentration increased immediately because of remobilization of manganese hydroxides or -oxides, the concentrations of iron and arsenic were nearly constant over the total delivery time. This result verifies the assumption of a high adsorption capacity in the oxidation zone for Fe(II) and As(V) with the consequence of a stable operation of *in situ* treatment for the removal of iron and arsenic (Rott and Meyerhoff, 1996).

Treatment Results of Plant B

As generally shown in Figure 1, Plant B consists of two wells of 5" diameter which are operated alternately for production and recharge with a flow of 3 L/s. A complete oxidation from As(III) to As(V) was obtained within the first few days of treatment. Figure 9 shows the total arsenic and iron concentrations always at the end of the delivery periods.

Corresponding to the removal of iron, the arsenic concentration decreased after several cycles of the *in situ* treatment. After approximately 20 treatment cycles the arsenic concentrations were continuously lower than the guideline limit of 0.01 mg/L (Rott and Meyerhoff, 1996).

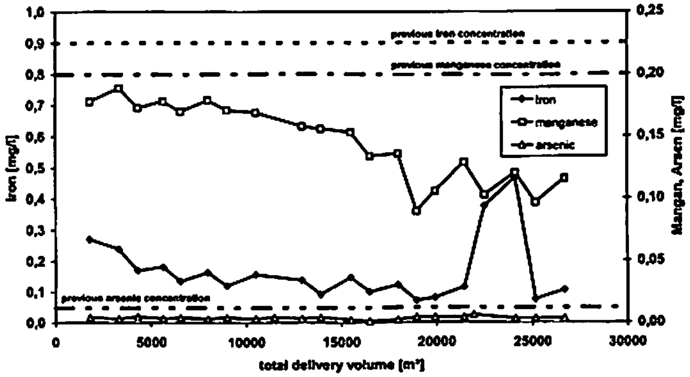


Fig. 7. Iron, manganese and arsenic in dependence of the delivery volume.

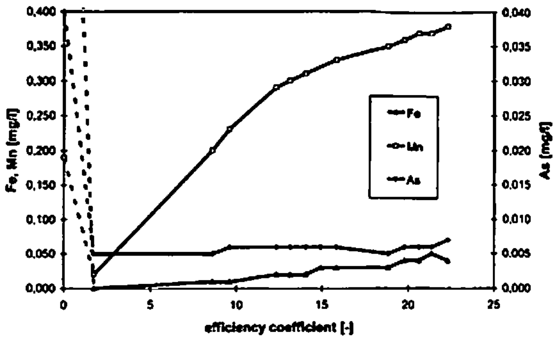


Fig. 8. As, Fe and Mn in delivered groundwater of plant A (long-term experiment).

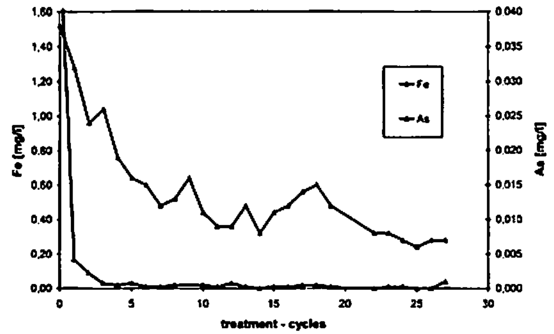


Fig. 9. Iron and arsenic concentrations at the end of the delivery period.

Treatment Results of Plant C

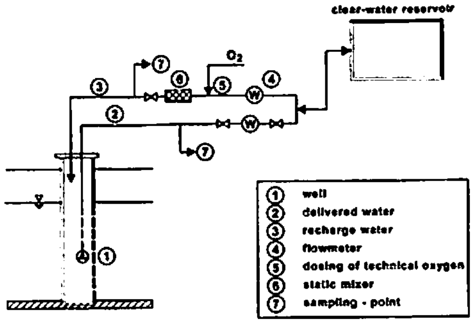
In the third case (Plant C) the application of *in situ* treatment is different to the generally normal technique represented in Fig. 10 because the experiment is practised with only one well. The infiltration water is taken from a clear water reservoir by gravity and is recharged by technical oxygen with a concentration of 12 mg/L. The water flows into the well by the natural hydrostatic pressure. Because of that, there are no additional energy costs for pumping. This technique variant requires a sufficiently sized drinking water tank for the provision of the enrichment water. Furthermore the delivery of drinking water is only possible from the reservoir during the infiltration phases.

As described in the second example (Plant B) the oxidation of arsenic(III) also took place in the first days of treatment, comparable with the removal of iron. Simultaneously to the removal of iron, the arsenic concentrations decrease from the beginning of *in situ* treatment. After 16 treatment cycles the arsenic values reached the guideline limit of 0.01 mg/L with deviation of ± 0.005 mg/L. After the starting period of some weeks, this plant was operated with recharge water from the reservoir and oxygen from the air only.

DISCUSSION

The three examples demonstrate the capability of *in situ* treatment. All field experiments which have been carried out by the Institute of Sanitary Engineering, Water Quality and Solid Waste Management achieved very good treatment results. While the removal of iron and arsenic normally starts after a few treatment cycles, the removal of manganese requires several weeks or months. The delayed beginning of the manganese removal is due to the

Fig. 10. Scheme of Plant C.



adjustment time of the micro-organisms which have to adapt to the varied surrounding conditions. However, it is confirmed that the removal of manganese and other oxidable substances improves with an increasing duration of *in situ* treatment and that by applying this method, drinking water can be supplied directly from the aquifer without any further above-ground treatment.

In order to obtain further findings of the chemical and biological mechanisms of *in situ* treatment a current research project titled "Analysis of physical, chemical and microbiological processes in order to optimise *in situ* treatment of reduced groundwater" is being carried out at the Institute of Sanitary Engineering, Water Quality and Solid Waste Management of the University of Stuttgart.

CONCLUSIONS

Assuming appropriate hydrogeological and geochemical conditions, *in situ* treatment using oxygen as the only reagent can be an alternative low-cost technique for drinking water treatment. The technique of subterranean treatment can be used for the removal of iron, manganese, arsenic, ammonia and organic substances. *In situ* treatment makes use of the aquifer as a natural reactor for physical, chemical and microbiological processes. In comparison to conventional treatment processes such as filtration and flocculation, *in situ* processes are often less expensive, both in investment and operating costs. In addition, wells and submersible pumps are protected against encrustations of ferric and manganese hydroxides and oxides (Rott and Meyerhoff, 1996). A great advantage of *in situ* treatment is the avoidance of any waste products and the resulting disposal problems as well as the use of only natural reactions without any treatment chemicals.

How far the described positive findings can be transferred to other habitats with differing aquifer- and raw water characteristics, particularly with different pH-values or iron-, manganese- and arsenic-concentrations, has to be checked with comparative field tests before a full-scale plant is built.

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Arsenic Exposure and Health Effects
W.R. Chappell, C.O. Abernathy and R.L. Calderon (Editors)

Mode of Action Studies for Assessing Carcinogenic Risks Posed by Inorganic Arsenic

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Janice W. Yager

ABSTRACT

Mode of action (MOA) is emphasized as a unifying concept in new U.S. EPA carcinogen risk assessment guidelines. Optimally, MOA hypotheses relate carcinogenicity to obligatory precursor effects, link cancer and non-cancer responses through common pathways, and predict dose–response relationships via biologically-based dose–response (BBDR) models. Inorganic arsenic (As_i) increases skin lesions, cardiovascular disease, and several types of cancers in humans. The MOA or MOAs for As_i toxicity/carcinogenicity is poorly understood. Multiple effects may be idiosyncratic, each with a distinct MOA. Alternatively, only a limited number of precursor steps may be involved in all tissues. This paper outlines proposed MOAs of As_i carcinogenesis—impaired DNA repair, altered DNA methylation, increased growth factor synthesis, and increased oxidative stress. Increasingly, MOA hypotheses are suggesting that concentrations of critical gene products, including growth factors, redox-sensitive proteins, and DNA repair/DNA methylating enzymes, may be altered by As_i. These alterations would enhance tumor promotion or progression. A potential MOA for As_i acting as a late-stage tumor progressor is evaluated in relation to specific data needs for an As_i risk assessment and to the development of a BBDR model for As_i-induced internal tumors in humans. MOA studies of transcriptional processes, measurements of As_i dosimetry in humans, and dose–response evaluations for precursor endpoints appear important for supporting public health decisions about the risks posed by human As_i exposures. Studies of the transcriptional/post-translational activities of arsenite and metabolites are likely to prove especially valuable for both cancer and non-cancer risk assessments.

Keywords: mode of action, arsenic carcinogenesis, BBDR modeling, tumor progression, cancer risk assessment

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In situ arsenic removal in an alkaline clastic aquifer

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Abstract

In situ removal of As from ground water used for water supply has been accomplished elsewhere in circum-neutral ground water containing high dissolved Fe(II) concentrations. The objective of this study was to evaluate in situ As ground-water treatment approaches in alkaline ground-water ($pH > 8$) that contains low dissolved Fe (<a few tens of μg/L). The low dissolved Fe content limits development of significant Fe-oxide and the high-pH limits As adsorption onto Fe-oxide. The chemistries of ground water in the two aquifers studied are similar except for the inorganic As species. Although total inorganic As concentrations were similar, one aquifer has dominantly aqueous As(III) and the other has mostly As(V). Dissolved O_2, Fe(II), and HCl were added to water and injected into the two aquifers to form Fe-oxide and lower the pH to remove As. Cycles of injection and withdrawal involved varying Fe(II) concentrations in the injectate. The As concentrations in water withdrawn from the two aquifers were as low as 1 and 6 μg/L, with greater As removal from the aquifer containing As(V). However, Fe and Mn concentrations increased to levels greater than US drinking water standards during some of the withdrawal periods. A balance between As removal and maintenance of low Fe and Mn concentrations may be a design consideration if this approach is used for public-supply systems. The ability to lower As concentrations in situ in high-pH ground water should have broad applicability because similar high-As ground water is present in many parts of the world.

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1. Introduction

In some geochemical conditions, dissolved As concentrations in ground water can be lowered by introducing O_2-rich water, reducing pH, increasing anion adsorption capacity of aquifer materials, or, some combination of these approaches. Adsorption or co-precipitation of As on Fe-oxides has been cited as a concentration-limiting process in ground water (see Matisoff et al., 1982; Robertson, 1989; Welch et al., 2003 among others). Adsorption of As onto Fe-oxide is affected by a variety of factors, including pH with high-pH conditions limiting adsorption of As and other anions. Introducing dissolved O_2 into ground water with high dissolved Fe(II) concentrations leads to formation of Fe-oxide (Appelo and deVet, 2003; Appelo et al., 1999; Meyerhoff and Rott, 1997; Rott and Friedle, 1999; Rott et al., 1996); thereby, increasing the

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adsorption capacity of an aquifer. Where dissolved Fe(II) concentrations are low, injection of Fe(II) and O_2 is an alternative approach for in situ removal of As. In alkaline aquifers lowering of the pH has been used to enhance As removal (Welch et al., 2003).

The concept of in situ remediation of Fe(II) has been practiced in Europe for decades where concentrations are lowered through introduction of atmospheric O_2 to Fe(II)-rich water (Hallberg and Martinell, 1976). The process is commonly cyclic, with a period of injection followed by a period of pumping. Along with lowering of Fe(II) concentrations, lowered concentrations of other inorganic constituents including Mn and As has been accomplished. The efficiency of removal has been noted to increase after continued cycles (Appelo and deVet, 2003; Rott and Friedle, 1999). In addition, even after operation of such systems for decades, clogging of wells or aquifer materials has not been reported (Appelo et al., 1999, 2002).

Methods for reducing As concentrations in high-pH ground water could have wide application because alkaline, high-As ground water is present in many parts of the United States (Focazio et al., 2000; Welch et al., 1988, 2000) and elsewhere, such as Argentina (Bundschuh et al., 2004; Smedley et al., 2002, 2005).

The present approach expands upon work of previous investigators that have described in situ As removal in aquifers containing naturally high-As and Fe(II) concentrations (Appelo and deVet, 2003; Appelo et al., 1999; Meyerhoff and Rott, 1997; Rott and Friedle, 1999; Rott et al., 1996). Because in situ As removal has not been widely adopted, it is appropriate to discuss some of the commonly expressed concerns with this approach. Among the concerns that seem to be more often expressed are:

1. Arsenic accumulates in the subsurface will reach unacceptably high concentrations in aquifer materials.
2. Increasing the Fe-oxide content of an aquifer will result in lowered yields from production wells.
3. Concentrations of As or other trace elements will increase in the ground water to values greater than before the removal efforts.

The first two issues are, at least in part, related to the amount of As and Fe that would be added to some volume of an aquifer. Current understanding of the fate of Fe entering an aquifer during in situ removal indicates that Fe-oxide is not concentrated near a well bore, but rather moves some distance out into an aquifer. This understanding is based on geochemical modeling of the reactions that result in the formation of the Fe-oxide (Appelo and deVet, 2003; Appelo et al., 1999), examination of aquifer material that has been affected by in situ removal for decades (Mettler, 2002; Mettler et al., 2001), and the observation that well yields have not been lowered (Mettler et al., 2001; Rott and Friedle, 1999 and references therein). Additionally, the volume of Fe and As removed are small compared with the volume of an aquifer that is likely to be affected. For instance, the aquifers within a 61 m (200 foot) radius surrounding a municipal well used in the experiments described below (well SAP#1) contain about 2.4×10^9 kg of sediment (this assumes: (1) a density of 2.6 gm/cc, which is the approximate density of quartz and feldspar, (2) a porosity of 0.3, and (3) an aquifer thickness of 111 m (364 feet), as indicated by the drilling log for South Airport well 1). The amount of Fe that would be added from the injection of water from the aquifer for a period of 100 a would be about 0.01% of this mass (assumes: (1) a flow rate of 3785 L/min, and (2) a concentration of 3.4 mg/L as indicated in Table 1). Iron added to aquifers during in situ remediation is largely associated with fine grained sediment indicating that treatments in higher permeability, coarser zones are less likely to have any significant reduction in permeability. This small amount of mass compared with the aquifer mass in the vicinity of a production well, and reported case histories of Fe in situ removal that have operated for decades lead to the conclusion that a significantly lowered hydraulic conductivity as a result of treatment is unlikely.

The amount of As added to the same volume would be much less than the amount of Fe added. Assuming complete removal of 36 μg/L (the maximum concentration in Table 1), the amount of As added would increase the As concentration in the sediment by about 15% (assumes an As content of the sediment equal to the geometric mean for the United States of 5.2 ppm for surficial sediments, Shacklette and Boerngen, 1984). This increase is expected to be incorporated in Fe-oxide, which becomes less soluble over time because of recrystallization, which has been observed over the time scales of in situ removal projects (Mettler et al., 2001). Laboratory experiments show that As is not

Table 1
Ambient geochemical conditions

	Units	EXP-2			SAP#1
		Shallow	Middle	Deep	
O_2	mg/L	0.2	0.2	0.2	0.2
pH		8.38	8.47	8.68	8.77
Ca	mg/L	25	30	16	14
Na	mg/L	35	34	38	38
Mg	mg/L	1.9	2.2	0.1	0.4
K	mg/L	1.5	1.4	0.9	1.0
Alkalinity, as $CaCO_3$	mg/L	93	99	73	75
Cl	mg/L	7.5	6.6	6.0	5.8
SiO_2	mg/L	36	26	42	36
SO_4	mg/L	30	33	30	28
P	mg/L	<0.01	0.01	0.01	0.01
As(V)	μg/L	27	17	2.6	0.9
As	μg/L	30	31	36	31
As(III)	μg/L	<0.6	9.5	29	29
Fe	μg/L	<6	<6	<6	<6
Mn	μg/L	36	12	17	8.4
DMA	μg/L	<0.6	0.5	1.1	1.0
MMA	μg/L	<1.2	<1.2	<1.2	<1.2

expelled during recrystallization of Fe-oxide (Ford, 2002). Because As is more tightly bound in these recrystallization products, release would be expected to be slow or insignificant.

A series of experiments were conducted to evaluate Fe-oxide in situ removal of As from alkaline ground water. The field experiment is located in an area that could be developed into a well field to replace water supplied by other wells that produce high-As ground water elsewhere in the northern part of Carson Valley. Arsenic concentrations in ground water beneath Carson Valley in the western USA are variable but commonly exceed the 10 μg/L US EPA drinking water standard (Fig. 1). Locally, high-As concentrations are present in alkaline ground water; the pH of the ground water at the locations shown in Fig. 1 that exceed the As standard ranges from 7.6 to 9.1.

2. Experimental methods

2.1. Field and laboratory methods

Ground-water samples were collected from 4 wells prior to conducting injection experiments. The wells include a public-supply well (South Airport well 1 – referred to here as SAP#1) and 3 nested 5 cm (inside diameter) wells (EXP-2 shallow, middle and deep) located about 490 m east of SAP#1. The EXP-2 wells were drilled to depths of 38, 62 and 99 m and fitted with 6.2 m screens at the bottom (Bugenig, 2003). The aquifer tapped by the 38 m EXP-2 shallow well is referred to as the shallow aquifer whereas the aquifer tapped by EXP-2 middle and deep wells and SAP#1 is referred to as the deep aquifer. Geochemical data for these sites are given in Table 1.

Measurements of temperature, specific conductance, pH, and dissolved O_2 were made in a flow-through chamber. During most injection experiments, temperature, specific conductance, pH, and dissolved O_2 data were recorded every 30 s. Field meters were calibrated daily. Chlorine was measured on site by colorimetry using *N*,*N*-diethyl-*p*-phenylenediamine (Franson, 1995). Iron was measured on site for the purpose of monitoring injection concentrations with a spectrophotometer using the phenanthroline method (Clesceri et al., 1998) although reported concentrations represent laboratory determinations using methods described below.

Laboratory analysis utilized ICP-MS (Lamothe et al., 2002) for Ca, Mg, K, Na, SiO_2, SO_4, P, As and Fe on filtered samples acidified with ultra pure HNO_3 to a pH of about two in the field. Chloride was determined using anion chromatography (Fishman, 1993). Filtered samples were collected by passing the water through a 0.45 μm pore-size capsule filter. Inorganic and organic As species were preserved in the field with EDTA, chilled and kept in the dark and then analyzed by John Garbarino using ICP-MS as described by Garbarino et al. (2002). Alkalinity was measured in the laboratory on filtered, chilled samples using an incremental titration (Wilde and Radtke, 1998). The sum of the As species tends to indicate slightly lower As concentrations compared with total As determined by ICP-MS (Fig. 2). Unless otherwise indicated, As concentrations discussed herein refer to values determined using methods described by Lamothe et al. (2002).

Field experiments included 12 cycles of injection into and withdrawal from the deep aquifer and 7 cycles in the shallow aquifer. These cycles are designated D1 through D12 and S1 through S7 for the deep and shallow experiments, respectively. Bucket and stop-watch measurements of injection rates were made prior to and after injection, and at various intervals during withdrawal. Injection rates were not varied during injection and measured rates of water pumped to waste before and after injection were generally very similar. Static water levels were

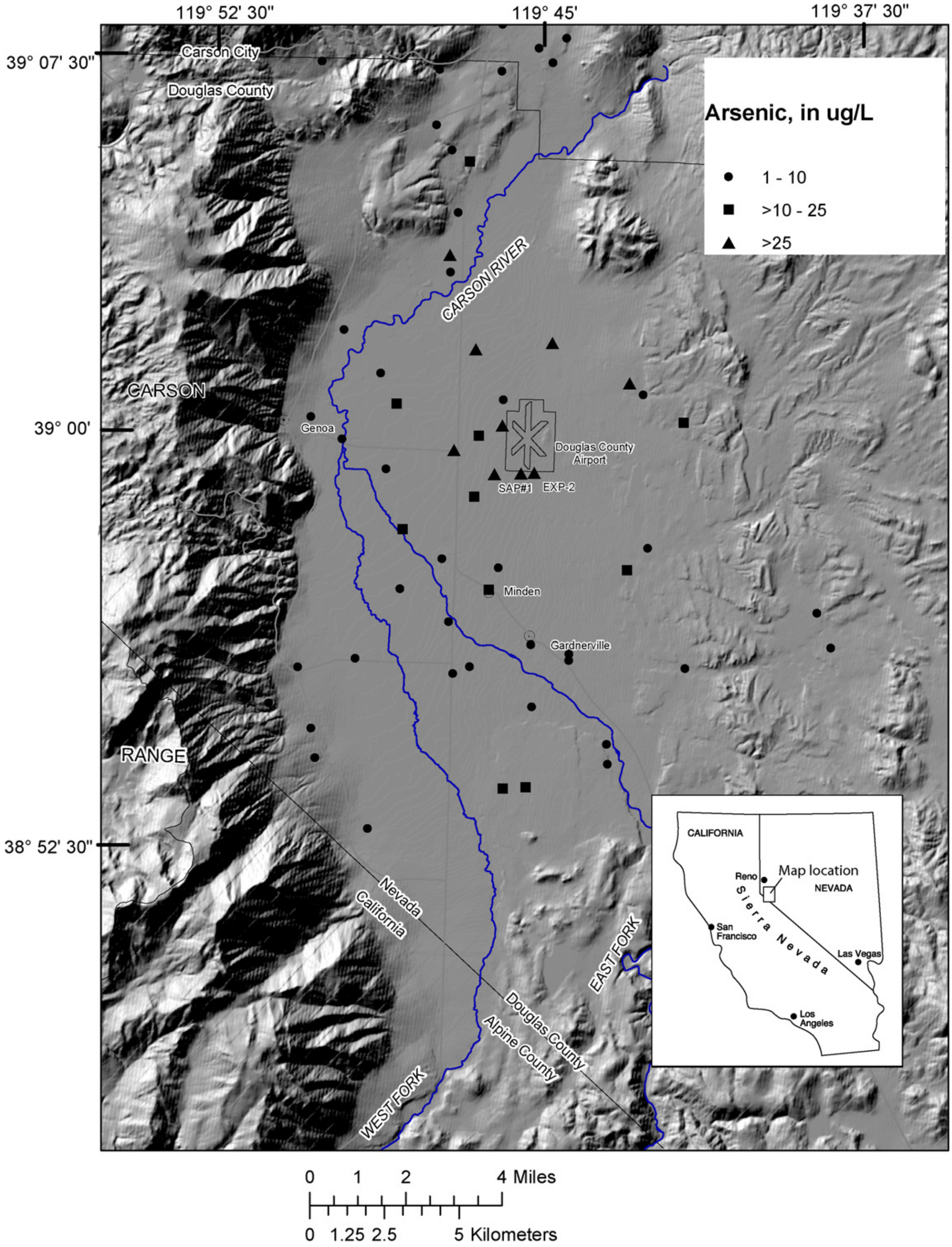

Fig. 1. Location of wells used in the As removal experiment and As concentrations in ground water tapped by wells with depths >30 m in Carson Valley, NV, USA.

measured each day of testing in the EXP-2 shallow and deep wells prior to injection and withdrawal. However, cascading water made accurate water-level measurements problematic during injection. Water levels during injection generally stabilized quickly to a level of ∼0.6 m below land surface.

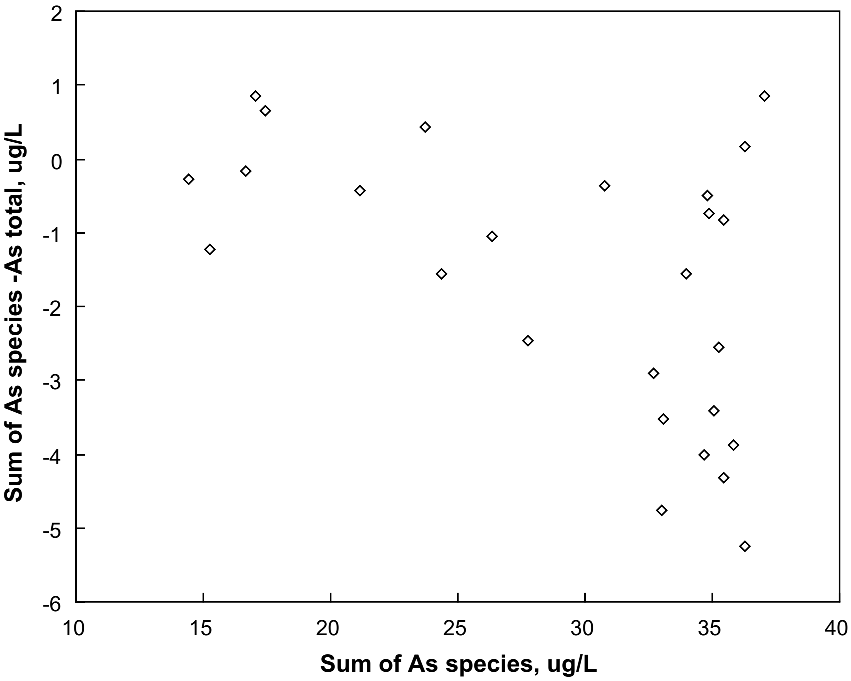

Fig. 2. Difference between the sum of As species [As(III) + As(V) + DMA] and total As.

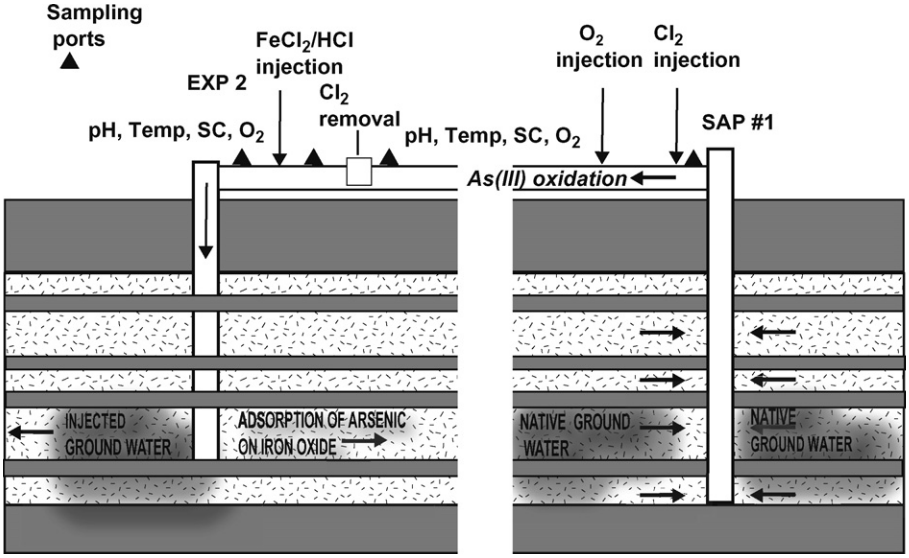

Fig. 3. Schematic diagram of injection scheme. This depiction does not represent subsurface conditions at the experiment site but is intended to broadly represent a sequence of aquifers and confining units. The vertical break between the blocks represents the distance between the well locations.

Water levels were measured at various intervals during withdrawal from the injection wells and were generally about 12 m below land surface in the deep well and about 8 m below land surface in the shallow well. After withdrawal, water levels in both wells recovered to near static after about 2 h; about

7 and 10 m below land surface in the shallow and deep wells, respectively. Water-level measurements were not made in SAP#1.

Water pumped from SAP#1 was piped about 0.5 km to the EXP-2 wells. Prior to injection the water was altered in several ways (Fig. 3). Chlorine was injected at SAP#1 and then removed by activated charcoal near the EXP-2 wells. The Cl_2 was removed prior to injection to minimize the production of any undesirable disinfection by-products. Chlorine addition is desirable because it rapidly converts As(III) to As(V) (Ghurye and Clifford, 2001). The residence time from injection to removal was about 10 min greater than the expected time for nearly complete oxidation of As(III) of less than a minute based on laboratory experiments (Ghurye and Clifford, 2001). Air was injected through a diffuser near the SAP#1 well for the purpose of increasing dissolved O_2. In-line valves were used near the EXP-2 wells to remove most excess air. Just prior to injection, HCl and $FeCl_2$ were added to lower the pH and increase the Fe(II) content. The treated water was injected into the deep (screened 93–99 m) and shallow (screened 32–38 m) wells. Finally, water was pumped from the EXP-2 wells some time later, generally about one hour. Injection rates and withdrawal rates were both about 20 Lpm.

For each experiment, weighed bottles of HCl acid and $FeCl_2$ of known concentration were used to supply injection solutions. The remaining solution and bottles were re-weighed to determine the amounts of HCl and $FeCl_2$ injected in each cycle during the experiments. The solutions were injected into the flow-line using peristaltic pumps. For most cycles, injection of solutions was halted 5 (for the shallow well) to 10 min (for the deep well) prior to the end of injection to flush the treated water from the well casing and into the aquifer.

3. Hydrology and geochemistry of the aquifer

3.1. Hydrologic and geochemical setting

Carson Valley is an alluvial basin that encompasses about 93,000 ha, in northwestern Nevada, USA (Fig. 1). The valley lies in the rain shadow of the Carson Range portion of the Sierra Nevada that bounds the valley on the west; the valley floor received only an average annual about 200 mm of precipitation during the period 1970–2000 (Maurer and Halford, 2004). The hydrology of Carson Valley is dominated by flow of the Carson River. Flow of the river is diverted through natural channels and a network of ditches to irrigate mainly alfalfa and native grasses. The site of the experiments is on the eastern side of the valley floor in an area of native vegetation consisting of rabbitbrush and greasewood.

Infiltration losses from the Carson River and irrigation ditches maintains a shallow depth to water of less than 1.5 m below land surface over much of the floor of Carson Valley. In the EXP-2 wells, depth to water varies annually in response to summer pumping of SAP#1. In early spring, depth to water in the shallow well is about 4 m below land surface, declining to about 9 m in late summer. An upward hydraulic gradient at the site is indicated by higher water levels with increasing depth of the EXP-2 wells. In the deep well, depth to water varies from about 1.6 m below land surface in early spring, declining to about 8 m in late summer. Water-level altitudes indicate that the local ground-water flow direction is toward the NW (Maurer, 1986).

Based on driller's and electric logs, aquifer materials consist of layers of sand and gravel from 3 to 30 m thick alternating with layers of clay and sandy clay of similar thickness. Sand and gravel layers generally correspond to the screened intervals of the EXP-2 wells from 30 to 40 m, 60 to 70 m, and 85 to 100 m. A sand and gravel layer 30 m thick was encountered from 80 to 115 m in depth at SAP#1. Sediment color, which provides an indication of redox state, was described as (1) 0–30 m – yellowish brown and light olive brown, (2) 32–52 m – interbedded greenish grey, light olive brown, and brown clay, and (3) 58–110 m – green, greenish grey and black. These colors indicate that Fe-oxide is present at depths of up to 58 m but absent below that depth. The age of the sediments has not been determined, but based on several assumptions regarding rate of uplift and other factors, the rate of sedimentation is estimated to be between 0.2 and 0.5 mm/a (Alan Ramelli, Nevada Bureau of Mines and Geology, 2007 pers, comm.). Using these rates, the estimated age of the sediments in well EXP-2 deep is about 200–500 ka.

Pumping from well SAP#1 and water-level changes in the EXP-2 wells during the period from January 1, 2005 to December 31, 2005 were interpreted as an aquifer test. Results of the aquifer test indicated the aggregate transmissivity of aquifer materials is about 680 m^2/d, the hydraulic conductivity of sand and gravel layers is as great as 9 m/d, the hydraulic conductivity of clay layers is as little as 0.0001 m/d, and the vertical-to-horizontal anisotropy is about 0.2.

Based on the hydraulic characteristics of the site and assuming a 6-m thick injectate zone, which is about the length of the well screens used in the EXP-2 well, the injected volumes of water could form cylinders around the screens that range from 1.2 to 2.4 m in diameter. Lateral displacement of the injectate was less than 0.1 m during a cycle, assuming the vertical migration of the injectate was limited by a vertical-to-horizontal anisotropy of 0.2. The interbedded silts and clays create more dispersion along the perimeter of the injectate zones (Vacher et al., 2006).

3.2. Initial geochemical conditions

The aqueous chemistry and geochemical processes occurring in the ground water of Carson Valley have been described by Welch (1994). Briefly, the ground water is generally of good quality from the standpoint of human consumption with the exception of high-As concentrations, particularly beneath the northern part of the valley (Fig. 1). The major element chemistry has been attributed largely to dissolution of minerals derived from granitic rocks present in the Sierra Nevada that bound the valley to the west. Calcite dissolution also appears to contribute to the observed water chemistry (Welch, 1994).

The aqueous geochemistry of ground water tapped by the 3 EXP-2 wells and SAP#1 is similar (Table 1), with the notable exception of the As species. The ground water is distinctly alkaline (pH ⩾ 8.4). Inorganic As concentrations range from 30 to 36 μg/L, which is much greater than the US EPA drinking water standard of 10 μg/L (Federal Register, 2001). The dominant inorganic As species changes from As(V) in the shallow well to As(III) in the deep well and SAP#1 (Fig. 4 and Table 1). Concentrations of DMA (dimethylarsinate) were low (~1 μg/L) in the deep aquifer and <0.6 μg/L in the shallow aquifer. Monomethylarsonate (MMA) concentrations were <1.2 μg/L in both aquifers. The ground water contains little or no dissolved O_2, Fe(II), or Mn(II) (Table 1). Sulfide odor was not noted in any of the samples, even after acidification. Concentrations of P, which can compete with As for adsorption sites, were low (⩽10 μg/L).

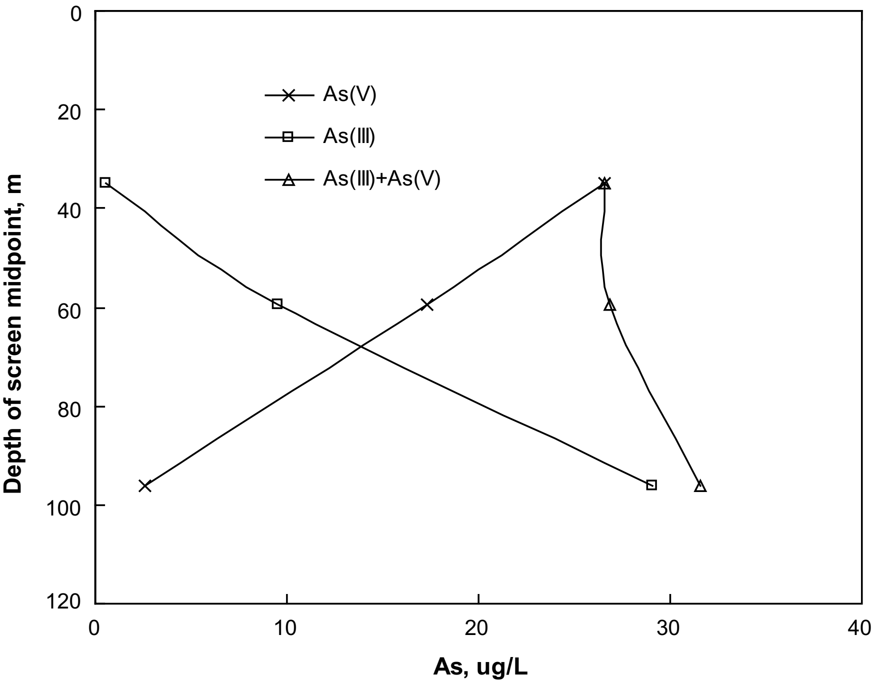

Fig. 4. Inorganic As species in ground water from wells EXP-2 shallow (35 m), middle (59 m), and deep (96 m).

4. Results and discussion

Alteration of the water chemistry from SAP#1 increased the dissolved O_2, Fe(II) and Cl concentrations, oxidized As(III) to As(V), and increased the Cl_2. DIC (dissolved inorganic C) concentrations initially decreased before and during injection because of CO_2 outgassing. Atmospheric gasses were injected at a rate that resulted in gas bubbles that were partially removed near the injection wells. Additionally, during injection the water was allowed to cascade down the open casing which allowed for further outgassing. Outgassing of CO_2 should increase after the addition of acid because a lower pH increases the pCO_2. Because outgassing continued during injection into the wells, the DIC of the water entering the aquifer is not known. Reaction with the aquifer sediments then increased the DIC after injection. A summary of the Fe(II) and O_2 concentrations, and pH in the injectate is presented in Table 2. Chlorine sampled prior to contact with the activated charcoal ranged from 0.4 to 0.8 mg/L, and <0.02 mg/L after reaction with the charcoal for all experiments. DMA was below detection (0.6 μg/L) in the injectate, presumably from either removal by the activated charcoal or reaction with Cl_2 to form As(V). No As(III) was detected in 3 samples of injectate collected immediately prior to injection. Chloride concentrations were well below the secondary standard of 250 mg/L in the injected and withdrawn water (Table 3).

Table 3
Injected Fe concentrations in selected cycles

Cycle	Average Fe concentration added to injectate (μg/L)	Average Cl concentration added to injectate (mg/L)
D2	270	25
D3	150	31
D5	5000	46
D7	4900	37
D8	3100	40
D9	280	40
D10	440	50
D11	350	40
S3	6400	56
S4	3300	40
S5	410	41
S7	370	44

4.1. *In situ experiments*

Arsenic removal experiments consisted of injection and withdrawal cycles using different Fe concentrations and pH values (Table 2). The first 3 injections into the deep aquifer consisted of lowering the pH from an original value greater than 8.0 by addition of HCl and relatively low concentrations of Fe(II) (from 150 to 560 μg/L). The next 5 cycles (cycles D4–D8) involved substantially higher Fe(II) concentrations ranging from 3100 to 5000 μg/L. A third set of cycles (D9–D11) again used modest Fe concentrations followed by a single cycle (D12) using an Fe concentration between that in the higher and lower Fe experiments. Experiments in the shallow aquifer consisted of 4 cycles with injection of relatively high Fe(II) concentrations (3300–6400 μg/L) and 3 cycles with lower values (370–410 μg/L; Table 2). Reaction periods (the time between the end of injection and the beginning of withdrawal) were generally about 1 h, except for cycles D11 and D12 that had a 2 h reaction period.

Table 2
Summary of injection experiment parameters

Cycle numbers	Injected volumes per cycle (L)	Withdrawn volumes per cycle (L)	Average injectate pH[a]	Average injectate O_2 (mg/L)[a]	Concentration of injected Fe(II) (μg/L)	Concentration of injected Cl (mg/L)	Comments
D1–D3	790–2880	1490–3460	5.3–6.4	6.1–6.9	150–560	9.2–31	Low Fe
D4–D8	1170–1580	1830–3900	5.5–5.9	6.5–9.8	3050–4960	34–46	High Fe
D9–D11	1300–1610	2450–3680	5.3–5.5	10.6–11.3	280–440	40–50	Low Fe, D11 – 2 h reaction time
D12	1680	2780	5.5	11.1	760	42	Moderate Fe, 2 h reaction time
S1–S4	1100–1470	1340–3050	5.3–6.2	7.0–9.7	3270–6350	34–56	High Fe
S5–S7	1210–1500	2860–2900	5.5–5.6	10.1–10.7	370–410	41–46	Low Fe

[a] Range of averages for the various cycles.

Dissolved O_2 concentrations decreased rapidly and early during the withdrawal periods involving both aquifers (Figs. 5A and 6A). Injected O_2 concentrations ranged from about 6–11 mg/L (Table 2) but were essentially absent in water withdrawn from the deep aquifer well before the amount of water withdrawn equaled the amount injected (Fig. 5A). The amount of water injected during each cycle is indicated by the solitary symbols in Fig. 5–13. This loss of O_2 early in the withdrawal period can be partly explained by reaction with injected Fe(II) to form Fe-oxide (reaction 1). From the stoichiometry in reaction (1), and for an injected Fe(II) concentration of 6000 μg/L (the upper limit during all cycles involving the deep aquifer), O_2 would be reduced by less than 1 mg/L. Clearly, O_2 reacts with some reductant present in the aquifer materials. One possibility is adsorbed Fe(II), which is consistent with greenish-gray, green, and black sediments that comprise the deep aquifer could react rapidly as indicated by the reaction of dissolved Fe(II) with O_2 (King et al., 1995; King, 1998). Sedimentary organic matter (SOM) could react with O_2, however, the age of the sediments (tens to hundreds of thousands of years based on the sedimentation rates discussed above) suggests that highly reactive SOM is unlikely to be present. This rapid decrease in O_2 was similar in successive injection cycles. The dissolved O_2

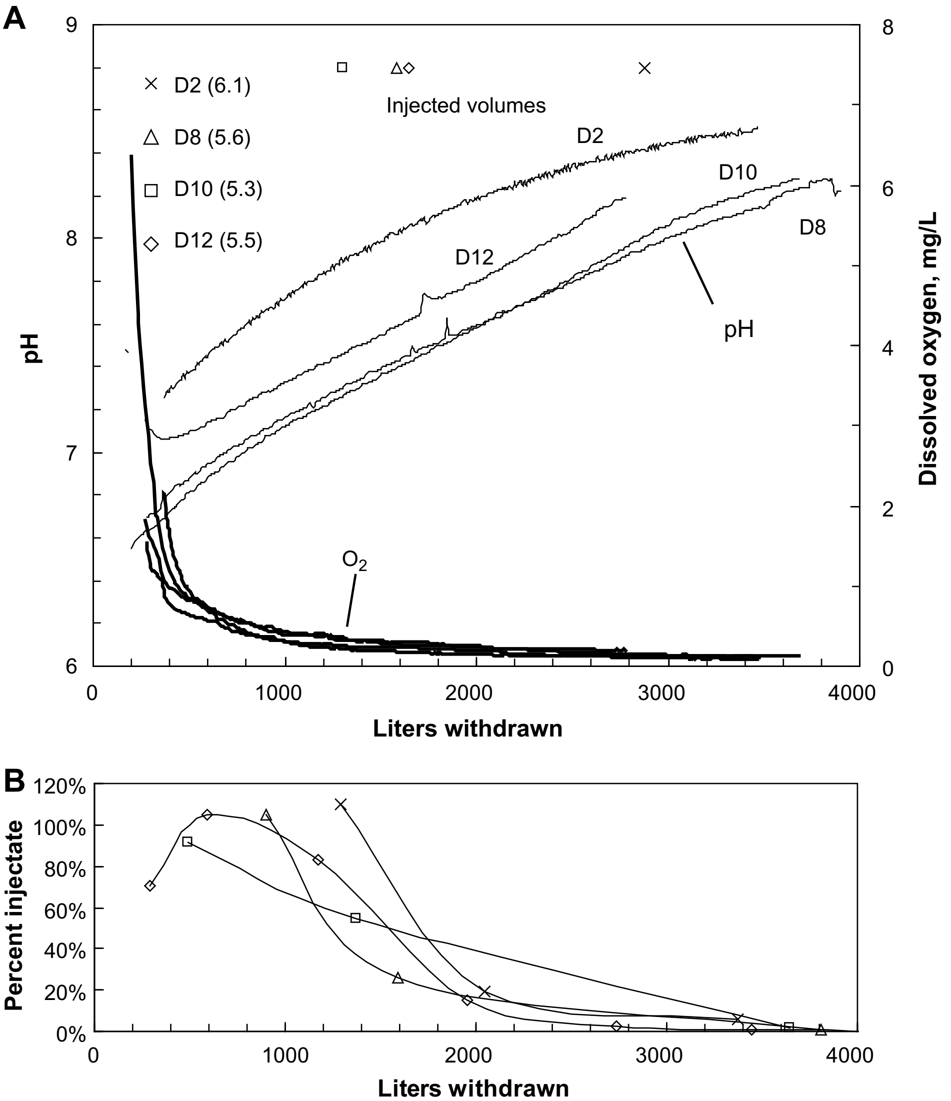

Fig. 5. Dissolved oxygen and pH in water withdrawn from the deep aquifer (A) and percent injectate in withdrawn water (B). Values in parentheses are the average injectate pH values.

concentrations remained measurable through longer withdrawal volumes from the shallow aquifer as compared to the deep aquifer (Fig. 6A). The presence of interbedded brown sediments in the shallow aquifer is compatible with less reducing conditions and consumption of O_2 compared with the deep aquifer.

$$\mathrm{Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+} \qquad (1)$$

An increase in pH early in the withdrawal periods (Figs. 5 and 6A) can be caused by mixing with ambient ground water and reactions with aquifer sediments. The amount of mixing of injectate with ambient ground water is estimated from Cl concentrations in the injectate and withdrawn water, and expressed as percent in Figs. 5B and 6B. Chloride concentrations were essentially equal to the injectate concentrations during withdrawal of water up to a volume near the injected volume. This indicates that the pH increase is partly from reaction with the deep aquifer sediments. As discussed below, increases in major ion concentrations also indicate that the pH is affected by reactions in the aquifer. In broad terms, pH values in the water withdrawn from both aquifers had similar trends (Fig. 6A and B). Recovery to ambient pH requires a greater amount of

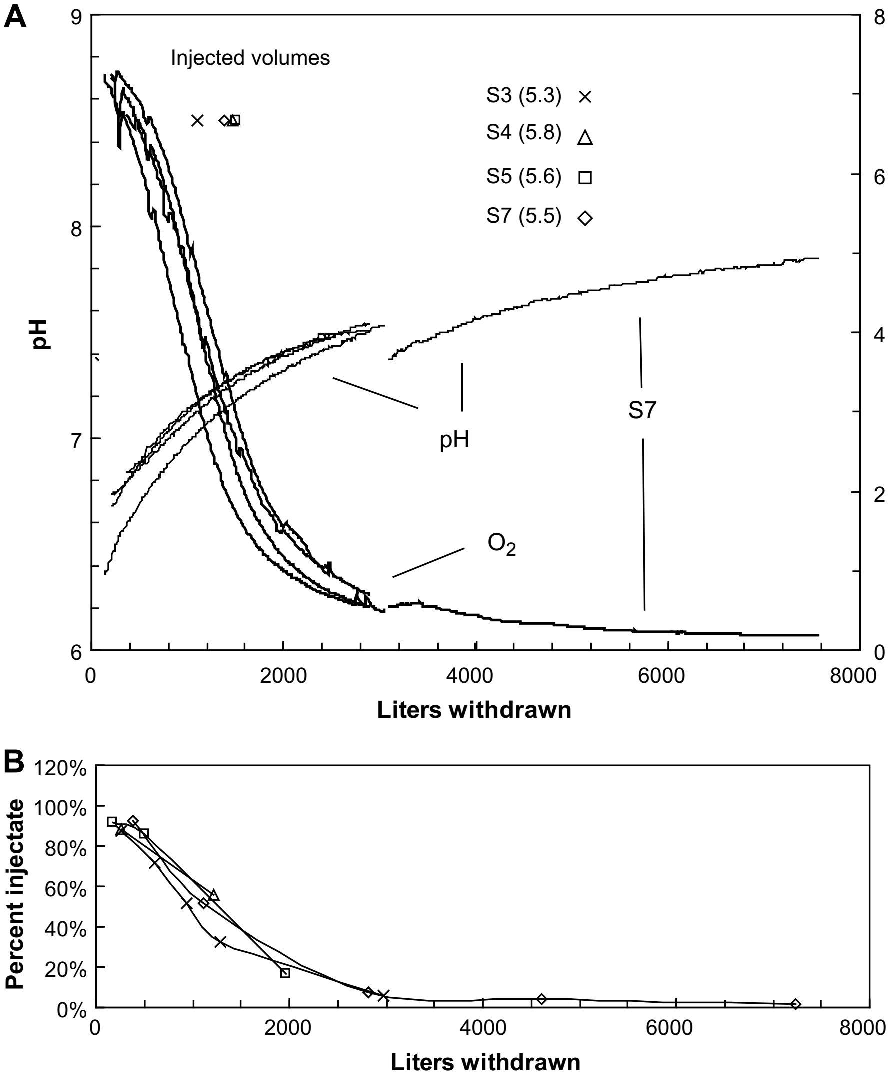

Fig. 6. Dissolved oxygen and pH in water withdrawn from the shallow aquifer (A) and percent injectate in withdrawn water (B). Values in parentheses are the average injectate pH values. The withdrawal period for cycle S7 extending beyond about 3000 L represents recovery after a 16 h period of no pumping.

water withdrawal from the shallow aquifer rather than the deep aquifer; the amount of water withdrawn was not sufficient to attain ambient pH values during all the cycles.

Arsenic concentrations in water pumped after injection during the cycles D1–D3 were similar to, or somewhat greater, than the concentrations in the aquifer prior to injection (Fig. 7). As(V) was the dominant inorganic As species during the early part of the withdrawal period. As(III) concentrations increased as the withdrawal period continued and became the dominant inorganic As species. Phosphorus concentrations during withdrawal were all <10 μg/L. Iron and Mn concentrations during withdrawal were < 50 μg/L.

Lack of As removal in initial cycles indicates that the amount of Fe(II) may have been insufficient. Experiments D4–D8 involved lowering the pH to values generally ranging from 5.4 to 6 with substantially higher Fe(II) concentrations of 3600 to 5900 μg/L (Table 2). Substantial removal of As occurred during the initial withdrawal (Fig. 8). Arsenic concentrations rose from <10 μg/L to about 15–25 μg/L at the point where the volume of withdrawn water equaled the amount of injected water. Arsenic concentrations approached the injected values after withdrawal of about twice the injected volume and increased only slightly thereafter. Inorganic As speciation data are not available for these experiments. Iron concentrations were high during the early part of the withdrawal period (Fig. 8) followed by a decrease to below the 300 μg/L secondary drinking water standard. Manganese concentrations also exceeded the secondary standard of 50 μg/L during the early part of the withdrawal period and then decreased below the standard. Both Fe and Mn concentrations were somewhat lower during the early withdrawal periods for successive cycles. Lower Fe concentrations in cycle D8 were partly from a lower injected Fe concentration of about 3100 μg/L compared to concentrations ranging from 4600 to 5900 μg/L in cycles D5–D7. A possible cause

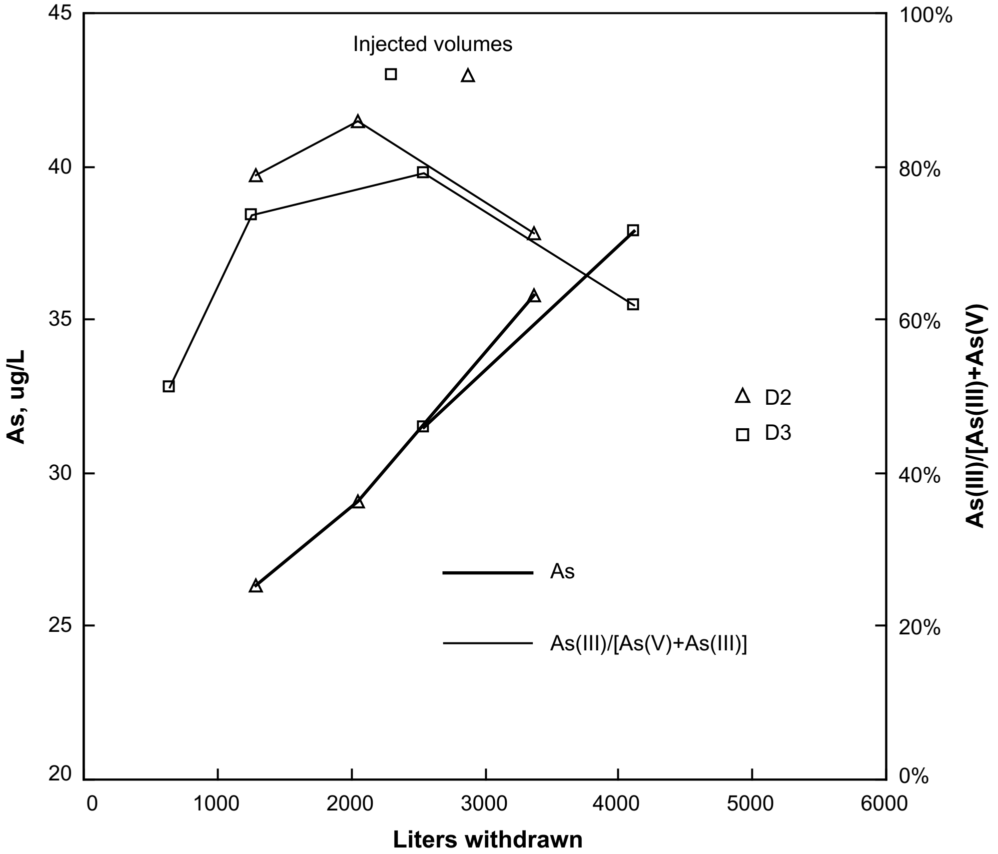

Fig. 7. Arsenic and As(III)/[As(III) + As(V)] in water withdrawn during cycles D2 and D3.

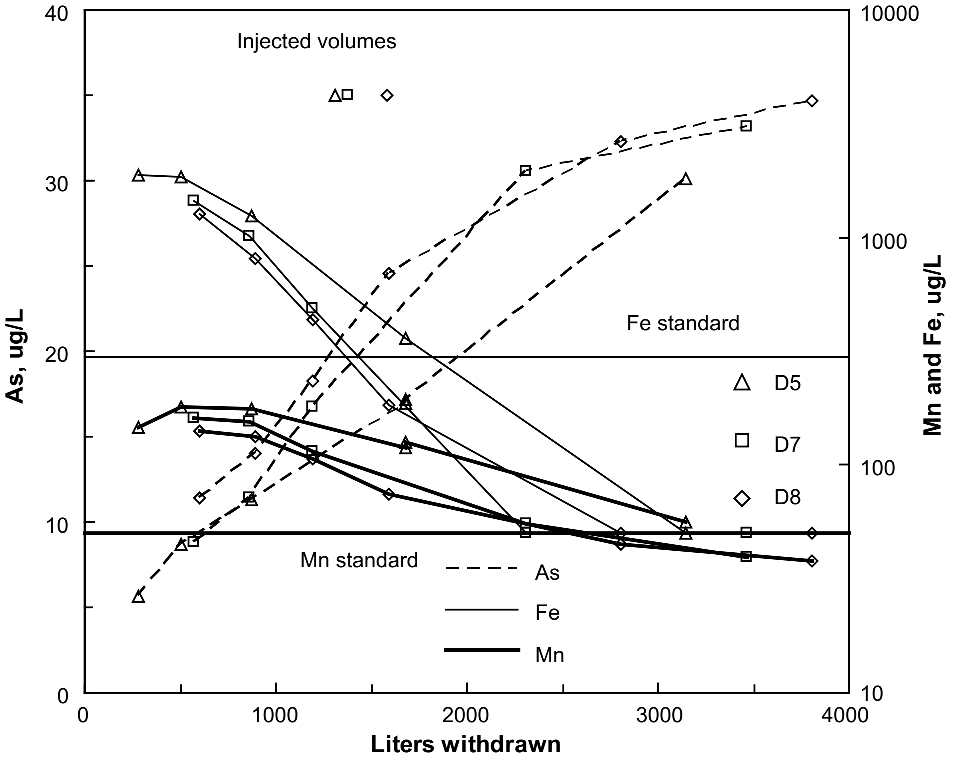

Fig. 8. Fe, Mn, and As in water withdrawn during cycles D5, D7, and D8.

of increased Mn concentrations is exchange of Mn(II) adsorbed onto aquifer materials for Fe(II) in the injectate. Increasing Fe-oxide content of the aquifer produces additional adsorption capacity with successive cycles which could reduce aqueous Mn(II) by adsorption.

Experiments D9–D11 involved lowering pH to about 5.4 and returning to low Fe(II) concentrations ranging from 380 to 440 μg/L (Table 2). Cycle D11 included injection of only HCl to maintain a pH of 5.4 for an additional 30 min and a 2-h reaction time between injection and withdrawal instead of the 1 h reaction time used for the cycles D9 and D10. Experimental conditions for cycle D12 were similar to D9 and D10 except for a higher injected Fe concentration (1450 μg/L; Table 2) and a longer withdrawal period. Resultant As concentrations ranged from about 15 to 25 μg/L during the initial withdrawal period (Fig. 9). As(V) was the dominant inorganic As species during the beginning of the withdrawal period and was generally below about 15 μg/L during the experiments. As(III) became dominant before one injection volume was pumped out. At about one volume removed, the As concentration was about equal to that present prior to the experiments. After initially low concentrations, As increased to values that were, at times, somewhat greater than that in the deep aquifer prior to the injection experiments. Continued pumping produced As concentrations near the 36 μg/L initially found in the aquifer (Table 1). Concentrations greater than the ambient values might be a result of a combination of increasing pH (Fig. 5A) and As(III) dominance causing some desorption from newly formed Fe-oxide. Iron(II) concentrations were a maximum of 170 μg/L at the start of withdrawal during cycle D9 and below 100 μg/L in all other samples. Manganese concentrations were below the 50 μg/L drinking water standard in all sampled water during these cycles.

Arsenic concentrations in water withdrawn from the shallow aquifer in experiments S1–S4 were much lower than the injected concentrations (Fig. 10A). Arsenic concentrations were below the drinking water standard in a volume of water slightly greater than that injected in experiments S3 and S4. However, Fe(II) and Mn(II) concentrations in most water sampled during the withdrawal period exceeded their

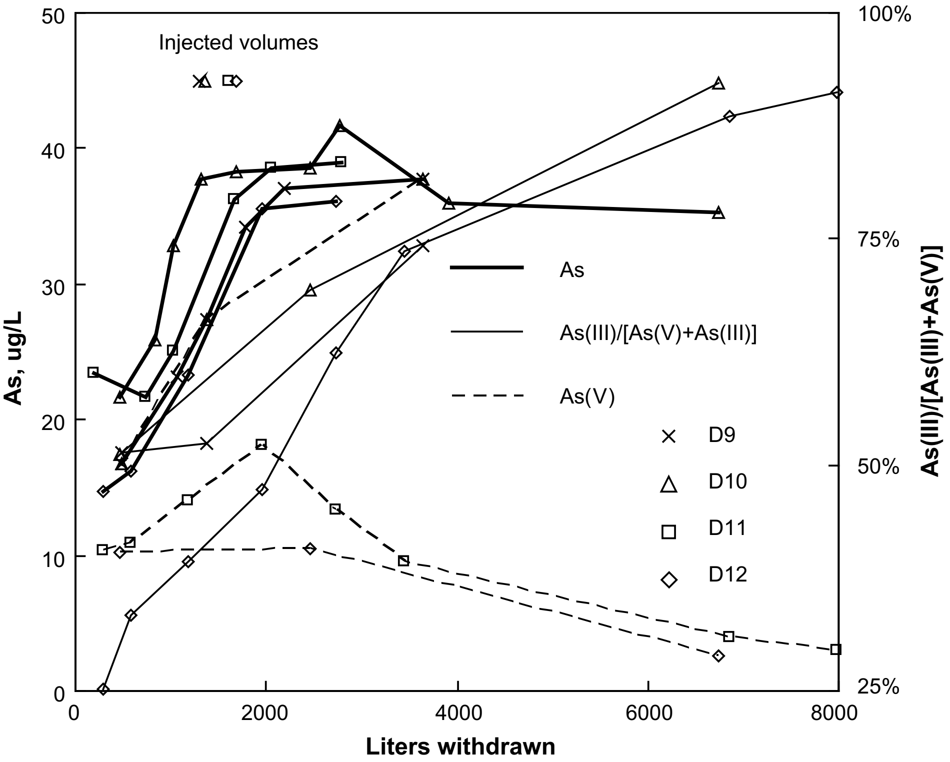

Fig. 9. Arsenic, As(V), and As(III)/[As(III) + As(V)] in water withdrawn during cycles D9–D12.

respective standards (Fig. 10B). Injection of water with lower Fe(II) concentrations in cycles S5–S7 resulted in less As removal but with lower Fe(II) and Mn(II) (Fig. 10B). Because As in the injected and ambient water in the shallow aquifer is predominantly As(V), a limited number of samples were analyzed for As species. Nearly all of the inorganic As was present as As(V).

Calcium and Na concentrations were higher in the early part of withdrawal periods (Fig. 11A) than initially in the deep aquifer and SAP#1 (Table 1). Carbonate alkalinity in water sampled during the early part of the withdrawal periods (Fig. 12A) were distinctly lower than in the deep aquifer (Table 1). The carbonate alkalinity of the injectate could not be quantified because of outgassing in the injection well. The injected water was allowed to cascade from near the top of the well to the top of the water column in the well which allows CO_2 outgassing because the CO_2 partial pressure is greater than atmospheric in the lower pH water. The greater Ca and Na concentrations can be attributed to calcite dissolution and cation exchange. The saturation index (SI) of calcite calculated using PHREEQE (Parkhurst and Appelo, 1999) is markedly undersaturated during the early part of the withdrawal periods (Fig. 12A). If cation exchange is the primary cause of the higher Na concentrations, then the amount of calcite dissolution should be equal to the amount involved in the exchange plus the increase in the aqueous Ca. Potassium and Mg concentrations were slightly higher during early withdrawal (Fig. 13). The Mg concentration in the earliest sample collected during the withdrawal period of cycle D10 was the same as the 0.4 mg/L concentration in the injected water from SAP#1 (Table 1) indicating that Mg was released from the sediments, most likely by cation exchange. Similarly, higher K concentrations observed during the early part of the withdrawal period are likely a result of cation exchange (Fig. 11A). The essentially constant SiO_2 concentrations show that silicate hydrolysis is not an important contributor to the increased dissolved solids. Sulfate concentrations during the early part of the D10 withdrawal period were as high-As 29 mg/L (Fig. 13) which is essentially the same as the injected concentration of 30 mg/L (Table 1). Sulfate concentrations were distinctly

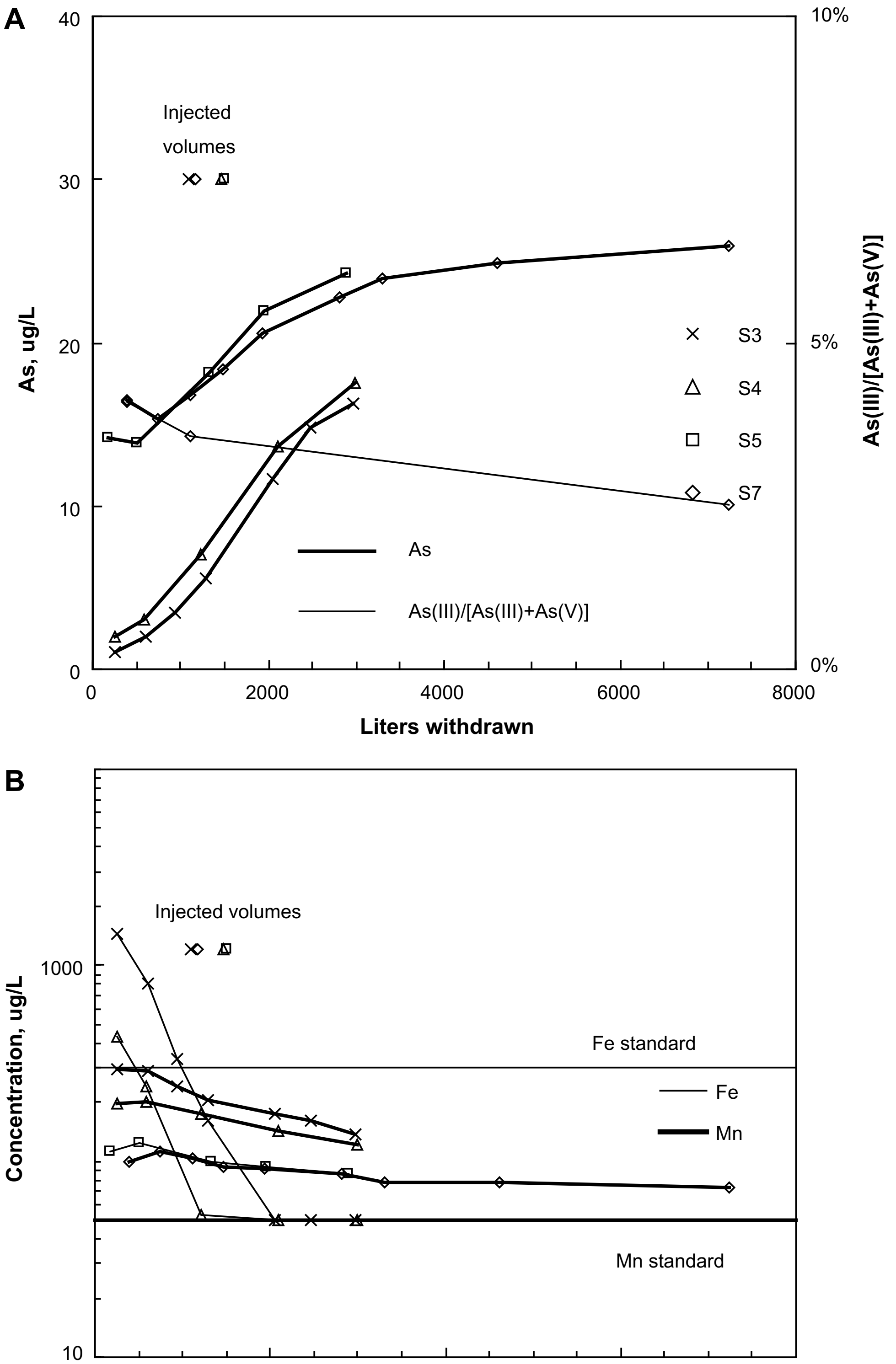

Fig. 10. Arsenic and percent As(III)/[As(III) + As(V)] (A) and Fe and Mn (B) in water withdrawn from the shallow aquifer.

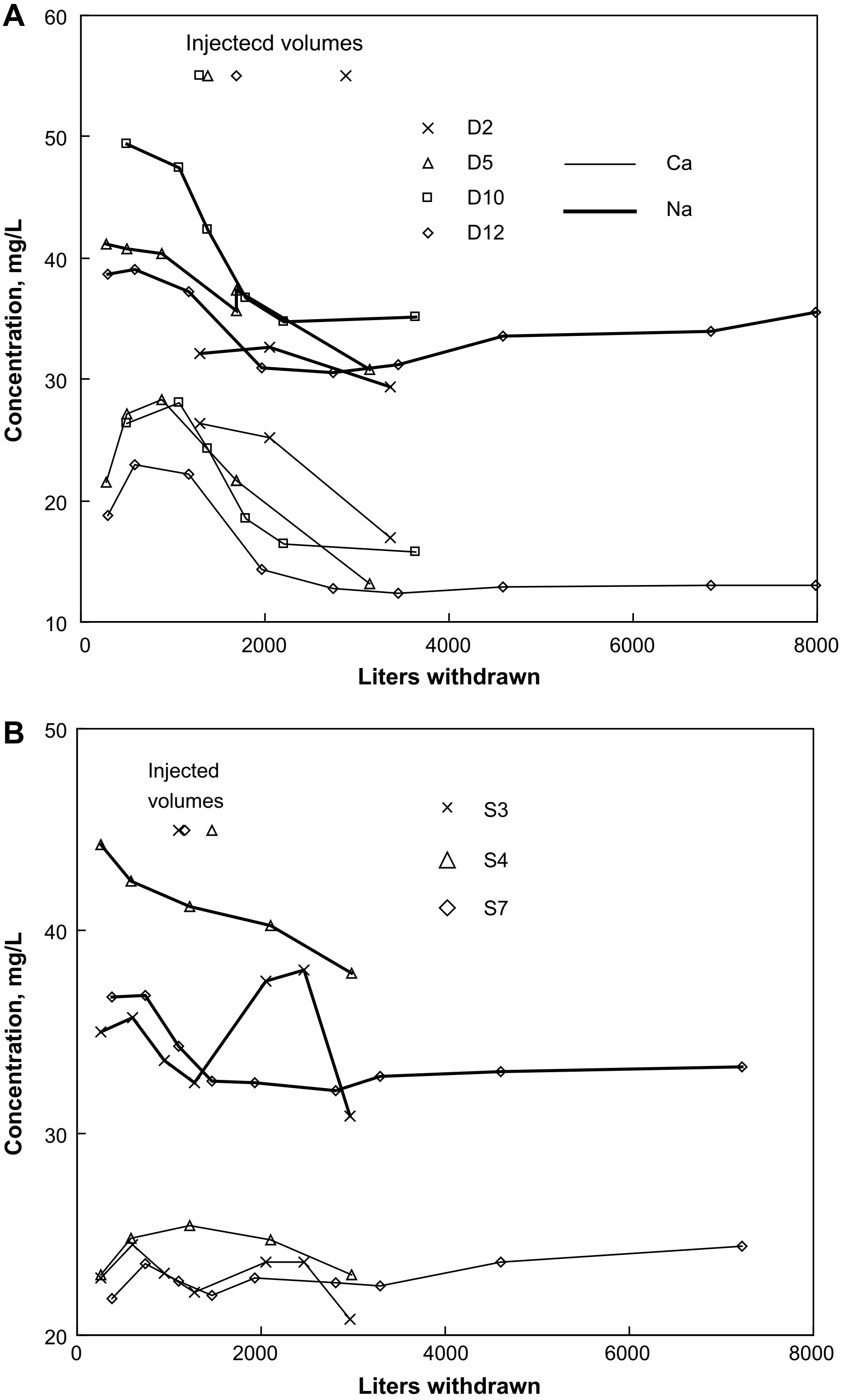

Fig. 11. Ca and Na concentrations in water withdrawn from the deep (A) and shallow (B) aquifers.

lower than the ambient values (28 mg/L) during the latter part of several withdrawal periods, including D10 (Fig. 13), indicating that anion adsorption might be occurring. Sulfate concentrations near

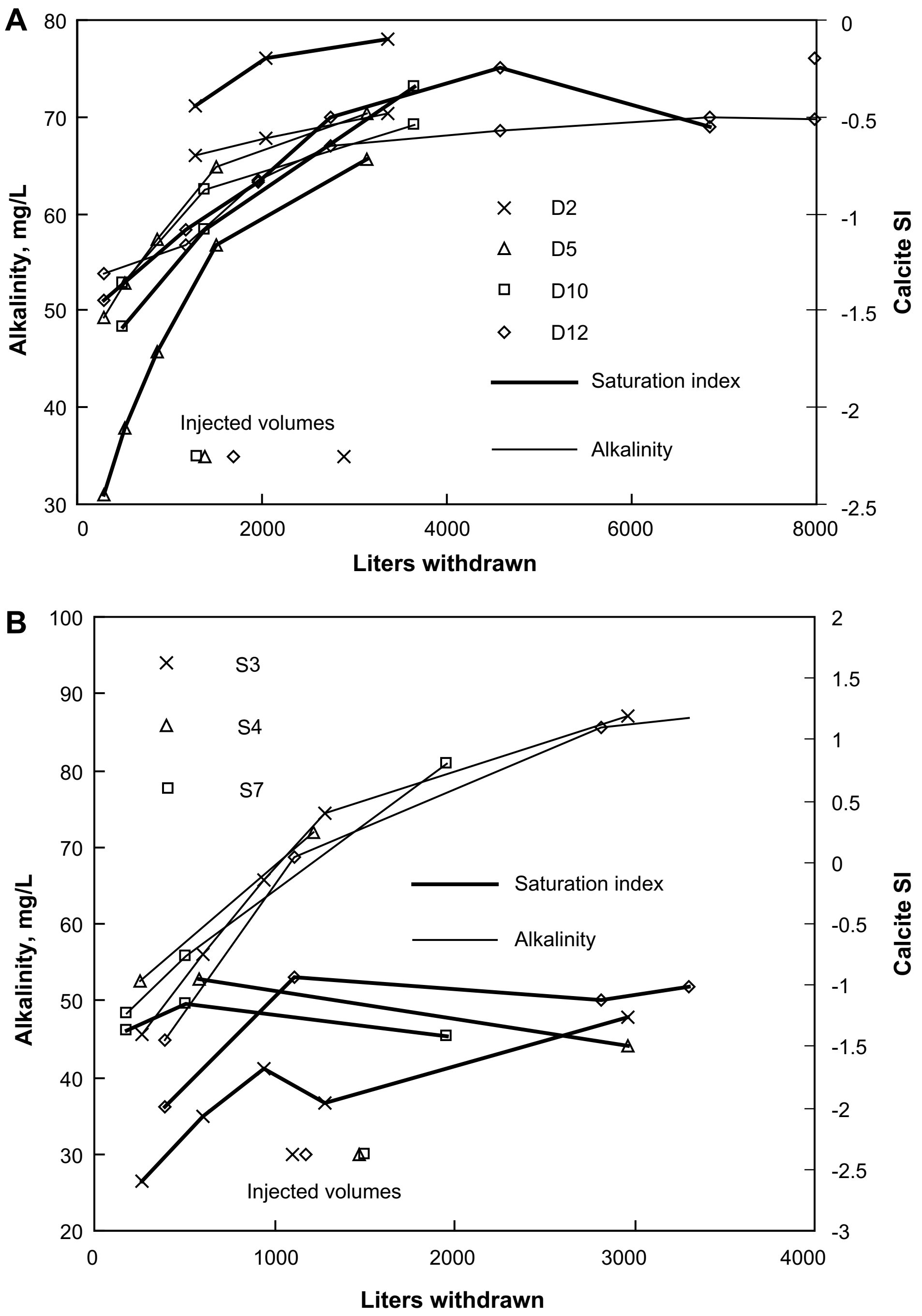

Fig. 12. Alkalinity and calcite saturation index (SI) for water withdrawn from the deep (A) and shallow (B) aquifers.

the end of D11 were about 24 mg/L, somewhat lower than the ambient concentrations which are likely from Fe-oxide introduced into the aquifer.

Sodium concentrations were higher during the early part of withdrawal from the shallow aquifer compared with later concentrations (Fig. 11B). Additionally, increasing alkalinity and the negative values of calcite saturation indices (Fig. 12B) indicate calcite dissolution. Although not shown for the purpose of brevity, K and Mg concentrations were slightly different from the injected and ambient concentrations. Sulfate concentrations show loss of

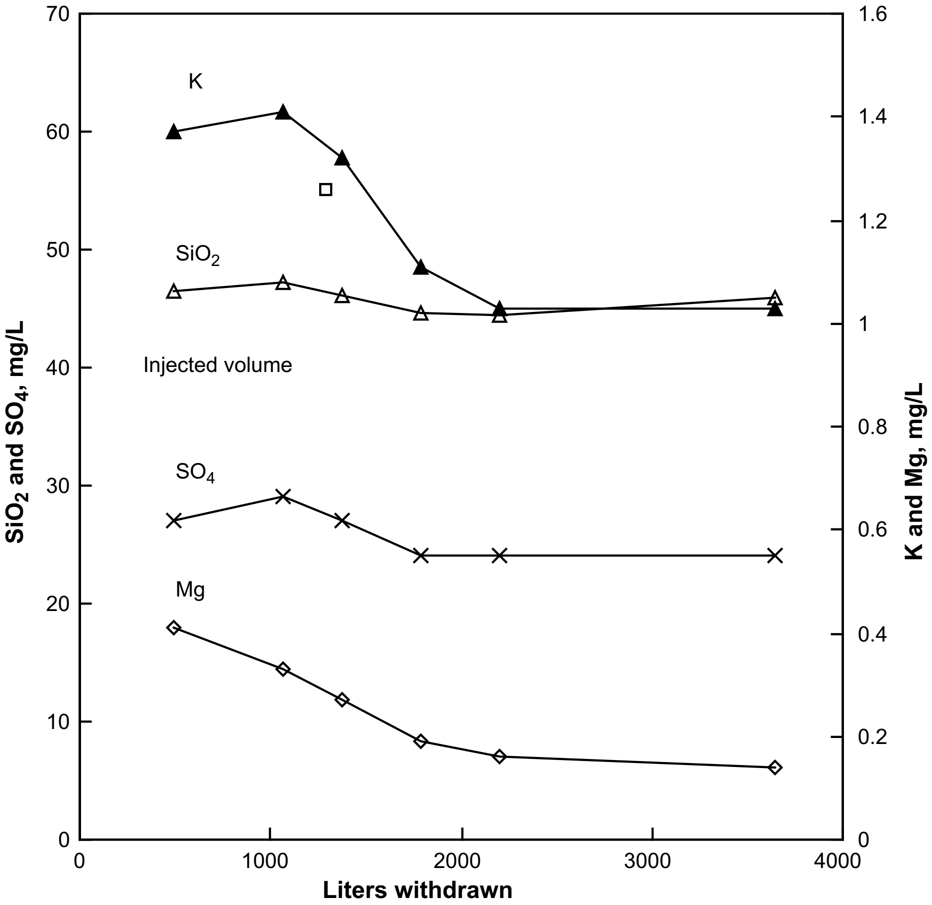

Fig. 13. Selected major ions in water withdrawn during cycle D10.

a few mg/L at most in the shallow aquifer. Silica concentrations were as much as 5–10 mg/L greater in the withdrawn water indicating that some silicate hydrolysis is occurring. Overall, the major element chemistry appears to be affected by calcite dissolution accompanied by lesser amounts of sulfate removal and silicate hydrolysis.

5. Conclusions

Experiments in two aquifers demonstrate substantial in situ As removal using Fe-oxide along with lowering the pH. This approach is particularly relevant in the western United States where high-As concentrations commonly are associated with alkaline ground water (Welch et al., 1988; Welch et al., 2000). The experiments involved a series of processes that modified the chemistry of the injectate that caused several reactions in the aquifers. Chemical and physical processes that affected the source water for the injection experiments included: (1) Injection of Cl_2 which oxidized As(III) to As(V) during a reaction time of about 7 min, (2) Cl_2 removal to prevent formation of undesirable disinfection by-products in the aquifers, (3) injection of Fe(II), HCl and atmospheric gas to add dissolved O_2, and (4) outgassing of CO_2. Dissolved O_2 and Fe(II) were added to form Fe-oxide in the aquifer. HCl was added to lower the pH. Reactions in the aquifer included reaction of O_2 with aquifer materials, formation of Fe-oxide, removal of As, dissolution of calcite, and cation exchange. Calcite dissolution could be reduced by injection of water below the water-level in the well at a depth that could prevent outgassing. Arsenic concentrations in the shallow and deep aquifers were as low as 1 and 6 μg/L, respectively, although Fe and Mn concentrations during some withdrawal periods exceeded secondary drinking water standards. Removal was greater in the shallow aquifer in terms of concentration as well as amount of water withdrawn with low As concentrations. Arsenic removal in the deep aquifer could improve if the reductive capacity of the aquifer materials can be exceeded by injection of more water with dissolved O_2. The volumes of water involved in this effort are modest compared with those used in a study of a highly reduced ground water system (Appelo and deVet, 2003). They describe a system involving about 1000 times as much water injected per cycle into a methanogenic aquifer. Iron and Mn concentrations in withdrawn water were lower for longer periods after 7 cycles compared with the first cycle. Evaluation of optimum design for limiting concentrations of Fe and pH is worth further evaluation. Among the factors that deserve investigation include the reductive capacity of the aquifer sediments, the effect of longer reaction times on Fe, Mn and As concentrations, and the effect of continued cycles of injection and withdrawal.

Injection zones likely will be well-defined if a production site is operated in the vicinity of the experiment site. Vertical migration of injectate will be limited because sand and gravel intervals are less than 30 m thick and isolated by silt and clay units that are 1000 times less permeable. Lateral migration and distortion of injectate also will be limited because ground-water velocities are not great enough to significantly displace injected water. Overall aquifer transmissivity of 700 m^2/d is great enough that injection and pumping are feasible.

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Subsurface iron and arsenic removal for shallow tube well drinking water supply in rural Bangladesh

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ABSTRACT

Subsurface iron and arsenic removal has the potential to be a cost-effective technology to provide safe drinking water in rural decentralized applications, using existing shallow tube wells. A community-scale test facility in Bangladesh was constructed for injection of aerated water ($\sim 1\ m^3$) into an anoxic aquifer with elevated iron ($0.27\ mmol\ L^{-1}$) and arsenic ($0.27\ \mu mol\ L^{-1}$) concentrations. The injection (oxidation) and abstraction (adsorption) cycles were monitored at the test facility and simultaneously simulated in the laboratory with anoxic column experiments.

Dimensionless retardation factors (R) were determined to represent the delayed arrival of iron or arsenic in the well compared to the original groundwater. At the test facility the iron removal efficacies increased after every injection-abstraction cycle, with retardation factors (R_{Fe}) up to 17. These high removal efficacies could not be explained by the theory of adsorptive-catalytic oxidation, and therefore other ((a)biotic or transport) processes have contributed to the system's efficacy. This finding was confirmed in the anoxic column experiments, since the mechanism of adsorptive-catalytic oxidation dominated in the columns and iron removal efficacies did not increase with every cycle (stable at $R_{Fe} = \sim 8$). R_{As} did not increase after multiple cycles, it remained stable around 2, illustrating that the process which is responsible for the effective iron removal did not promote the co-removal of arsenic. The columns showed that subsurface arsenic removal was an adsorptive process and only the freshly oxidized adsorbed iron was available for the co-adsorption of arsenic. This indicates that arsenic adsorption during subsurface treatment is controlled by the amount of adsorbed iron that is *oxidized*, and not by the amount of *removed* iron. For operational purposes this is an important finding, since apparently the oxygen concentration of the injection water does not control the subsurface arsenic removal, but rather the injection volume. Additionally, no relation has been observed in this study between the amount of removed arsenic at different molar Fe:As ratios (28, 63, and 103) of the groundwater. It is proposed that the removal of arsenic was limited by the presence of other anions, such as phosphate, competing for the same adsorption sites.

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1. Introduction

Arsenic contamination of shallow tube well drinking water in Bangladesh is an urgent developmental and health problem (British Geological Survey/DPHE, 2001; WHO, 2001; Smith et al., 2002), disproportionately affecting the rural poor, i.e., those most reliant on this source of drinking water. The water treatment option presented in this article, subsurface iron and arsenic removal, relies on the existing infrastructure of a hand-pump/shallow tube well and retains iron and arsenic in the subsurface. As such, it has crucial advantages over other household and community arsenic removal systems, such as SONO and Alcan (Sutherland et al., 2002):

- no costly filter media and maintenance is needed;
- the tube well is the 1st preferred option for drinking water in rural Bangladesh (WSP/Worldbank, 2003); and available to a majority of the rural poor in their household;
- (minimal) additional hardware beyond the existing hand pump is affordable and locally available/repairable;
- iron is also removed which improves colour and taste of the water; greatly enhancing potential for social acceptance;
- iron could be a visible indicator for arsenic presence (and aid in post-deployment monitoring of water quality);
- groundwater-irrigation leading to arsenic accumulation in crops (rice) may also be mitigated.

The principle of subsurface iron removal is that aerated water is periodically injected into an anoxic aquifer through a tube well (Fig. 1, left), partially displacing the iron-containing groundwater. The injected water oxidizes adsorbed ferrous iron on the soil grains, resulting in a surface area of ferric iron hydroxides for adsorption of soluble ferrous iron and oxyanions, such as arsenic (van Beek, 1985; Rott and Friedle, 1985; Rott et al., 2002; Appelo and de Vet, 2003). When the flow is reversed, soluble ferrous iron in the abstracted groundwater is adsorbed onto the ferric iron coated soil grains and water with reduced iron concentrations is abstracted (Fig. 1, right). Injection is started again once elevated iron levels arrive at the well. The affected area in the subsurface around the tube well is referred to in this article as the *oxidation zone*.

By injecting oxygen-rich water into an anoxic aquifer, both homogenous and heterogeneous oxidation of ferrous iron will occur in the aquifer. Homogeneous oxidation of ferrous iron takes place in solution, and predominantly occurs at the interface of injected water and original, anoxic groundwater. Based on the large surface area of iron hydroxides on the soil grains in the subsurface, it is thought that the heterogeneous reaction of ferrous iron oxidation on the surface of ferric iron hydroxides is dominant during subsurface iron removal. In literature, the system's efficacy is explained by adsorptive-catalytic oxidation (van Beek, 1985; Rott and Friedle, 1985), where adsorbed ferrous iron is oxidized to form new adsorption sites. On its way into the aquifer, the injected water oxidizes adsorbed ferrous iron and thus "regenerates" the subsurface for adsorption during abstraction:

$$\equiv \mathrm{Fe^{III}OFe^{II}OH(s)} + 0.25\mathrm{O_2} + 0.5\mathrm{H_2O} \rightarrow \equiv \mathrm{Fe^{III}OFe^{III}OH(s)} + \mathrm{OH^-} \quad (1)$$

Due to the rapid consumption of oxygen during injection of aerated water, the oxygen front will lag behind the injected water front. When heterogeneous ferrous iron oxidation is complete, the iron hydroxide surface is available for adsorption of ferrous iron and oxyanions, such as arsenic(III), during groundwater abstraction:

$$\equiv \mathrm{Fe^{III}OH(s)} + \mathrm{Fe^{II}} + \mathrm{H_2O} \leftrightarrow \equiv \mathrm{Fe^{III}OFe^{II}OH(s)} + 2\mathrm{H^+} \quad (2)$$

$$\equiv \mathrm{Fe^{III}OH(s)} + \mathrm{H_3AsO_3} \rightarrow \equiv \mathrm{Fe}^{III}\mathrm{H_2AsO_3(s)} + \mathrm{H_2O} \quad (3)$$

Once the iron oxyhydroxide surface is exhausted, no more iron(II) or arsenic will be adsorbed and iron/arsenic breakthrough will be observed in the produced water (Dzombak and Morel, 1990). Hence, during abstraction the iron/arsenic front is retarded and more iron-free water can be produced than was injected. Every period of injection-abstraction is referred to as a *cycle*, with the first injection-abstraction period being cycle 1. More water with reduced iron/arsenic concentrations can be abstracted (volume V) than was injected (volume V_i), i.e., this volumetric ratio (V/V_i) determines the efficiency of the system.

Subsurface or in-situ iron removal has been used in central Europe for many decades (Hallberg and Martinell, 1976; Boochs and Barovic, 1981; Jechlinger et al., 1985; Rott and Friedle, 1985; van Beek, 1985; Appelo et al., 1999; Mettler, 2002), but the application of subsurface treatment for the

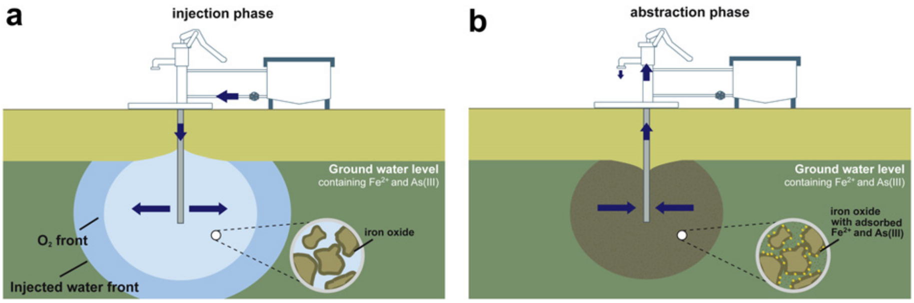

Fig. 1 – Principle of small-scale subsurface iron and arsenic removal.

removal of arsenic from groundwater is a relatively new approach (Rott et al., 2002; van Halem et al., 2009). This technology has the potential to be a cost-effective way to provide safe drinking water in rural areas in decentralized applications. With minimal investments in additional equipment, the existing infrastructure (hand pumps/shallow tube wells) can be modified to be operated under injection and abstraction conditions. In literature, a reduction of arsenic concentrations from maximum 40 $\mu g\,L^{-1}$ to below the WHO guideline (10 $\mu g\,L^{-1}$, WHO, 2006) has been reported with the injection of aerated water into the aquifer (Rott et al., 2002; Appelo and de Vet, 2003). In Bangladesh the subsurface removal of higher arsenic levels was investigated by Sarkar and Rahman (2001), namely, 500–1300 $\mu g\,L^{-1}$. In that study concentrations as low as 10 $\mu g\,L^{-1}$ were not reached, nevertheless, more than 50% removal was observed. In the absence of naturally occurring soluble ferrous iron, other researchers have studied the simultaneous injection of aerated water with ferric or ferrous iron (Welch et al., 2000; Miller, 2006). Preliminary results showed reduction of 100 $\mu g\,L^{-1}$ arsenic(V) to below the WHO guideline. Although these results are promising, only little is known about the limitations of this technology in the diverse geochemical settings of Bangladesh. The focus of this article was to identify the dominant processes in subsurface iron and arsenic removal in order to assess the applicability for rural Bangladesh. The methodology included (1) a field study with a community-scale facility in Manikganj, Bangladesh to assess the potential of decentralized subsurface iron and arsenic removal, and (2) anoxic column experiments with natural groundwater to simulate the shifting redox conditions in the oxidation zone during subsurface iron and arsenic removal. The column experiments provided controlled conditions for the investigation of the adsorptive-catalytic oxidation mechanism, whereas the test facility enabled to study subsurface treatment in the complex subterranean environment.

2. Materials and methods

2.1. Community-scale test facility, Bangladesh

Household shallow tube wells with suction hand pumps are widely distributed in Bangladesh and the objective of subsurface iron and arsenic removal is to use this existing infrastructure. The Manikganj district, 40 km west of Dhaka, was selected for this study, since the area is known to have high iron and arsenic concentrations in the groundwater. A site was selected with elevated iron concentrations (0.27 $mmol\,L^{-1}$) and arsenic concentrations (1.94 $\mu mol\,L^{-1}$). Unlike other parts of the Manikganj district, manganese concentrations were not found to be high (5.46 $\mu mol\,L^{-1}$) at this particular location. For phosphate, however, the groundwater did show elevated levels (52.6 $\mu mol\,L^{-1}$). The OR potential of the groundwater was measured to be on average −170 mV and the pH of the groundwater was 6.85.

The experimental set-up (Fig. 2) was connected to an existing hand pump with tube well in the upper aquifer. The 1.5-inch tube well had a depth of 31 m and a perforated well length of 3 m. As an added precaution, the set-up was placed with a family who already had arsenic treatment since 2001 (SIDKO system, BCSIR, 2003). For the purpose of subsurface treatment, the existing situation was modified with a pipe and valve for injection. After subsurface treatment, the groundwater was pumped (electrical suction pump) into the SIDKO system for aeration, sand filtration and Granular Ferric Hydroxide filtration (AdsorpAs, Harbauer GmbH). The treated water, low in arsenic and iron, was collected in a 1 m^3 storage tank and used for injection into the aquifer. The maximum injection volume was therefore limited to 1 m^3. Analysis of the water samples was done with field test kits (Wagtech International: Palintest and Arsenator) and confirmed in the laboratory (Perkin–Elmer Flame AAS 3110; Perkin–Elmer GF-AAS 5100PC). Duplicates or triplicates were taken to check the method of sampling and accuracy of analysis. Arsenic speciation was done with a field method (Clifford et al., 2004) using anion exchange resin columns (Amberlite IRA400). Multimeters (HACH 340i) were fixed inline to the experimental set-up to monitor pH (WTW SenTix 41), dissolved oxygen (WTW Cellox 325), OR potential (WTW SenTix ORP) and electric conductivity (TetraCon 325). Measurements were registered on a computer with Multilab Pilot v5.06 software. The injection and abstraction volumes were monitored using water meters. Operation started in October 2008, just after the monsoon season, and continued until May 2009. The family shared their arsenic treatment facility with their community and the weekly water consumption was 2.4–2.9 m^3. Operational conditions, such as injection frequency and production discharge, varied due to irregular operation. Normally the set-ups were used for the families' water production, however, during research periods the operation was intensified. Injection was done the night before, and abstraction was started at least 12 h after injection.

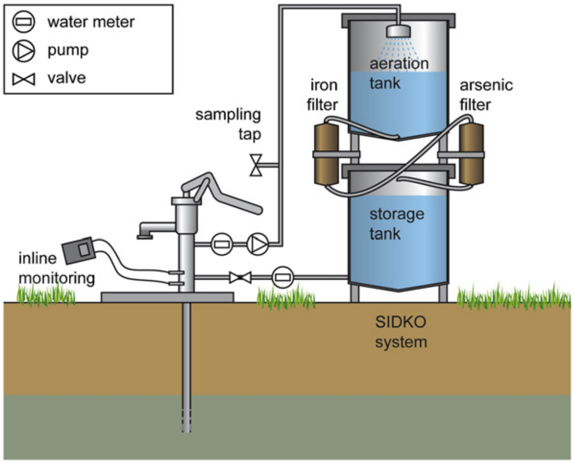

Fig. 2 – Small-scale test facility in Manikganj, Bangladesh.

2.2. Anoxic column experiments with natural groundwater

The raw groundwater of Oasen Drinking Water Company drinking water treatment plant Lekkerkerk in the Netherlands was used as influent for the column experiments. In addition, spikes of arsenic(III) ($NaAsO_2$, Fisher) were added to simulate high arsenic conditions as found in Bangladesh. Additionally, to evaluate the effect of different Fe:As ratios in the groundwater, several lower arsenic concentrations were dosed. During the research period the groundwater had an average pH of 7.1, a nearly constant temperature of 12 °C, iron concentration of 94.9 $\mu mol\,L^{-1}$, manganese concentration of 11.1 $\mu mol\,L^{-1}$ and phosphate concentration of 33.3 $\mu mol\,L^{-1}$. The groundwater was pumped onto the columns during the abstraction phase of a cycle, and the injection phase consisted of drinking water. The drinking water had an oxygen concentration of 0.28 $mmol\,L^{-1}$, a slightly higher pH of 7.4, and iron, manganese and arsenic were below detection limits.

The experimental set-up (Fig. 3) consisted of duplicate transparent PVC columns with a length of 80 cm and an inner diameter of 36 mm (wall thickness 2 mm). The columns were filled with washed (24 h with 3% HCl) filter sand (grain size = 0.6–1.2 mm, $D_{10} = 0.75$ mm) that contained 48.4 $\mu mol\,Fe\,g^{-1}$ ds after total iron extraction with 5 M HCl. The push–pull operational mode of injection–abstraction at the test facility was simulated in the 2D plug flow environment of the columns with down flow ($1.0\,L\,h^{-1} \pm 0.05$) for both injection and abstraction. Switching of flow direction was not required to simulate adsorptive-catalytic oxidation, since for oxygen breakthrough of $C/C_0>0.8$ was allowed during the injection phase. At the start of the experiments the columns were conditioned with groundwater, until complete breakthrough of iron occurred. Anoxic conditions were maintained in the columns by using an airtight FESTO system (6 x 1 PUN, I.D. 4 mm) with matching connectors and valves. The flow rate in the columns ($2.16\,m\,h^{-1} \pm 0.11$) was controlled with a multi-channel pump and PVC tubing with low gas permeability. The set-up remained under constant positive hydrostatic pressure to prevent oxygen. An injection-abstraction cycle started with 1.5 pore volume of (oxic) injection water and subsequently the influent was switched to (anoxic) groundwater for multiple pore volumes. Electrical conductivity was used as a conservative tracer from which the pore volume could be calculated to be on average 0.37 L (±0.005). For the columns, the V/V_i was calculated by dividing the produced water (V) by one pore volume (V_i), since the latter corresponds to the actual oxidized volume of sand in the column. The water quality parameters were monitored until at least $C/C_0 = 0.8$ was reached for iron and arsenic (C = measured concentration, and C_0 = original concentration), and runtimes of the columns per cycle varied between 9.2 and 16.1 pore volumes.

During the experiments samples were taken for iron analysis (Perkin-Elmer Flame AAS 3110) and arsenic analysis (GF-AAS; Perkin–Elmer 5100PC). Arsenic speciation was done with a field method (Clifford et al., 2004) using anion exchange resin columns (Amberlite IRA400). On-line measurements were done for dissolved oxygen (WTW Cellox 325), OR potential (WTW SenTix ORP), pH (WTW SenTix 41), and electrical conductivity WTW (TetraCon 325). Measurements were registered on a computer with Multilab Pilot v5.06 software.

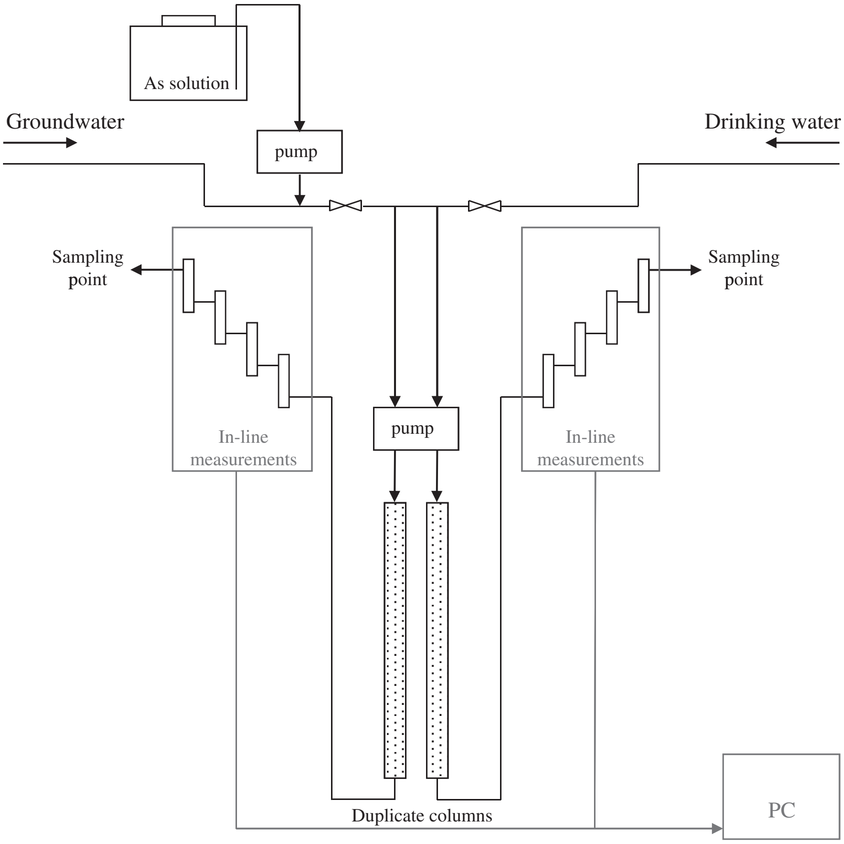

Fig. 3 – Experimental column set-up at Oasen, the Netherlands.

3. Results and discussion

3.1. *Arsenic and iron breakthrough curves*

3.1.1. *Community-scale test facility*

A dimensionless retardation factor (R) has been defined to represent the delayed arrival of iron or arsenic in the well compared to the original groundwater. R is equal to the V/V_i when the C/C_0 ($C =$ measured concentration, and $C_0 =$ original concentration) for iron or arsenic equals 0.5 divided by the V/V_i for a conservative tracer, e.g., electrical conductivity, at $C/C_0 = 0.5$. The determination of the retardation factor is illustrated in Fig. 4 for cycle 6 at the community-scale test facility in Manikganj, in this case the R_{Fe} for iron is 4.5.

Fig. 5 depicts the breakthrough of total arsenic, arsenic(III) and iron during cycle 20 at the test facility in Bangladesh. The graph clearly shows that iron breakthrough was retarded significantly, since the background concentration of 0.27 mmol L^{-1} was not reached at $V/V_i = 7.5$. The retardation factor (R_{Fe}) for iron has an estimated value of 13. It can be calculated that the total amount of removed iron would in that case be approximately 2.6 moles. The volume of injected water for this particular cycle was 827 L and had an oxygen concentration of 0.17 mmol L^{-1}, which adds up to a total amount of injected oxygen of ±0.14 moles. In the case that all injected oxygen was consumed by subterranean adsorbed ferrous iron, and thus used for the formation of new iron hydroxide surfaces, the measured iron removal does not even closely correspond to the equation that 1 mol of oxygen can oxidize 4 moles of ferrous iron (Eqs. (1) and (2)). In other words, iron removal at this particular site was much more effective than can be explained by the theory of adsorptive-catalytic oxidation.

Arsenic breakthrough started immediately at $V/V_i = 0$ and reached complete breakthrough before $V/V_i = 5$. During this cycle, the retardation factor for arsenic did not even reach 2. In the initial stage of the cycle all arsenic that breaks through is arsenic(III), but after $V/V_i = 4$ arsenic(V) also arrived at the well. In total, 2.6 mmol of arsenic is removed during this cycle, of which 1.1 mmol is arsenic(V). This gave an arsenic adsorption ratio of 1.0 mmol As/mol of removed iron. It may be concluded that the efficient iron removal does not promote the equivalent co-removal of arsenic. Also, iron does not provide a visible indicator for arsenic presence at this site – which could have been an aid in post-deployment monitoring of the water quality.

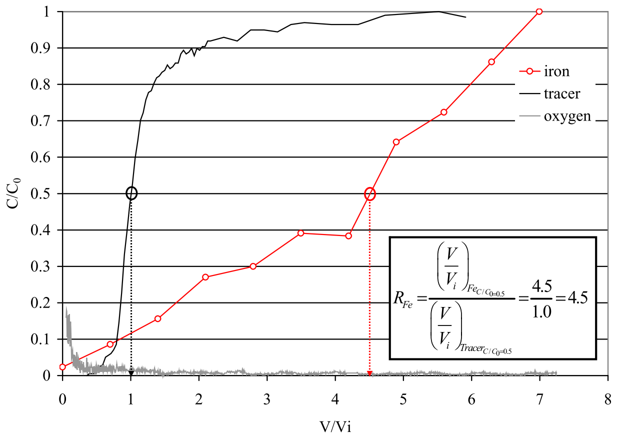

Fig. 4 – Typical breakthrough curve for electrical conductivity, dissolved oxygen, and iron, including determination of the retardation factor.

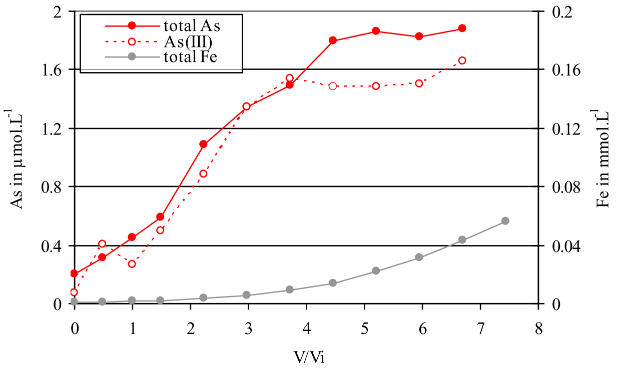

Fig. 5 – Breakthrough of arsenic and iron at the test facility in Manikganj, Bangladesh (cycle 20).

3.1.2. *Anoxic column experiments*

In the columns, oxygen-rich drinking water was dosed to the columns for 1.5 pore volume and remained in the columns overnight (16 h). In the morning, columns were re-started with natural groundwater and monitored for the retardation of arsenic and iron. Since the columns were operated under strict plug flow conditions, it can be assumed that homogeneous oxidation and precipitation were very limited and that heterogeneous oxidation and adsorption processes, and thus adsorptive-catalytic oxidation, dominated. The typical breakthrough curves of arsenic and iron are depicted in Fig. 6 for one of the columns (cycle 14). The arsenic concentration spiked to the influent consisted of 3.7 μmol L^{-1}, of which 2.8 μmol L^{-1} was arsenic(III). The graph shows that the original arsenic concentration was reached just before $V/V_i = 7$, with a retardation factor (R_{As}) of 2. Like in the test facility, arsenic(V) was initially completely removed, but passed the columns around $V/V_i = 4$. The iron content of the natural groundwater was 94.9 μmol L^{-1} and in the columns this concentration was reduced with a retardation factor of 7. The total amount of removed iron was 0.21 mmol, which yields an arsenic adsorption ratio of 24.8 mmol As per mol of removed iron.

During injection the amount of consumed oxygen can be registered by the retardation of the oxygen curve compared to the conservative tracer, electrical conductivity. The total oxygen consumption during injection was 0.05 mmol, which corresponds to approximately 1/4 of the amount of removed iron (Eq. (1)). Based on this mass balance, it can be concluded that the oxygen retardation was indeed caused by heterogeneous oxidation of ferrous iron in the column. The results for iron retention in the column therefore support the theory of adsorptive-catalytic oxidation.

3.2. *Retardation factors over successive cycles*

3.2.1. *Community-scale test facility*

Subsurface iron removal has been frequently reported to increase in efficacy with every successive cycle (Hallberg and

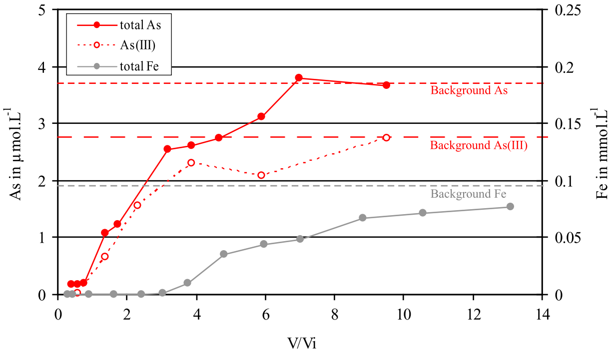

Fig. 6 – Breakthrough of arsenic and iron in the columns (cycle 14).

Martinell, 1976; Rott and Friedle, 1985; van Beek, 1985; Jechlinger et al., 1985; Boochs and Barovic, 1981; Mettler, 2002; Braester and Martinell, 1988). Fig. 7 shows that this was also the case for the test facility in Bangladesh, hence R_{Fe} increased from 2 to 15 after multiple cycles. It is noteworthy that the injection volume at this facility was limited to only 1 m^3, which can be considered very small-scale compared to existing treatment plants in Europe where injection volumes typically vary between 500 and 1000 m^3 (van Beek, 1985; Appelo and de Vet, 2003). It is therefore an important finding that, even at small-scale, subsurface iron removal is effective and could provide iron-free water in decentralized facilities in rural areas. R_{As} did not increase with every successive cycles, it remained stable at around 2, illustrating that the process which is responsible for the increasingly effective iron removal during subsurface treatment did not promote an equally effective co-removal of arsenic. There is a general consensus in the literature that adsorptive-catalytic oxidation is the dominant mechanism in subsurface iron removal, but the *increasing efficacy* of subsurface iron removal has also been attributed to bacterial activity (Hallberg and Martinell, 1976; Jechlinger et al., 1985; Rott and Friedle, 1985; Grombach, 1985), occurrence of dead-end pores or stagnant zones (Boochs and Barovic, 1981), growth of the oxidation zone with every cycle (Appelo et al., 1999), and oxidation of reductants other than iron(II) during initial cycles (van Beek, 1985).

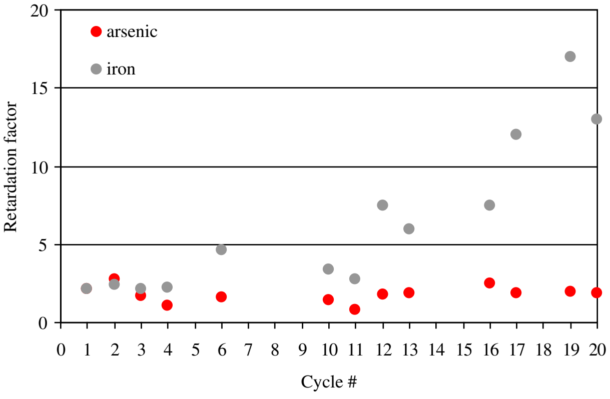

Fig. 7 – Retardation factors for iron and arsenic during successive cycles at the test facility in Manikganj, Bangladesh.

Heterogeneous oxidation of iron(II) is extremely fast, so oxidation of other reductants is unlikely to be favored. Nevertheless, oxidation of, e.g., pyrite could be a secondary reaction, resulting in elevated iron (and sulphate) concentrations in the produced water. Such mobilization of iron could underestimate the actual iron removal efficiency through adsorptive-catalytic oxidation during initial cycles. In the columns, only the adsorptive-catalytic oxidation mechanism within the oxidation zone was simulated. The clean filter sand did not contain other reductants that consume oxygen during initial cycles and changing transport mechanisms are unlikely to be relevant in the columns, since the conservative tracer tests confirmed stable plug conditions after multiple cycles. Bacterial activity was checked by Phase Contrast Microscopy of the produced water during cycle 21 and no iron oxidizers like *Gallionella ferruginea* were found. In other words, the adsorptive-catalytic oxidation process during subsurface iron and arsenic removal is expected to be the dominant process in the columns.

3.2.2. *Anoxic column experiments*

The retardation factors for iron and arsenic for the different injection-abstraction cycles in the columns are depicted in Fig. 8. It should be noted that dosing of arsenic to the natural groundwater was started after 7 cycles; therefore the arsenic retardation factors for the initial cycles are not included in the graph. Successive cycles in the columns show similar retardation factors for arsenic as the test facility. R_{As} remained around 2 and did not increase after multiple cycles. In the columns, the removal of arsenic is expected to be purely adsorptive, and the strong correlation with the results from the test facility suggests that those results were also achieved with adsorptive arsenic removal. Iron retardation in the columns did increase initially, but remained more or less stable at $R_{Fe} = 8$ after the first 6 cycles. The efficacy did not improve with every cycle as was found in the test facility, and since the dominant mechanism in the columns was adsorptive-catalytic oxidation it can be concluded that this mechanism was not responsible for increasing efficacies at the test facility. Apparently this mechanism does not provide sufficient new adsorptive surface area through freshly formed iron hydroxides to improve the system's efficacy with every cycle. Hence, the mechanism which was responsible for improved iron removal with every successive cycle in the field situation does not prevail in the columns. Unlike in the columns, at the test facility bacterial activity and/or occurrence of stagnant zones may control the improved iron removal efficacy with every cycle.

3.3. *Fe:As ratio of the groundwater*

The total amount of arsenic removed per cycle in the duplicate columns varied between 1.6 and 3.6 µmol/cycle and did not increase with every successive cycle. It appears that the sites available for arsenic adsorption are regenerated during every injection phase, but the number of sorption sites does not seem to increase due to the freshly retained iron in the columns. On average, the amount of removed arsenic per mol of removed iron is 8.4 and 10.0 mmol As/mol Fe for the duplicate columns. This is valid for an arsenic concentration

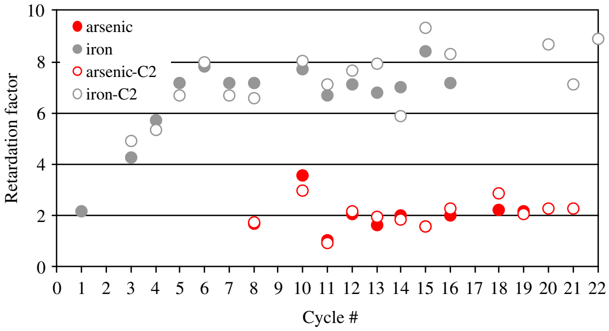

Fig. 8 – Retardation factors for iron and arsenic during successive cycles in the duplicate columns (C1 and C2).

of 3.1 µmol L^{-1} and an iron concentration of 94.9 µmol L^{-1}. The amount of available sorption sites appears stable with every cycle, so the breakthrough of arsenic would, in theory, be delayed in case of lower arsenic concentrations (Eq. (3)). To study the effect of the molar Fe:As ratio in groundwater on the adsorptive removal efficiency of arsenic, the column experiments were repeated with different arsenic(III) concentrations: 3.1, 1.5, and 0.9 µmol L^{-1}. Iron concentrations in the groundwater remained constant at 94.9 µmol L^{-1}, thus the Fe:As ratios were 28, 63, and 103. The results for arsenic breakthrough in the duplicate columns are depicted in Fig. 9. It clearly shows that, independent of arsenic concentration, the breakthrough trend and retardation factor ($R_{As} = \sim 2$) were the same at the different Fe:As ratios. In other words, the percent breakthrough curves for arsenic at different Fe:As ratios matched exactly. This implies that although the amount of removed iron was equal per cycle, the total amount of removed arsenic was not. At a Fe:As ratio of 28, 63, and 103, the total amount of removed arsenic was 3.9, 1.6, and 1.1 µmol, respectively. The sorption sites on the freshly formed iron hydroxide surfaces were apparently only available for arsenic adsorption up to a V/V_i of 7–9, independent of the Fe:As ratio. This indicates that the available sorption sites may have been occupied by other sorbates in the groundwater, such as competing anions (e.g., phosphate), which limited the adsorption of arsenic. It is noteworthy that the Fe:As ratio at the test facility was even higher than in the columns (Fe:As = 140) and also complete arsenic breakthrough occurred around V/V_i of 5–6.

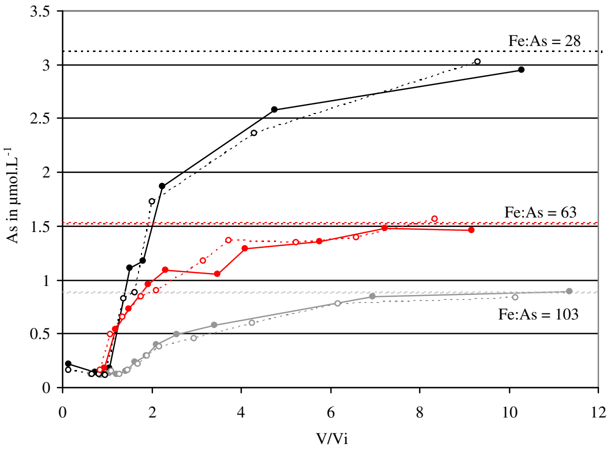

Fig. 9 – Arsenic breakthrough curves for duplicate columns at Fe:As ratio of 28 (black circles), 63 (red circles) and 103 (grey circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. *General discussion*

The total amount of iron that was removed per cycle was stable over time at an average of 0.30 and 0.29 mmol for the duplicate columns. The retardation curve for oxygen showed that only a portion of the injected oxygen was consumed for oxidation of adsorbed ferrous iron. After one pore volume, with a travel time of approximately 22 min, the oxygen concentration had reached 82% of its original concentration again. Of the total amount of injected oxygen (155 µmol) around 75–105 µmol passed the column. Only 50–80 µmol O_2/cycle was consumed during the injection phase in the columns, corresponding to the molar $Fe:O_2$ removal ratio of 4 and thus consistent with the theory of adsorptive-catalytic oxidation (Eqs. (1) and (2)). In other words, the oxidation of adsorbed ferrous iron was complete during the injection phase, illustrating that the iron oxidation reaction was fast and the adsorbed ferrous iron reacts with only a portion of the total amount of injected oxygen. For operational purposes this is an important finding, since, above a certain threshold value, the *oxygen concentration* does not control the adsorption-catalytic oxidation, but rather the *injection volume*. The key is to oxidize as much soil grain surface area as possible, since this will provide new sorption sites for iron and arsenic. It is thus unlikely that injection of chemical oxidants (such as permanganate) will improve subsurface iron removal efficiencies. Such chemicals may even inhibit any bacterial activity that could be responsible for the improved iron removal efficiency with every successive cycle. Although only a portion of injected oxygen is used for rapid heterogeneous iron oxidation, the surplus oxygen in the oxidation zone is available for consumption by other adsorbed compounds – such as iron-oxidizing bacteria.

Freshly formed iron hydroxides usually have high (adsorptive) surface areas (Cornell and Schwertmann, 1996) and enhance the removal of ferrous iron. Interfacial Electron Transfer (IET, Jeon et al., 2001, 2003) has been proposed to describe the "loss" of ferrous iron in an ferrous/ferric iron system. IET entails the transport of an electron to adsorbed ferrous iron from the incorporated iron hydroxide, creating new sorption sites at the surface. The theory of IET could provide an explanation for the improved subsurface iron removal efficiency at the test facility; however, these results were not reproduced by the adsorptive-catalytic oxidation in the columns. It is therefore more likely that other processes, such as bacterial activity or transport phenomena, are responsible for the enhanced iron removal in full-scale facilities.

The community-scale test facility in Manikganj has shown that iron removal increases after multiple cycles, but arsenic removal remains stable at a retardation factor of 2. Hence, the amount of arsenic removed per mol of removed iron reduces with every successive cycle. This indicates that arsenic adsorption during subsurface treatment is controlled by the amount of *oxidized* iron, and not by the amount of *removed* iron. In the columns, the arsenic adsorption is also stable at $R_{As} = 2$ but, unlike at the test facility, iron removal does not improve with every successive cycle. The mechanism of adsorptive-catalytic oxidation is isolated in the columns from other potential removal processes, showing that subsurface arsenic removal is, indeed, controlled by the amount of oxidized iron per cycle. In the field, enhancement of subsurface arsenic removal can therefore only be achieved by increasing the oxidation zone, i.e. the volume of injected water. A high molar Fe:As ratio of the groundwater has not been shown to promote improved co-removal of arsenic with the iron. A proposed explanation for this finding is that arsenic removal is limited by the presence of other compounds in the natural groundwater, competing for the same adsorption sites. The process of arsenic adsorption is not limited by ferrous iron sorption (Dixit and Hering, 2006), but may be limited by the presence of competing anions in the multi-component environment, such as phosphate (Stachowicz et al., 2008). In the columns, phosphate concentrations were 10–37 times higher than the arsenic concentrations, and phosphate adsorption may thus dominate over arsenic adsorption. In practice, competing anions will frequently co-occur in the groundwater with arsenic and could therefore locally threat the efficacy of subsurface arsenic removal. One could overcome this limitation by improving the current design to reach larger injection volumes through utilizing rainwater for injection. In areas with heavy rainfall during the monsoon season(s), it could even be considered to combine subsurface arsenic removal with artificial rainwater recharge and recovery. With such a design, the oxidation zone is scaled-up and arsenic/iron adsorption would occur in a much larger area around the well.

4. Conclusions

- At the community-scale test facility in Bangladesh, subsurface *iron* removal showed great potential for decentralized application in rural areas. The efficacies were much higher than could be explained by the adsorptive-catalytic oxidation in the column experiments and therefore other ((a)biotic or transport) processes must contribute to the system's efficacy.
- Unlike iron removal, subsurface arsenic removal did not increase after multiple cycles, illustrating that the process which is responsible for the effective iron removal did not promote an equally effective co-removal of arsenic. The strong correlation between field and column results indicates that arsenic adsorption during subsurface treatment is controlled by the amount of adsorbed iron that is *oxidized*, and not by the amount of *removed* iron. For operational purposes this is an important finding, since apparently the oxygen concentration of the injection water does not control the arsenic removal, but rather the injection volume.
- No relation has been observed in this study between the amount of removed arsenic and the Fe:As ratio of the groundwater. It is proposed that the removal of arsenic is limited by the presence of other anions, such as phosphate, competing for the same adsorption sites.

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IN SITU TREATMENT OF ARSENIC CONTAMINATED GROUNDWATER

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ABSTRACT

Groundwater in a sand and gravel aquifer was contaminated by arsenic compounds. The extent and the As concentration of the polluted groundwater plume decreased from 1971 to 1975, whereas the content of free dissolved oxygen increased. High As concentrations (>1 mg/l) occured in groundwater with typical characteristics of a "reduced" water with negative Eh values and high concentrations of dissolved iron (up to 140 mg/l in 1971). When plotted into an As stability field diagram, the higher values (>1 mg As/l) coincided with the fields of trivalent As species, whereas the lower values (<0.1 mg As/l) fitted to the fields of the pentavalent arsenic species. Therefore it was concluded that an improvement of the oxygen supply should accelerate the natural precipitation processes. By injection of 29,000 kg $KMnO_4$ into 17 wells and piezometers the soluble As (III) species were oxidized to As (V) species, which were precipitated as $FeAsO_4$ or $Mn_3(AsO_4)_2$ or co-precipitated with Mn- and Fe-hydroxides.

INTRODUCTION

The groundwater in the vicinity of a zinc ore smelter near Cologne, West-Germany, which operated from 1913-1971, was contaminated by arsenic compounds. They originated from the flue gas wash, which used sulphurous acid solution. Its effluent was treated with $Ca(OH)_2$ solution at pH >8 to precipitate As_2O_3 as $Ca_3(AsO_4)_2$. However due to the fairly high solubility of $Ca_3(AsO_4)_2$ traces of arsenic remained in solution and seeped from the cribs into the aquifer. The contaminated groundwater plume was detected in 1971 (Ref.1). Detailed studies and efforts for removing the dissolved As from groundwater followed in the interval 1971-1979.

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HYDROGEOLOGICAL AND HYDROGEOCHEMICAL CONDITIONS

The aquifer consists of Pleistocene sands and gravels with intercalated layers of silt, clay and coarse gravels. It is underlain at 18.5 - 27 m depths by silty fine sands of Oligocene age. The average hydraulic conductivity of the Pleistocene aquifer is $2.6.10^{-3}$ m/s (range $0.5.10^{-3}$-$3.7.10^{-3}$ m/s). For the underlying Oligocene clayey and silty fine sands an average value of 1.10^{-5} m/s is quoted (Ref.1). The groundwater flow direction and velocity is controlled by the water table in the river Rhine. At mean and low discharge it flows towards the river, however during floods river water infiltrates and groundwater flows for some time landwards. Nevertheless over the whole year a general, but retarded net groundwater inflow in the river occurs. The average flow velocity is 0.9 m/d (Ref.1), but higher flow velocities and even stagnant conditions are observed at times.

In the contaminated zone 41 piezometers of different lengths were installed, some of them as piezometer nests (2 nests with 4 piezometers, 2 nests with 3 piezometers and 11 nests with 2 piezometers). In addition five injection wells were drilled in 1976/77. Thus it was possible to investigate the spatial distribution of the contaminant.

Near the cribs the sediment grains were found to be coated by yellow and brown As containing precipitates (Ref.1). The As concentration in the sediments varied in horizontal and vertical direction. In a drill hole in the centre of the contaminated zone 10 to 170 mg As/kg sediment (average 78 mg/kg) were measured, with the highest values in the lower part of the Pleistocene aquifer. With help of selective extraction methods it could be shown that As was present in form of water soluble oxides, as sulphides insoluble in dilute acids and as compounds of the type FeAsS (arsenopyrite) poorly soluble in dilute acids. Realgar (AsS), a calcium arsenate ($CaAs_2O_6$, $CaAs_2O_7$) and gypsum (containing 50 mg As/kg) could be identified mineralogically. Besides these phases microcrystals and poorly crystallized As bearing substances were observed.

The contaminated groundwater plume was characterized by reducing conditions shown by elevated contents of dissolved ferrous iron (up to 140 mg Fe^{2+}/l in 1971), negative Eh and low pH values (Table 1). This reducing condition are presumable due to the oxidation of sulphurous to sulphuric compounds which in 1971 were present in concentrations up to 2010 mg/l.

In 1971 the As concentrations were as high as 56 mg/l at 20 m depth near the source of contamination, in contrast to a natural background of $<$0.01 mg/l. The contaminated groundwater plume diminished during the

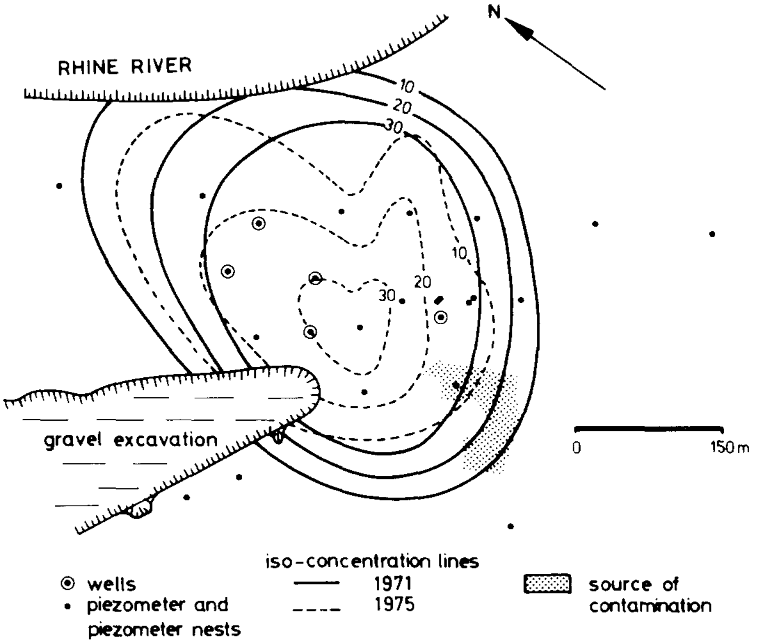

Fig. 1. As concentrations in the lower part of the aquifer

time interval 1971/1975, but the highest concentration, 26.4 mg/l, was still found in the same piezometer nest. In January 1975 Eh and pH measurements were performed together with simultaneous determination of dissolved arsenic. The observed pH-, Eh- and As-values were plotted on a stability field diagram (Ref.3). It turned out that the higher As contents (> 1 mg As/l) fell into the $HAsO_{2aq}$ field, whereas the lower contents (< 0.1 mg As/l) lie in the fields of the pentavalent arsenic species $H_2AsO_4^-$ and $HAsO_4^{2-}$. Water samples with As contents between 0.1 and 1 mg/l lie on or close to the boundary between trivalent and pentavalent As species. Therefore it was concluded that the dissolved As was present in a trivalent state and that the transfer into pentavalent species in presence of Ca^{2+}- and Fe^{2+}-ions would produce an appreciable precipitation of dissolved As. Another diagram of Hem (personal communication) including CO_2 and S species shows that at low Eh and pH values As sulphides are stable. Under oxidizing conditions the As sulphides will be oxidized to arsenate and sulphuric acid (1).

$As_2S_3 + 8O_2 + 4H_2O \rightarrow 2HAsO_4^{2-} + 3H_2SO_4$ (1)

The free acids will react with dissolved or solid substances, e.g. calcium carbonate, calcium and iron II ions.

PROCEDURES AND RESULTS

The observation that during the interval 1971/1975 the As concentration and the extension of the contaminated plume were diminished, together with a shift of the pH and Eh to higher values led to the notion to accelerate this movement toward oxidizing conditions. Therefore various oxidizing chemicals were tried out (H_2O_2, NaOCl, $KMnO_4$). It could be shown that $KMnO_4$ is a strong oxidizing agent even in dilute solution, which oxidizes As (III) in acid and basic solution to As(V). For acid solutions its effect can be described by equation (2)

$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ (2)

and for basic solutions by equation (3)

$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4OH^-$ (3)

In the contaminated groundwater plume acid and neutral pH conditions could be observed. Therefore both reactions may occur. The Mn^{2+} ions according to equation 2 may combine with the oxidized As species to form the fairly insoluble Mn II-arsenate $Mn_3(AsO_4)_2$ ($K_{SP} = 2.10^{-29}$) (Ref.5) or with Fe^{3+} ions to Fe III-arsenate ($FeAsO_4$) ($K_{SP} = 5.7.10^{-21}$) (Ref.2). Furthermore the As species may be coprecipitated with MnO_{2aq} according to equation 3 or with iron III hydroxides. Gulens et al. (Ref.4) indicated that As (V) and As (III) form complexes with Fe (III) in solution, with Fe (III) - As (III) complex being more soluble than the Fe (III)-As (V) complex. The consumption of H^+ (eqn.2) or production of OH^- (eqn.3) may shift the pH to a higher value.

After some laboratory experiments with sand filled lysimeters and some preliminary field experiments which proved that $KMnO_4$ is an effective, persistent oxidizing agent, it was decided to use a solution of about 2 g $KMnO_4$/l for the injection. This solution minimized the clogging effect close to the well screens which is due to the precipitation of iron III hydroxide and other substances. From December 1976 to May 1977 29.000 kg $KMnO_4$ were dissolved and injected into 17 wells and piezometers. The demand of $KMnO_4$ was calculated for each injection well using the measured average $KMnO_4$ demand of the water filled sediment of 0.472g $KMnO_4/m^3$. In the following time the injection water mixed with the contaminated groundwater due to dispersion in the aquifer, in which changing groundwater flow directions are typical.

TABLE 1:

pH, Eh, As-, Fe^{2+} contents and specific electrical conductance in the contaminated groundwater plume in 1971, 1975 and 1977.

	1971	1975	1977	1979
ph	3.1 - 7.0	4.8 - 7.0	5.5 - 7.8	5.8 - 8.2
Eh mV	-	-110 -+20	-100 -+440	-120 -+440
As mg/l	<0.01- 56	<0.01 - 26	<0.01 - 0.3	<0.01 - 5.6
As average mg/l	22.7	13.6	0.06	0.4
Fe^{2+} mg/l	0.2-140	<0.1 - 93.3	-	-
SO_4^{2-} mg/l	152-2010	80 -1670	-	-
Spec.electrical conductance μS/cm	-	440 -2300	600 -2250	650 -2150

The values vary according to the site and depth of the observation wells. The improvement of the groundwater quality is obvious, but as the negative Eh-values in 1977 and 1979 and the locally higher As concentrations (> 1 mg/l) in 1979 show no total mixing of contaminated water and injection water could be achieved up to now. Therefore the respective wells will be subject to new injections.

TABLE 2:

Supply of As into the river Rhine

Width of the contaminated plume	m	266
Thickness	m	20
Groundwater flow velocity	m/d	1
Groundwater discharge	m^3/d	5320
Average As concentration	g/m^3	0.06
As discharge	g/d	319.2
	g/s	$3.69 . 10^{-3}$
Rhine discharge (Emmerich) average	m^3/s	2330
Increase of As-concentration	g/m^3	$1.6 . 10^{-6}$

The As discharge, calculated for the data of 1977 (Table 2), is under the level of detection for the usual As measurement. It is about 0.01% of the up to date As discharge of the Rhine river (calculated for average discharge) and 0.3% of the natural background (Table 3, Ref.6).

Table 3:
Comparison of As discharge of the river Rhine (kg/a) and the As concentration (mg/l) (Ref. 6) with the As discharge from the contaminated groundwater plume.

		kg/a	g/s	mg/l
As discharge of the Rhine river at average discharge ($2330\ m^3/s$)	dissolved	375,000	11.89	$5.1.10^{-3}$
	suspended	500,000	15.85	$6.8.10^{-3}$
	total	875,000	27.74	$11.9.10^{-3}$
Natural background		34.000	1.08	$0.46.10^{-3}$
As discharge from Nievenheim		116.5	0.0037	$0.0016.10^{-3}$

CONCLUSIONS

The considerable reduction of the As concentration and the total amount of dissolved As species between 1971 and 1975 obviously occured without human contribution due to a gradual oxidation of trivalent to pentavalent As species and of ferrous to ferric iron species as oxygen was supplied by the seepage, the intermixture of oxygenated groundwater and gas exchange with the ground air. This oxidation favoured the precipitation of the fairly unsoluble $FeAsO_4$. This natural process was accelerated by the addition of $KMnO_4$ solution, which improved the removal of dissolved As by precipitation of $FeAsO_4$ and $Mn_3(AsO_4)_2$, by coprecipitation and adsorption of As on $Fe\ (OH)_3$ and $MnO_2\ n\ H_2O$

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