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Tailored Collaboration

In-situ Arsenic Removal During Groundwater Recharge Through Unsaturated Alluvium

Web Report #4299

Subject Area: Water Quality

In-situ Arsenic Removal During Groundwater Recharge Through Unsaturated Alluvium

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The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

In-situ Arsenic Removal During Groundwater Recharge Through Unsaturated Alluvium

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FOREWORD

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This publication is a result of a research project fully funded or funded in part by WRF subscribers. WRF’s subscription program provides a cost-effective and collaborative method for funding research in the public interest. The research investment that underpins this report will intrinsically increase in value as the findings are applied in communities throughout the world. WRF research projects are managed closely from their inception to the final report by the staff and a large cadre of volunteers who willingly contribute their time and expertise. WRF provides planning, management, and technical oversight and awards contracts to other institutions such as water utilities, universities, and engineering firms to conduct the research.

A broad spectrum of water supply issues is addressed by WRF's research agenda, including resources, treatment and operations, distribution and storage, water quality and analysis, toxicology, economics, and management. The ultimate purpose of the coordinated effort is to assist water suppliers to provide a reliable supply of safe and affordable drinking water to consumers. The true benefits of WRF’s research are realized when the results are implemented at the utility level. WRF's staff and Board of Trustees are pleased to offer this publication as a contribution toward that end.

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EXECUTIVE SUMMARY

OBJECTIVES

The purpose of this study was to determine the feasibility and sustainability of *in-situ* removal of arsenic from water infiltrated through unsaturated alluvium.

BACKGROUND

Arsenic is naturally present in aquifers throughout the southwestern United States and elsewhere. In January 2006, the U.S. Environmental Protection Agency (EPA) lowered the Maximum Contaminant Level (MCL) for arsenic from 50 to 10 micrograms per liter (μg/L). This raised concerns about naturally-occurring arsenic in groundwater. Although commercially available systems using sorbent iron or aluminum oxide resins are available to treat high-arsenic water, these systems are expensive to build and operate, and may generate hazardous waste.

Iron and aluminum oxides occur naturally on the surfaces of mineral grains that compose alluvial aquifers. In areas where alluvial deposits are unsaturated, these oxides may sorb arsenic in the same manner as commercial resins, potentially providing an effective low-cost alternative to commercially engineered treatment systems.

APPROACH

The Antelope Valley within the Mojave Desert of southern California contains a shallow water-table aquifer with arsenic concentrations of 5 μg/L, and a deeper aquifer with arsenic concentrations of 30 μg/L. Water was pumped from the deep aquifer into a pond and infiltrated through an 80 m-thick unsaturated zone as part of field-scale and laboratory experiments to treat high-arsenic groundwater and recharge the shallow water table aquifer at the site.

The field-scale recharge experiment included the following steps:

1) construction of a recharge pond
2) test drilling for sample collection and instrument installation adjacent to the pond
3) monitoring downward migration of water infiltrated from the pond
4) monitoring changes in selected trace-element concentrations as water infiltrated through the unsaturated zone

Data from instruments within the borehole adjacent to the pond were supplemented with borehole and surface geophysical data to evaluate the lateral spreading of water as it moved downward through the unsaturated zone.

Three laboratory studies were undertaken. Sequential extraction was used to evaluate the abundance of iron, aluminum, and manganese oxides and selected trace elements on operationally defined sites on the surfaces of mineral grains collected before and after infiltration from the pond. Secondly, radio-labeled arsenic-73 microcosm experiments evaluated the potential for incorporation of arsenic sorbed to exchange sites on mineral grains into less reactive crystalline mineral structures with time. Finally, column studies evaluated arsenic sorption and the pH dependence of sorption for selected unsaturated zone materials.

RESULTS/CONCLUSIONS

Between December 2010 and July 2012, more than 120,000 cubic meters (m^3) (about 97 acre-feet) of high-arsenic groundwater was pumped from the deep aquifer into a 0.11 hectare (about 0.27 acres) pond and infiltrated though an 80-meter (about 260 feet) thick unsaturated zone to recharge a water-table aquifer.

Arsenic concentrations were lowered from 30 to 2 μg/L as water infiltrated though the unsaturated zone at the site. Some uranium, possibly associated with past agricultural land use at the site, was mobilized to concentrations as high as 66 μg/L within the unsaturated zone during the experiment. Uranium was resorbed and the high uranium concentrations did not reach the water table at the site. Concentrations of other trace elements, including antimony, chromium, vanadium, and selenium were low throughout the study.

Infiltration rates from the pond were as high as 0.4 meters per day (1.1 feet per day, ft/d), and the wetting front moved downward about 25 centimeters per day (cm/d) (0.8 ft/d) to a depth of about 50 m (about 165 feet). Clay layers at that depth slowed the downward movement of the wetting front to about 5 cm/d (0.16 ft/d). Lateral movement of the wetting front was monitored using sequential direct-current (DC) surface and sequential electromagnetic (EM) and DC borehole resistivity. Most lateral movement occurred on a clay layer about 50 m (about 165 feet) below land surface. Infiltrated water reached the water table in January 2013. At the water table, the "wetted footprint" of water infiltrated from the pond, indicated by surface resistivity data, was about 13 hectares (about 32 acres). On the basis of data collected at the site, there is enough sorbent material to operate this pond and treat groundwater having an arsenic concentration of 30 μg/L to 2 μg/L for about 500 years. Toxicity Characteristic Leaching Procedure (TCLP) data showed arsenic concentrations to be below hazardous levels beneath the pond after the experiment. Pond maintenance may be required to keep infiltration rates high, and prevent accumulation of organic material on the pond bottom, although organic material on the pond bottom may increase removal of other trace elements in infiltrated water including chromium, selenium, and vanadium.

Laboratory results are consistent with the field data and show sorption of arsenic in 10 cm (0.3 feet) columns to about 2 μg/L over a pH range of 6 to 8, and at influent arsenic concentrations as high as 300 μg/L, without breakthrough in 50 pore volumes. Column results suggest that the *in-situ* treatment may remove arsenic in a range of hydrogeologic settings, and would not necessarily be restricted to alkaline alluvial aquifers common throughout the southwestern United States. Radiolabeled arsenic-73 experiments show that although arsenic is initially weakly sorbed (and potentially mobile), with time arsenic is incorporated into amorphous materials. One year after sorption onto surface exchange sites, most sorbed arsenic is incorporated into crystalline oxide minerals on the surfaces of primary mineral grains and is less mobile.

Results of the study suggest that long-term land use restrictions on sites used for *in-situ* treatment of arsenic may not be needed to control water applied to surface materials. This minimizes some regulatory concerns about future land use at sites used for *in-situ* arsenic treatment. However, future land uses that may alter reduction-oxidation conditions in the subsurface should be avoided, such as infiltration of stormwater recharge or recharge with other water having high organic carbon concentrations (including unsewered residential land use, dairy or other confined animal operations).

APPLICATIONS/GUIDANCE

Results of this study provide an inexpensive arsenic treatment method for water utilities. The approach is especially attractive for aquifers that can no longer be used as a source of public supply because of regulatory changes. These aquifers can once again be pumped, treated using *in-situ* methods, and ultimately used for public supply. Some deeper aquifers have higher heads than shallower aquifers. In such cases, pumping deeper aquifers to recharge shallower aquifers reduces the pressure in the deeper aquifer. This minimizes potential water quality degradation in the shallower aquifer from movement of poor-quality water from depth through wells and other connections between the aquifers. Pumping for groundwater recharge does not need to meet the peak capacity demands required by public-supply wells. This can be accomplished less expensively with smaller wells than those needed for public supply that can be pumped during off-peak periods of lower electrical costs. The approach was intended for arid areas of the southwestern United States having thick unsaturated zones and multiple aquifer systems. Laboratory column experiments suggest this approach also will be effective in other hydrogeologic settings outside the arid southwestern United States.

RESEARCH PARTNERS

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PARTICIPANTS

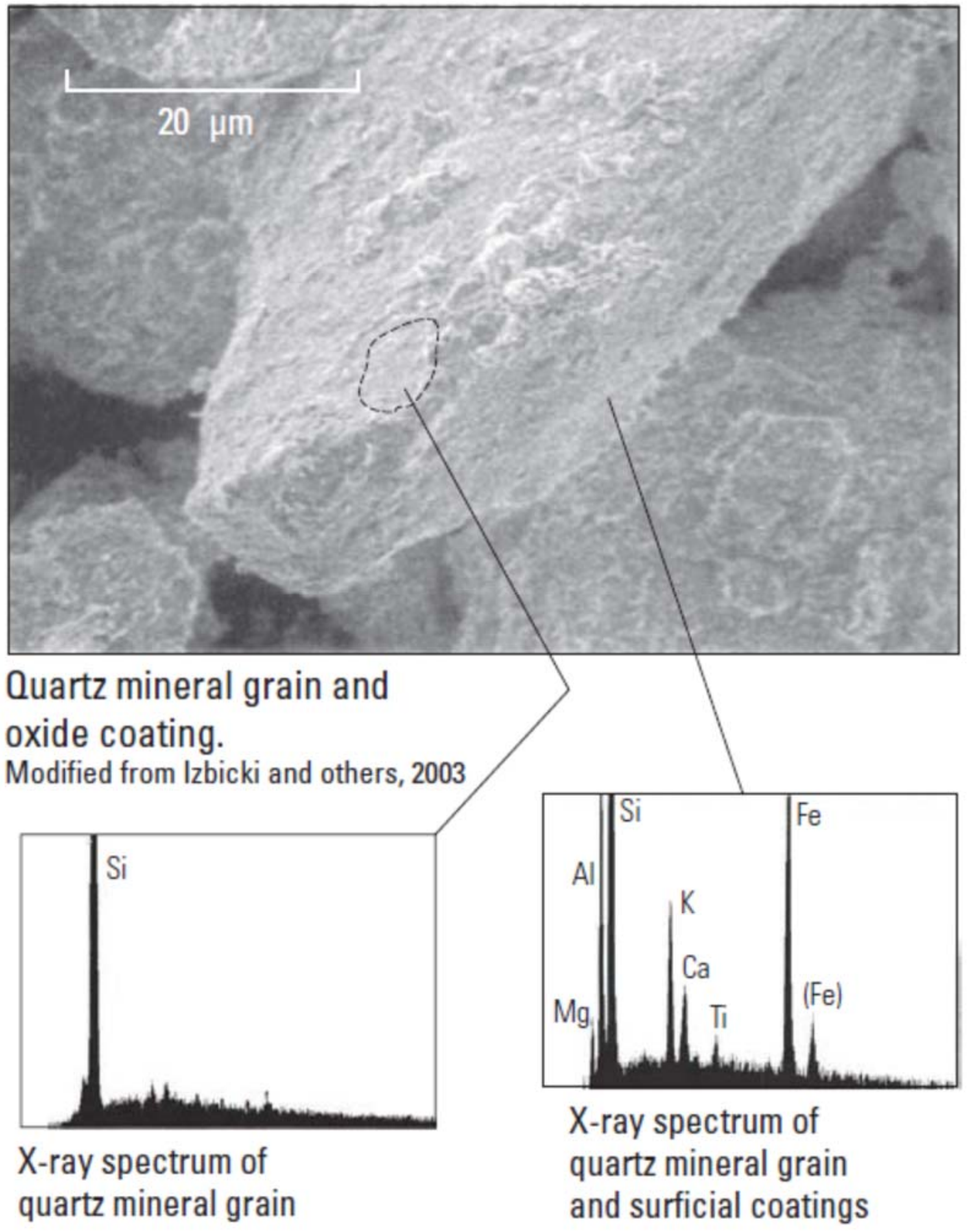
Field studies including test-drilling, instrument installation, site characterization, and monitoring were conducted by the U.S. Geological Survey, California Water Science Center. Column studies were conducted by Donald Suarez at the U.S. Agricultural Research Service, Riverside, Calif. Arsenic-73 experiments were conducted by Thomas Kulp, U.S. Geological Survey, National Research Program, Menlo Park, Calif.

Field support including use of the study site, and pumping of high-arsenic groundwater, was provided by the Antelope Valley-East Kern Water Agency (AVEK).

CHAPTER 1: INTRODUCTION

Arsenic occurs naturally in groundwater within the United States (Focazio, et al., 1999; U.S. Geological Survey, 2000) and throughout the world (Smedley and Kinniburgh, 2002) at concentrations of concern for human health. The mobility of arsenic is influenced by reduction-oxidation (redox) conditions, and arsenic can be present in water in either the reduced form arsenite, As (III), or in the oxidized form arsenate, As (V). The potential for acute arsenic poisoning has been known more the 2,400 years (Ravenscroft, 2007). Chronic exposure to arsenic in drinking water can contribute to lung and bladder cancer (Morales et al., 2000), and recent data show the health of more than 137 million people worldwide may be affected by arsenic in drinking water (Ravenscroft, 2007). Regulatory concern over naturally-occurring arsenic concentrations in groundwater within the United States resulted in a decrease in the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) for arsenic in drinking water from 50 to 10 micrograms per liter (µg/L), effective January 2006 (Federal Register, 2001).

Although ultimately the source of naturally-occurring arsenic in groundwater is mineral weathering, arsenic is concentrated by natural processes within iron, aluminum, and manganese oxides present on the surfaces of mineral grains within aquifers (Figure 1.1). Changes in the equilibrium between groundwater and these oxide coatings can mobilize arsenic either through 1) changes in pH that allow arsenic to desorb, or 2) changes in redox conditions that dissolve oxide coatings; thereby liberating sorbed arsenic and arsenic incorporated within the oxides (Stollenwerk, 2003). Although commercial application of iron, aluminum, and manganese oxides to remove arsenic from groundwater in engineered treatment systems is widespread, the use of naturally-occurring, ubiquitous iron, aluminum, and manganese oxides to sorb arsenic *in situ* within natural systems has not been previously studied.



Source: Adapted from Izbicki et al. 2003

Figure 1.1 Iron and aluminum oxide coatings on the surface of a mineral grain

Arsenic, primarily as As (V) is naturally occurring in groundwater at concentrations of about 30 µg/L in the deep aquifer underlying the western part of the Antelope Valley, approximately 100 kilometers (km) north of Los Angeles (Figure 1.2) (Pedersen and Ariki, 2007; Halford et al., 2010). Arsenic is present at lower concentrations, about 5 µg/L, in groundwater in the overlying shallow water-table aquifer. Since implementation of the 10 µg/L MCL for arsenic in January 2006, water from the deeper aquifer is no longer suitable as a source of public supply without treatment or blending. Throughout the Antelope Valley, loss of supply from deep aquifers and subsequent increased pumping from shallow aquifers occurred while the area was undergoing adjudication as a result of pumping in excess of recharge and subsequent water-level declines. To further complicate water-supply issues, imported water from the California Aqueduct is increasingly less available, while the demand for water is increasing as a result of population growth in nearby Palmdale and Lancaster.

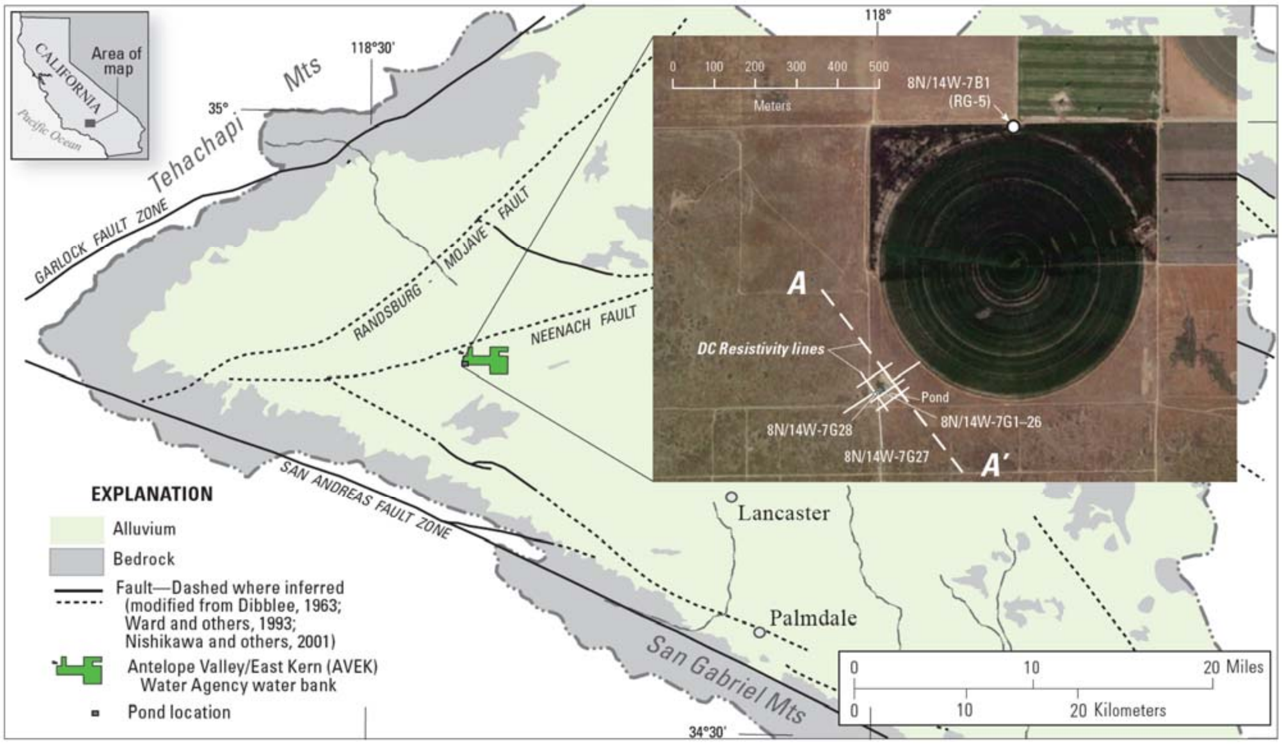


Figure 1.2 Study area location

Previous work showed that naturally occurring iron, aluminum, and manganese oxides on the surfaces of mineral grains sorb arsenic as water infiltrates through the unsaturated zone (Izbicki et al., 2008a). Thus, it may be possible to pump groundwater from deeper aquifers into ponds and treat the water to remove arsenic by infiltrating it through the unsaturated zone. After infiltration through the unsaturated zone, high-arsenic groundwater from the deep aquifer would serve as a source of low-arsenic recharge water to the shallow aquifer, where it could be pumped for public supply without additional arsenic removal or blending.

HYDROGEOLOGIC SETTING

The study site is located in the western part of the Antelope Valley, in the Mojave Desert about 100 km north of Los Angeles (Figure 1.2). Climate of the area is cold and wet in winter, and hot and dry during summer. Low temperatures are commonly below freezing during the winter, and daytime high temperatures commonly exceed 38° Celsius (about 100° Fahrenheit) during the summer. Average annual precipitation is about 190 mm, with most precipitation falling between

December and March. Like most areas of the Mojave Desert, areal recharge from infiltration of precipitation to depths below the root zone did not occur prior to development (Izbicki et al., 2000a; Izbicki 2002b and 2007). After development for agriculture, naturally occurring soluble salts, such as chloride, that accumulated in the unsaturated zone since areal recharge last occurred were leached from the subsurface. These naturally-occurring salts were replaced with salts derived from irrigation return that accumulated in low-permeability layers within the unsaturated zone.

The study site is on alluvial fan deposits eroded from granitic rocks in the San Gabriel Mountains (Figure 1.2). The alluvial fan deposits consist of a heterogeneous mixture of gravel, sand, silt, and clay. Fine-grained, low-permeability deposits occupy low-lying areas near the margin of the fan to the north of the site. Lacustrine deposits associated with dry lake beds that form the "blue clay" which separates upper and lower aquifers in much of Antelope Valley are not present in this area. The extent of the alluvial fan deposits and the position of finer-grained deposits near the fan margin changed through geologic time as a result of changes in relative erosion rates from mountains surrounding the valley. For example, in the past when the altitude of the San Gabriel Mountains was lower, less alluvial material was eroded from this source, the alluvial fan was smaller, and the fan margin was closer to the mountain front to the south of its present location. As uplift in the San Gabriel Mountains continued, more material was eroded and carried farther into the valley. As the alluvial fan extended farther into the valley, previously deposited fine-grained fan margin deposits were buried—creating thick, areally-extensive clay layers at depth.

For purposes of this study an unlined 0.11 hectare pond, dug to a depth of about 2 meters (m), was constructed (Figure 1.3). The pond was oriented with a longer axis (49 m) perpendicular to the slope of the alluvial fan, and a shorter axis (22.5 m) parallel with the slope of the fan. The pond is on the southwestern corner of 600 hectares of land developed as a water bank by the Antelope Valley-East Kern (AVEK) Water Agency (Figure 1.2). Soil at the pond is a fine-sandy loam (U.S Department of Agriculture, 2009), having a hydraulic conductivity of 4.4 x 10^{-3} centimeters per second (cm/s) at the surface, and 1.1 x 10^{-3} cm/s at a depth of 1 m (Peter Martin, U.S. Geological Survey written comm., 2010). Although currently fallow, the land was previously irrigated and farmed for row crops and alfalfa. Alfalfa farming continued during this study to the north (Figure 1.2).

Figure 1.3 Photograph showing recharge pond used for *in-situ* removal of arsenic, July 2011, and the fine-grained organic layer with "gleyed" (a discoloration associated with reduced conditions) alluvium, near Palmdale, California, August 2013

Depth to water is about 80 m. On the basis of test-drilling data collected for site characterization at the AVEK water bank (Peter Martin, U.S. Geological Survey written comm., 2010), alluvial deposits consist of interbedded, heterogeneous mixtures of silt, sand, and gravel, and are divided into a shallow and a deep aquifer. The shallow aquifer, from the water table to a depth of about 98 m, contains groundwater having an arsenic concentration of about 5 µg/L. Groundwater deeper than 98 m has arsenic concentrations greater than the U.S. Environmental Protection Agency MCL for arsenic of 10 µg/L. Hydraulic conductivities are higher in the shallow aquifer and lower in the deeper aquifer. Water for the experiment was piped to the pond from well 8N/14W-7B1 (7B1, locally known as RG-5), 830 m to the northeast of the pond (Figure 1.2). Water from the well has an arsenic concentration of about 30 µg/L.

PURPOSE AND SCOPE

The purpose of this study was to determine the feasibility and sustainability of *in-situ* removal of arsenic from water infiltrated through unsaturated materials in the western Antelope Valley, California. The scope of the study included a field-scale recharge experiment and laboratory data collection. The field-scale recharge experiment included: 1) construction of a recharge pond, 2) test drilling for sample collection and instrument installation adjacent to the pond, 3) monitoring downward migration of water infiltrated from the pond, and 4) monitoring changes in selected trace-element concentrations as water infiltrated through the unsaturated zone. Data from instruments within the borehole adjacent to the pond were supplemented with borehole and surface geophysical data to evaluate the lateral spreading of water as it moved downward through the unsaturated zone. Laboratory studies included: 1) sequential extraction to evaluate the abundance of iron, aluminum, and manganese oxides and selected trace elements within operationally defined sites on the surfaces of mineral grains collected before and after infiltration from the pond, 2) radiolabeled arsenic-73 microcosm experiments to evaluate potential for incorporation of arsenic sorbed to exchange sites on mineral grains into less reactive crystalline mineral structures with time, and 3) column studies to evaluate arsenic sorption and the pH dependence of sorption for selected unsaturated zone materials.

CHAPTER 2: METHODS

DRILLING, INSTRUMENT INSTALLATION, AND FIELD DATA COLLECTION

An instrumented borehole was installed through the unsaturated zone into the water table adjacent to the pond location prior to pond construction. Drilling was done using the ODEX (Overburden Drilling EXploration) technique (Hammermeister et al., 1986; Izbicki, et al., 2000b). The technique uses air as a drilling fluid rather than water, which would alter water content and matric potential of unsaturated deposits. During ODEX drilling, the hole was stabilized by a 22-cm-diameter steel pipe inserted into the borehole behind an eccentric drill bit that drills a hole slightly larger than the outside diameter of the pipe.

Cuttings from the drill holes were logged at 0.3-m intervals. The lithology of drill cuttings was described in the field. Subsamples of cuttings were mixed with distilled water on an approximate one-to-one per weight basis, and the specific conductance of the leachate was measured in the field (Figure 2.1). Subsamples of cuttings were saved for laboratory analysis of physical properties, and soluble anions (chloride, nitrate, and sulfate) using procedures described by Izbicki et al. (2000b). Trace element concentrations in sequential extracts from these materials were determined using procedures modified by Chao and Sanzolone (1989) and Wenzel et al. (2001). Cores were collected at selected depths using a 0.6-m-long, 10-cm-diameter piston core barrel. Cores were capped, labeled, wrapped in plastic, and stored in heat-sealable aluminum pouches immediately after collection according to procedures described by Izbicki et al. (2000b) and Hammermeister et al. (1986). Cuttings and cores were used for laboratory analysis of physical and hydraulic properties, and chemical concentrations including soluble salts and trace elements.

In addition to sample collection during ODEX drilling, samples of organic material on the pond bottom, and samples of alluvium were collected 1) immediately beneath the organic layer within gleyed alluvium (discolored by redox processes), 2) within iron-enriched alluvium beneath the gleyed layer and 3) using hand augers at a depth of 1 m below the pond (Figure 1.3) were collected in August 2012 after infiltration from the pond ceased. These samples were handled using the same methods as the ODEX cuttings and used for laboratory analysis of trace-element concentrations, including Toxicity Characteristic Leaching Protocol analyses for arsenic.

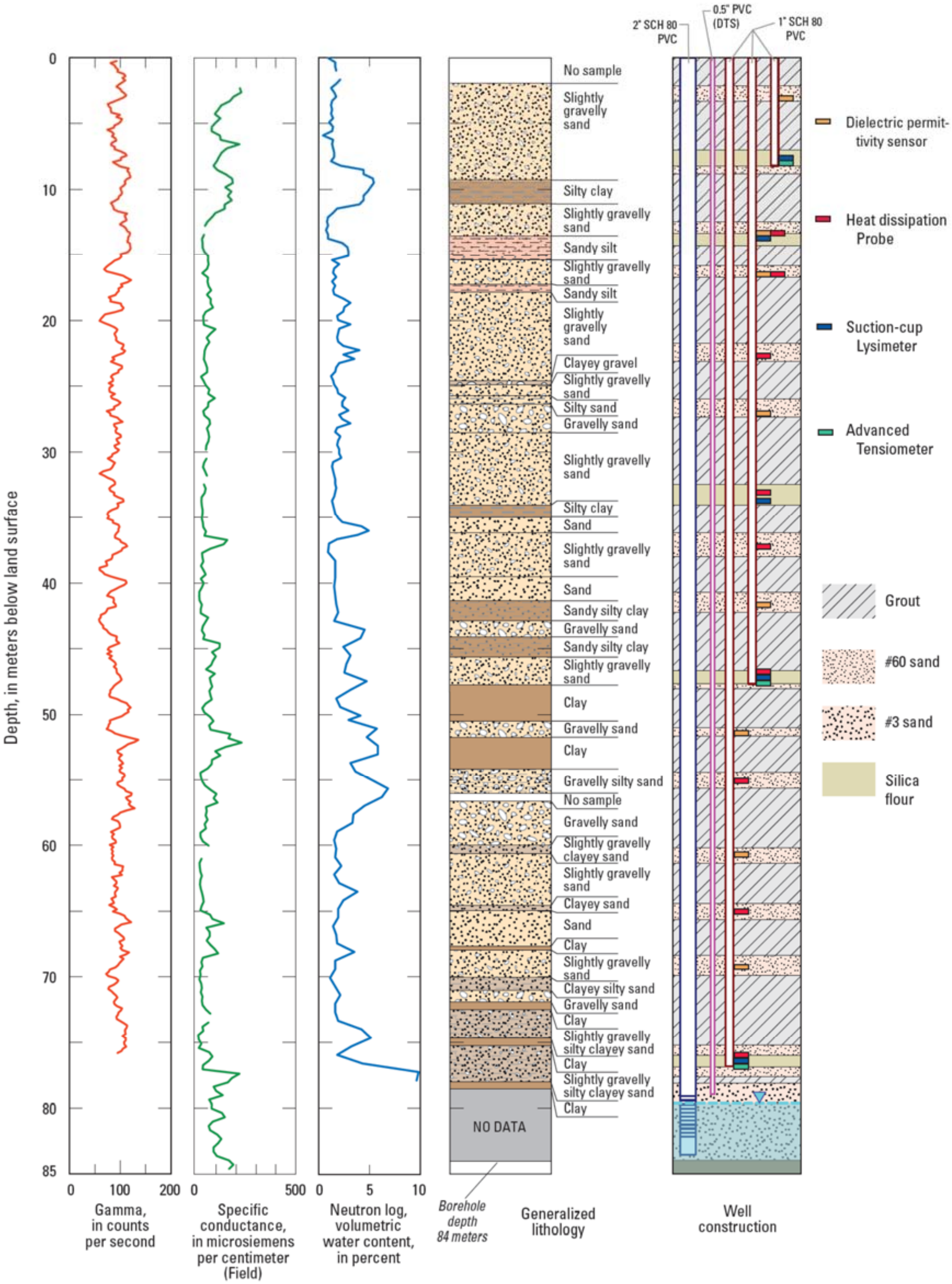


Figure 2.1 Simplified lithology, selected geophysical logs, and instrumentation installed within an unsaturated zone monitoring site adjacent to a recharge pond used for *in-situ* removal of arsenic, near Palmdale, California

Natural gamma and neutron logs (Figure 2.1) were collected from the borehole while the ODEX pipe was still in the ground. Although attenuation of the gamma and neutron signal occurs through the steel pipe, relative changes in the logs were used to identify clay layers, and materials having higher water content. Instruments were installed in the borehole on the basis of lithologic, geophysical, and chemical data collected during test drilling. Instruments included a 5-cm diameter polyvinyl chloride (PVC) well that was screened at the water table. In addition to measurements of water-levels and water-quality sample collection, the well provided access for repeated geophysical measurements of using an electromagnetic (EM) resistivity tool.

Matric potential sensors, including advanced tensiometers (Hubble and Sisson 1998), heat-dissipation probes (Reece 1996), and dielectric-permittivity sensors (Decagon Devices, Inc., 2011), were installed at selected depths within the borehole (Figure 2.1) to measure changes in matric potential before, during, and after infiltration from the pond. Matric potential is a measure of how tightly water is held within unsaturated material (Jury et al., 1991). Each instrument was packed within fine-grained rock flour or sand to ensure hydraulic contact with the surrounding unsaturated zone (Figure 2.1). A mixture of low-permeability bentonite grout and coarse sand (for structural support) was used to seal the borehole between instruments and prevent downward movement of water through the borehole. The bentonite was installed dry. Repeated neutron logging at similar sites in the Mojave Desert showed the bentonite hydrates within several months after installation to ensure an adequate seal between instruments within the borehole prior to recharge (Izbicki et al., 2008b).

Pressure transducers within the advanced tensiometers measure negative pressure (matric potential) within the tensiometer range between 0 and about -8 m of water (Cassell and Klute 1986). These transducers also measure positive pressures as great as 8 m of water. Advanced tensiometers were installed above clay layers where the downward movement of water would be impeded, and wet (or even saturated) conditions were expected to develop during recharge. The advanced tensiometers were connected to the surface through a 2.5-cm-diameter PVC pipe, so that only a limited number (usually not more than three) could be installed in a single borehole.

Heat-dissipation probes measure the rate of movement of heat in a calibrated ceramic; in which, heat movement varies with water content (Phene et al. 1971a, 1971b). The probes are individually calibrated to allow the raw data to be converted to matric potential (Flint et al. 2002). The range of matric potential for the probes is from about -10 to -2,500 kiloPascals (kPa) (equivalent to -1 to -255 m H_2O), which is drier than the tensiometer range. Heat-dissipation probes were commonly installed below clay layers, and in more massive lithologic units where saturated conditions were not likely to develop during recharge.

Dielectric-permittivity sensors measure the ability of a calibrated ceramic to store an electric charge, which varies with water content (Decagon Devices, Inc., 2011). These probes were individually calibrated in a manner similar to heat-dissipation probes. The range of matric potentials for calibrated probes is from greater than -10 to -500 kPa (equivalent to -1 to -51 m H_2O), and is between the tensiometer range and the heat-dissipation probe range.

Advanced tensiometers, heat-dissipation probes, and dielectric-permittivity sensors were controlled by data loggers in a vault at land surface, and data were collected at 4 hour intervals during the study. Arrival of the wetting front was identified by increases in matric potential (less negative values), and in some cases the development of perched conditions (positive pressure) measured by the tensiometers.

Suction-cup lysimeters installed within the borehole using procedures described by Izbicki et al., (2000b) enable collection of water-quality samples during recharge. Suction-cup lysimeters, 4.8 centimeters (cm) in diameter and 77 cm long, were commonly paired with advanced tensiometers, heat-dissipation probes, or dielectric-permittivity sensors to relate changes in water quality with changes in matric potential (or pressure) data. The suction-cup lysimeters were rinsed repeatedly with a mild acid solution and water was extracted and analyzed prior to installation to ensure trace-element concentrations were below reporting levels. Suction-cup lysimeters were sampled at approximately 6-week intervals during the study. Depending on the water content in the surrounding material, the lysimeters may yield as much as 250 milliliters (ml) of water. Arrival of the wetting front was easily identifiable as lysimeters which did not previously yield water began to yield water.

In addition to the instrumented ODEX borehole, two 10-cm diameter mud-rotary boreholes were drilled 7.6 and 15 m southwest of the ODEX borehole (Figure 1.2). A 5-cm diameter PVC access tube was installed within each borehole to a depth of 24 m to provide access for sequential EM resistivity data collection. In addition, a direct-current (DC) resistivity cable having electrodes spaced at 1-m intervals was attached to the PVC access tube and installed within each borehole. Because these boreholes were drilled using mud (rather than air) as a drilling fluid, they could be drilled and instrumented in less time and for less money than the ODEX boreholes. However, fewer instruments could be installed within the mud-rotary boreholes, and water-quality data could not be collected from these boreholes.

A Century 9511 EM tool was used to collect sequential EM resistivity data from the borehole adjacent to the pond. The tool is sensitive to differences in the lithology and water content of unsaturated materials within a donut-shaped torus having an inner diameter of about 46 and an outer diameter of about 127 cm (Century Geophysical Corp., 2008). As a consequence the tool is relatively insensitive to the borehole fill material adjacent to the PVC access tube (McNeill, et al., 1990). Because the lithology of the material within the unsaturated zone stays constant, changes in EM resistivity measured during this experiment were the result of changes in water content resulting from infiltration of water from the pond. This is similar to the approach used to monitor movement of water infiltrated from ponds by Ferre et al. (2007), and to measure changes in water quality within aquifers by Metzger and Izbicki (2013). Sequential EM resistivity logs also were collected from access tubes within the mud-rotary boreholes drilled at the site.

Information on the downward and lateral movement of the wetting front from the pond also was obtained using surface Direct-Current (DC) resistivity data collected using an Advanced Geosciences Inc. (AGI) SuperSting R8 imaging system along lines parallel to and perpendicular to the pond (Figure 1.2). Electrode spacing along the lines ranged from 2 to 10 m. The 2-m spacing provided detail to evaluate lateral movement of water from the pond at depths from 10 to 17 m below land surface. The 10-m spacing enabled greater penetration of the electrical current to collect data throughout the 80 m thick unsaturated zone. Electrodes were placed in holes filled with bentonite hydrated with saline water to ensure electrical contact with the dry surficial material typical of the Mojave Desert. Data were collected using Dipole-Dipole and Wenner arrays using command files generated by the manufacturer's software (AGI SuperSting Administrator - v1.3.5.215), and interpreted using AGI EarthImager 2D software v2.4.0. In addition to surface DC-resistivity data, borehole DC-resistivity data were collected from custom-built cables, having an electrode spacing of 1 m, buried within the mud-rotary boreholes to provide additional depth-dependent data on changes in electrical resistivity within the subsurface. The DC-resistivity approach measures changes in electrical resistance of the unsaturated zone at greater distances from the borehole than the EM resistivity approach. Borehole DC resistivity data were processed manually. Surface DC-resistivity lines and cables installed within the mud-rotary boreholes were periodically reoccupied during the course of the study to evaluate changes in apparent resistivity with time. Similar to the approach used for borehole EM-resistivity data collection and interpretation, changes in EM resistivity measured during this experiment were interpreted as changes in water content, assuming lithology remained constant. Signal penetration and data quality (dependent on the electrical properties of the subsurface near each line) increased during the experiment as infiltration from the pond wetted the unsaturated materials.

Water-quality data were collected periodically from the discharge of production well 7B1 that supplied water to the pond, from within the pond, and from the water-table monitoring well within the instrumented borehole, 7G1. Samples from the water-table well were collected using a temporary pump. Samples from suction-cup lysimeters were collected using procedures described by Izbicki, et al. (2000b). Samples from the production well, pond, and monitoring well were filtered in the field and field parameters (pH, alkalinity, specific conductance, temperature, and dissolved oxygen) were measured. Samples from lysimeters were not filtered, as the porous ceramic cup provided filtration for the sample prior to collection. Field parameters (pH, were specific conductance) were measured, assuming sufficient sample volume was obtained. Samples for cation analysis were preserved in the field to a pH less than 2 using nitric acid. Samples were chilled on ice. Samples for trace elements discussed in this paper were analyzed at the U.S Geological Survey National Water Quality Laboratory (NWQL) using methods described by Fishman and Friedman (1989), Fishman (1993), and Garbarino et al. (2006). Not all analyses on sample water collected at the site are discussed in this paper; however, those data are available on-line from the U.S. Geological Survey's computerized data base National Water Information System (NWIS) at http://waterdata.usgs.gov/nwis.

SEQUENTIAL EXTRACTION PROCEDURES

Selected trace elements were extracted from sorption sites, amorphous oxides, and crystalline oxides on the surfaces of mineral grains from alluvium collected during test drilling. Selected samples of alluvium were homogenized and split using a soil splitter at the U.S. Department of Agriculture Soil Salinity Laboratory, Riverside, Calif. The homogenized, split samples were used for sequential extractions, arsenic-73 batch experiments, and column experiments discussed later in this paper.

The sequential extraction procedure used in this study was modified from procedures described by Chao and Sanzolone (1989) and Wentzel et al. (2001), and the extractions were done at the U.S. Geological Survey Laboratory in San Diego, Calif. Each step within the procedure is intended to extract trace elements from operationally-defined sorption sites on the surfaces of the mineral grains. Prior to the initial extraction, the alluvium was weighed, air-dried, reweighed (to determine initial moisture content), gently crushed to break-up aggregates (if required), and sieved through a #18 mesh to provide a consistent matrix for analysis and for comparison of data from different samples. In addition to environmental samples sequential extractions also were done on alluvium (from 19.9 to 20 m) that had been washed in 10 percent HCl for 2 weeks to remove iron, aluminum, and manganese oxides on the mineral surfaces. These samples were intended as controls for the extraction procedure but the results were not suitable for this purpose. The authors suggest the use of artificial material such as glass beads as controls for future work of this type.

For the first extraction, 20 grams (g) of sample was mixed with 100 ml of 0.25M potassium chloride (KCl) solution and shaken at 20°C for 4 hours on a wrist-action shaker. Operationally, this step was intended to extract "non-specifically sorbed" trace elements associated with dissolved and water-soluble material within the sample. For the second extraction, sample material recovered from the first extraction was mixed with 100 ml of 0.05 M ammonium dihydrogen phosphate (ADP) [$(NH_4)H_2PO4$], solution and shaken at 20°C for 16 hours. This step was intended to extract "specifically-sorbed" trace elements that may be mobilized by changes in pH or by exchange with more strongly sorbed oxyanions. After the second extraction, the sample was split into two 10 g subsamples. For the third extraction, one 10 g split of sample material recovered from the second extraction was mixed with 50 ml of 0.2M ammonium-oxalate buffer [$(NH4)_2C_2O_4 \cdot H_2O$] at pH 3.25 and 20° C, and shaken for 4 hours in the dark. This step was intended to extract trace elements associated with poorly-crystalized (amorphous) iron, aluminum, and manganese oxides on the surfaces of mineral grains. For the fourth extraction, the 10 g split recovered from the third extraction was mixed with 50 ml of a 0.2M ammonium-oxalate and 0.1M ascorbic acid [$C_6H_8O_6$] solution at pH 3.25 and 96°C, and shaken for 30 minutes. This step was intended to extract trace elements associated with well-crystalized iron, aluminum, and manganese oxides on the surfaces of mineral grains. A fifth extraction using 50 ml of 4M nitric acid [HNO_3] (Chao and Sanzolone, 1989) was done the material recovered from the fourth extraction to ensure dissolution of trace elements associated with iron, aluminum and manganese oxides. This extraction was incorporated into the procedure after it was apparent from arsenic-73 experiments and comparison with similar sequential extraction data (Izbicki, et al., 2008a) that the fourth extraction step (Wenzel et al., 2001) was not sufficiently vigorous to extract the trace elements associated with well-crystalized iron, manganese, and aluminum oxides on mineral surfaces within the sample. An additional sixth extraction on the other 10 g sample split obtained after the second extraction also was done. Results from this additional extraction are comparable to 4M HNO_3 extraction data collected elsewhere in the Mojave Desert (Izbicki et al., 2008a) using procedures described by Chao and Sanzolone (1989). More vigorous extractions, using hydrofluoric acid and aqua regia (Chao and Sanzolone, 1989) or nitric acid with hydrogen peroxide and microwave digestion (Wenzel et al., 2001), intended to dissolve sulfide, and silicate minerals were not done.

Between each extraction, the solid material was separated from the supernatant by centrifugation. The centrifuged sample material was rinsed with 30 ml of deionized water, and centrifuged after each rinse. The rinse water was decanted to waste. The sample was air-dried and weighed to track sample mass recovery through the various extraction steps. The supernatant was filtered through 0.45 µm pore-sized filters, preserved with HNO_3, and analyzed using Inductively coupled plasma mass spectrometry (ICP-MS) (Fishman and Friedman, 1989; Fishman, 1993; Garbarino and others, 2006) for Al, Fe, Mn, As, Cr, V, and U at the U.S. Geological Survey National Water Quality (NWQL) in Denver, Colo. Equipment blanks done at the time of the extractions showed all trace element concentrations to be less than their respective reporting limits.

Trace-element concentrations in sequential extraction data reported in Tables 3.2-3.4 (later in this paper) are reported in µg/L of extractant. Results are discussed in the paper as mg/kg of alluvium. To convert between the values the elemental mass in the extract (concentration in milligrams per liter divided by the volume of extractant in liters) is divided by the mass of alluvium (in kilograms) used to prepare the extract.

ARSENIC-73 EXPERIMENTS

Arsenic-73, a man-made radioactive isotope of arsenic having a half-life of 80.3 days, was added as a tracer to microcosms prepared from samples of alluvial material obtained from eight depths during drilling. The sample depths were selected to cover a range of textures and colors (presumably reflecting ranges in iron oxide surface coating abundance and mineralogy). Alluvium from each sample depth was homogenized and split at the USDA Soil Salinity Laboratory in

Riverside, Calif. and is a replicate of the material used for sequential extractions. Four complete sets of microcosms were prepared; each set included duplicate microcosms representing each of the eight sample depths (16 microcosms per set). The microcosms were prepared in 50 ml Nalgene centrifuge tubes, using 10 cm^3 of alluvium and 10 ml of water prepared to match the major-ion, arsenic (30 µg/L) concentration, and pH (8.0) of water from well 7B1 used for the recharge experiment. Each microcosm set also contained duplicate microcosms prepared from acid-washed alluvium (from 19.9 to 20 m) similar to controls used for the sequential extraction procedures. The authors suggest artificial material, such as glass beads would be more suitable for this purpose in future studies.

The microcosms were incubated at room temperature, loosely capped during the experiment to allow exchange with atmospheric oxygen (preventing development of anaerobic conditions during the experiment), and stored in a lead-lined box. One complete set of microcosms was harvested at each of four predetermined time-steps during the 1 year experiment (0 days, 1 month, 6 months, and 12 months). The activity of arsenic-73 added to the microcosms at the beginning of the experiment ranged from 3 to 78 microCurries (µCi). More arsenic-73 was added to microcosms intended to be held for the longer time-steps, with the intent that approximately 3 µCi would be present after decay when the samples were analyzed. The experiment could not be run for longer than one year because of radiation safety concerns associated with the arsenic-73 activities needed for a longer experiment.

Arsenic was extracted from alluvium in two microcosms harvested at each time-step according to the sequential extraction procedure modified from Chao and Sanzalone (1989) and Wenzel et al. (2001) described previously. Following each step of the extraction, the extract solution was separated from the sediment pellet by centrifugation and decanted into a scintillation vial for measurement of arsenic-73 activity. Arsenic-73 activity was measured by gamma spectroscopy using a Wallac Wizard 1480 gamma counter (Perkin Elmer Inc., Waltham, MA). In addition to the activity of each extract, arsenic-73 activity in water incubated within the microcosm and in residual alluvium after the last extraction also was measured.

For each sample, the activity of arsenic-73 from each extraction was summed and compared to the decay-corrected, arsenic-73 activity expected in the sample to determine the efficiency of arsenic-73 recovery. Recovery of arsenic-73 from individual samples ranged from 84 to 99 percent. Arsenic-73 recoveries for each time-step ranged from 91 to 96 percent with an overall recovery of 94 percent. Arsenic-73 recoveries were greater during the 6 month and 1 year timesteps (95 and 96 percent respectively), possibility from increased proficiency in handling the samples. Replicate data agreed with a median precision of ± 2 percent.

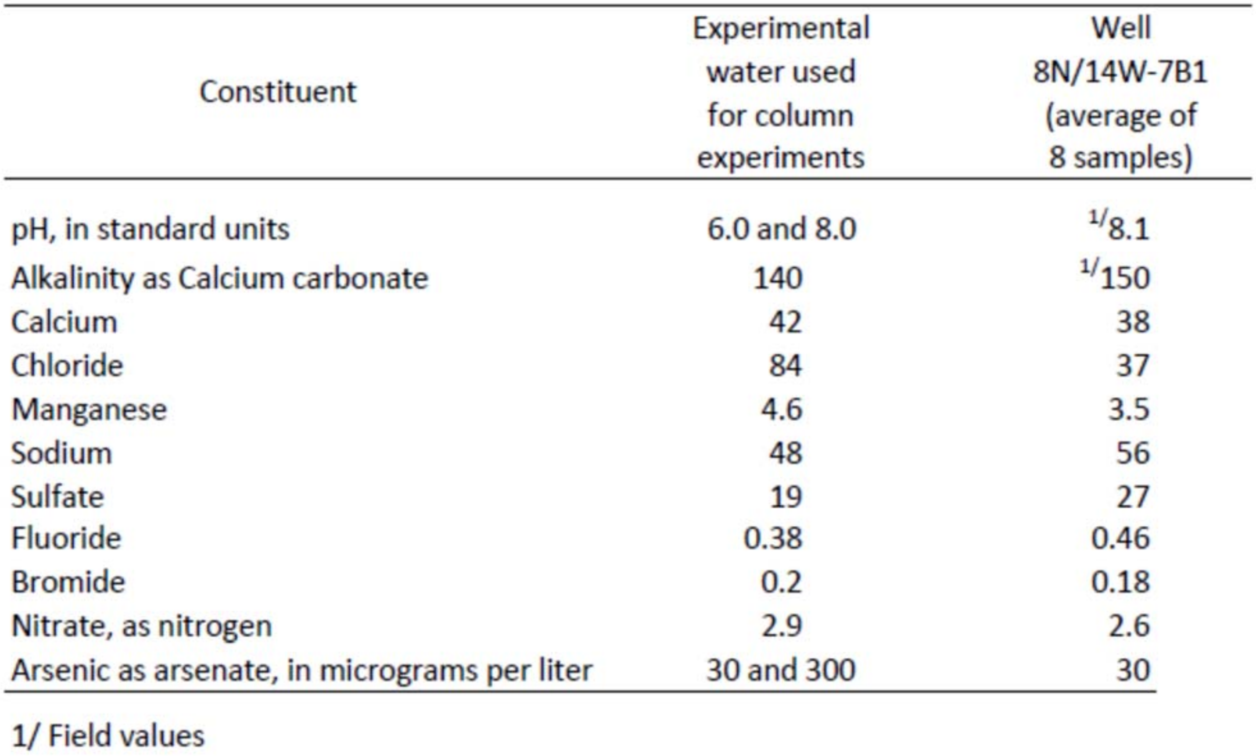
It was concluded that the ammonium-oxalate and ascorbic acid extraction was not sufficiently vigorous to extract arsenic and other trace elements associated with well-crystalized iron, manganese, and aluminum oxides, and the more aggressive strong acid (4M HNO_3) extraction (Chao and Sanzalone, 1989) was incorporated into the arsenic-73 and sequential extraction procedures. However, the samples having the largest percentage of arsenic-73 in the residual solid at time = 0 had the largest silt and clay fractions, suggesting that sorption to clay minerals also may be important.

COLUMN EXPERIMENTS

Column experiments were done at the USDA Soil Salinity Laboratory in Riverside, Calif. Air-dried alluvium from ODEX cuttings from depths of 8.5 to 9.8, 14.6 to 15.6, and 20.7 to 22.3 m were divided using a soil splitter in the same manner as alluvium used for sequential extractions and arsenic-73 microcosm experiments. Alluvium from each sample was lightly-packed into polycarbonate columns having an inside diameter of 5 cm to a height of approximately 31 cm. Bulk densities of packed columns were approximately 1.45, 1.48, and 1.86 grams per cubic centimeter (g/cm^3), respectively. These bulk densities are less than typical bulk densities for unsaturated alluvium in the Mojave Desert (Izbicki et al., 2000b) and may have (along with sample disturbance during drilling) permitted greater contact between sample material and column test solutions than occurred during the field-scale experiment.

Twelve columns were prepared for each sample to allow for three replicate column experiments using four test solutions having arsenic, as (V), concentrations of 30 and 300 µg/L, and pH's of 6 and 8. The 30 µg/L test solution approximated the arsenic concentration in water from well 7B1. The 300 µg/L test solution was used evaluate arsenic retention in the columns in the event breakthrough did not occur at the concentration in groundwater pumped into the pond. Major-ion composition of the test solutions was similar to the composition of water from well 7B1 used for the field-scale experiment (Table 2.1). However, 200 µg/L of bromide was added to the solutions to evaluate conservative breakthrough of the test solutions within the column. Prior to the experiment, polycarbonate columns, Teflon-lined tygon tubing, and other material in contact with samples and test solutions were tested to ensure there was no release or sorption of arsenic.

Table 2.1
Composition of selected constituents in water used for column experiments and water delivered to the *in-situ* arsenic treatment pond from well 8N/14W-7B1, near Palmdale, California, December 2010 to January 2013



Constituent	Experimental water used for column experiments	Well 8N/14W-7B1 (average of 8 samples)
pH, in standard units	6.0 and 8.0	$^{1/}$8.1
Alkalinity as Calcium carbonate	140	$^{1/}$150
Calcium	42	38
Chloride	84	37
Manganese	4.6	3.5
Sodium	48	56
Sulfate	19	27
Fluoride	0.38	0.46
Bromide	0.2	0.18
Nitrate, as nitrogen	2.9	2.6
Arsenic as arsenate, in micrograms per liter	30 and 300	30

1/ Field values

After the columns were packed, they were slowly saturated, from the bottom up, with a solution having the same major-ion composition as the test solutions, but without arsenic or bromide. After the columns were saturated, flow through the columns was reversed and the columns were flushed with the saturating solution. After 4 pore volumes of the saturating solution passed through the columns, the test solution containing arsenic and bromide was introduced into the columns. For the first set of columns, depth 8.5-9.8 m, the material in the columns was not flushed with saturating solution prior to addition of the test solution containing arsenic and bromide. As a consequence, bromide concentrations greater than the concentration in the test solution were measured in the column effluent until between 1 to 1.5 pore volumes moved through the columns, and naturally occurring bromide was flushed from the sample. These results prompted rinsing the column with saturating solution to remove weakly sorbed arsenic and bromide prior to the addition of the test solution.

During the experiments, 50 pore volumes were passed through each column, with the exception of the first set of columns, depth 8.5-9.8 m, which had 56 pore volumes. The flow rate during the experiments was approximately 30 ml per hour. At night, the flow rate was reduced to about 15 ml per hour, and on weekends to about 7 ml per hour. Almost 6 months were required to obtain 50 pore volumes from some columns. Samples were collected at every hour for the first 3 pore volumes and at every pore volume thereafter. Arsenic concentrations in column effluent were determined using ICP-MS with a reporting limit at or below 1 µg/L. Arsenic concentrations in effluents from triplicate columns agreed with a standard deviation of ± 5 percent.

CHAPTER 3: RESULTS

INFILTRATION OF WATER

About 121,500 m^3 of groundwater from well 7B1 was infiltrated from the pond between December 2010 and July 2012 (Figure 3.1). No water was infiltrated from the pond between March 3 and June 15, 2011 because of a pump failure in the well supplying water to the pond. Most water, about 110,000 m^3, was infiltrated between June 15, 2011 and July 19, 2012 after the pump was repaired. Water was pumped into the pond intermittently at a rate of about 38 liters per second. Infiltration rates, determined from measured inflows, from the pond were initially as high as 0.4 m/d, and declined to less than 0.2 m/d by the end of the test. Given the 0.11 ha size of the pond, the height of water infiltrated through the pond was about 100 m. On the basis of measured evaporative losses from a similar recharge pond in the Mojave Desert near Victorville, CA about 100 km east (Izbicki et al., 2008b), evaporative losses from the pond surface were estimated to be about 3.3 m/yr. Despite the desert climate, evaporative losses were not considered important compared to the volume of water infiltrated through the pond. Reduced infiltration from the pond is apparent as the change in slope of the cumulative infiltration line beginning in October 2011 (Figure 3.1).

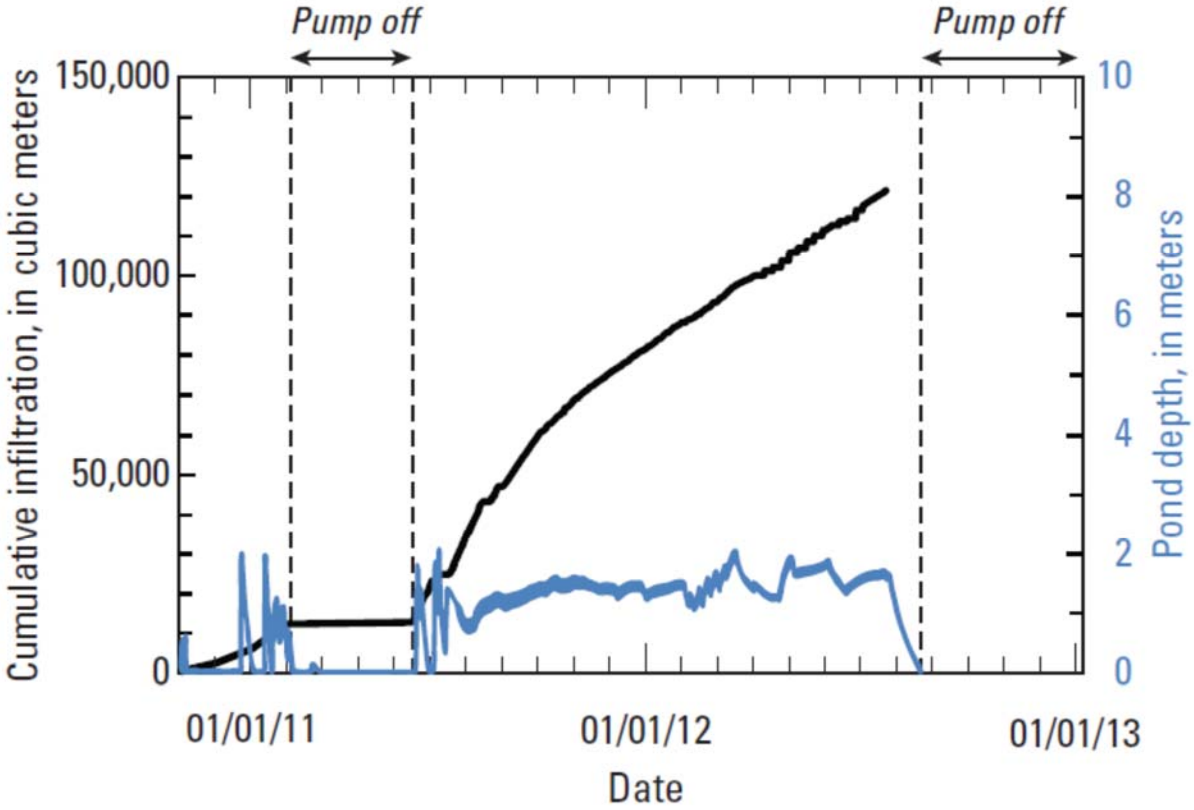


Figure 3.1 Cumulative infiltration and pond water levels from a groundwater recharge pond used for *in-situ* removal of arsenic, near Palmdale, California, December 2010 to January 2013

Reduced infiltration from the pond resulted from accumulation of fine-grained material and organic (algal) debris. By the end of the experiment, an organic layer about 1 cm thick was present at the bottom of the pond (Figure 1.3). Similar accumulations of organic material have been observed to reduce infiltration and change redox conditions in the unsaturated zone beneath recharge ponds; thereby, increasing arsenic concentrations in water recharged from ponds (Greskowiak, et al., 2005; McNab, et al., 2009; O'Leary, et al., 2012).

Downward Movement of Infiltrated Water

Downward movement of the wetting front through the unsaturated zone was measured on the basis of changes in matric potential data from instruments within the ODEX borehole adjacent to the pond, arrival of water in lysimeters within the borehole, and sequential EM-resistivity log data collected from the 5-cm diameter PVC water-table well within the borehole.

Downward movement of the wetting front beneath the pond was initially about 25 cm/d (Figure 3.2). The rate of downward movement was as high as 75 cm/d after application of water in June 2011, because the unsaturated zone beneath the pond had been previously wetted. The downward rate of movement decreased only slightly with time as a result of limited lateral spreading of water at depth within the unsaturated zone as the wetting front moved downward to a depth of about 50 m. However, the rate slowed abruptly to about 5 cm/d because of low-permeability clay layers present at this depth (Figure 2.1). The wetting front reached the water table in about November 2012 (Figure 3.2). The water table beneath the pond rose prior to the arrival of the wetting front as a result of recharge associated with nearby water banking.

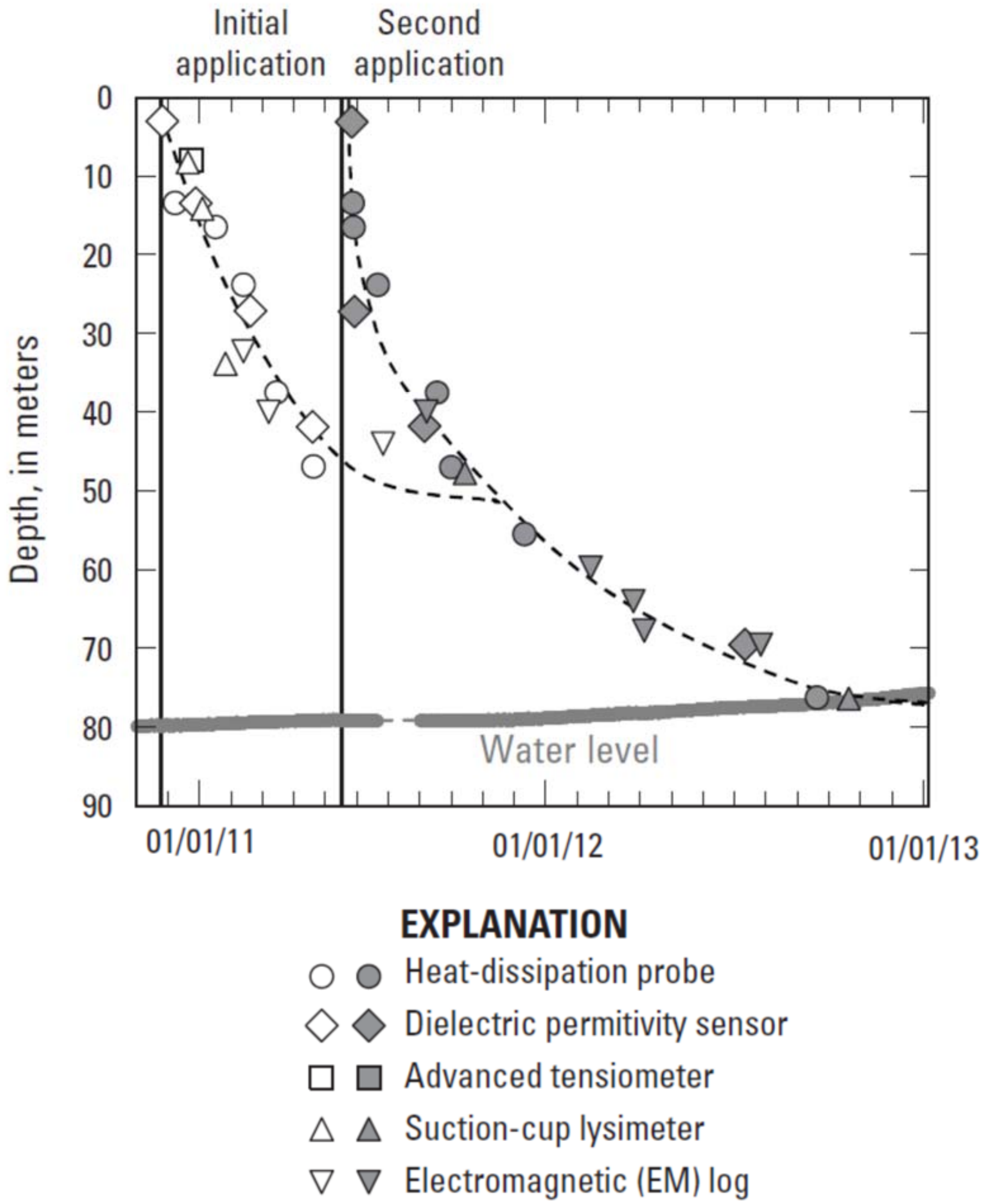


Figure 3.2 Downward movement of wetting front from a recharge pond used for *in-situ* removal of arsenic, near Palmdale, California December 2010 to January 2013

Lateral Movement of Infiltrated Water

Lateral movement of the wetting front in the unsaturated zone to depths less than 30 m was identified on the basis of surface DC-resistivity data (2-m electrode spacing), and DC-resistivity data from cables installed within mud-rotary boreholes 7.6 and 15 m away from the pond. Surface DC-resistivity data (10-m electrode spacing) were used to identify lateral movement of the wetting front at depths greater than 30 m to the water table 80 m below land surface. The underlying assumption in interpretation of these data is that the lithology of unsaturated material remains constant, and measured changes in electrical or electromagnetic resistivity are the result of changes in water content due to infiltration of water from the pond.

By July 2011, following infiltration from the pond beginning in December 2010 with sustained infiltration beginning in June 2011 (Figure 3.1), surface DC-resistivity data (2-m electrode spacing) showed lower electrical resistivity consistent with lateral movement of water from the pond at a depth of about 10 m (Figure 1.2), 15 m downslope from the pond. This may have occurred as a result of saturated (perched) conditions, with subsequent mounding and lateral movement of water infiltrated from the pond, on the sandy silt layer at 14.3 m below land surface. Changes in apparent resistivity associated with fine-grained layers at 9.2 or 14.3 m also were not observed in data collected upslope from the pond along line 4.2 (about 30 m downslope from the pond), or along other lines measured as part of this study.

By February 2012 and August 2012, DC resistivity data collected using the 10-m electrode spacing, show changes in apparent resistivity near clay layers between 48 and 60 m below land surface, consistent with movement of infiltrated water as far as 200 m from the pond (Figure 3.4). These changes occurred as a result of perched conditions on thick clay layers encountered at those depths during drilling (Figure 2.1). These clay layers are the thickest and finest-grained deposits encountered at the site. Consistent with the geology of the area, these clays may be similar to fine-grained deposits to the north of the fan. These materials would have been deposited at a time when alluvial fan deposits along the flanks of the San Gabriel Mountains were smaller, and the fan margin farther south beneath the present-day pond. Consistent with the geologic setting, these clay layers would be more areally extensive, and a greater impediment to downward flow, than fine-grained units within shallower alluvial fan deposits.

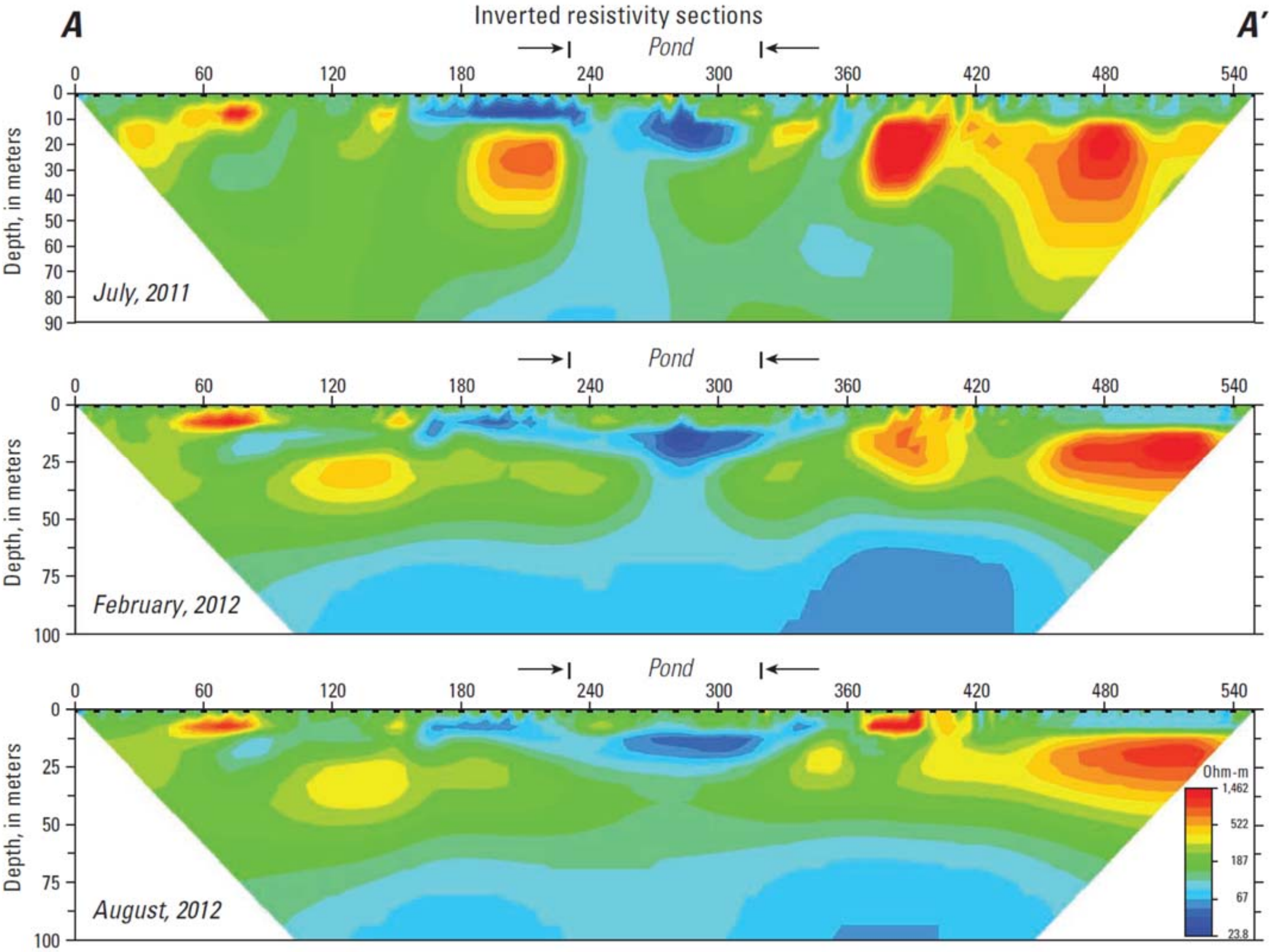


Figure 3.3 Direct Current (DC) resistivity data, 10-m electrode spacing, near a pond used for *in-situ* removal of arsenic, near Palmdale, California, December 2010 to January 2013

The surface DC resistivity data are consistent with the rapid, uniform rate of downward movement of the wetting front to clay layers at a depth of about 50 m measured by instruments within the ODEX borehole adjacent to the pond and with the slower movement of water measured below that depth (Figure 3.1). A diagram of wetting within the unsaturated zone as a result of infiltration from the pond is shown in Figure 3.4. Assuming uniform spreading around the 0.11 ha pond (1,100 m^2), about 4.5 x 10^6 m^3 of alluvial material was wetted as water infiltrated from the pond through the unsaturated zone to the water table, and the wetted "footprint" of the pond on arrival at the water table was about 13 ha.

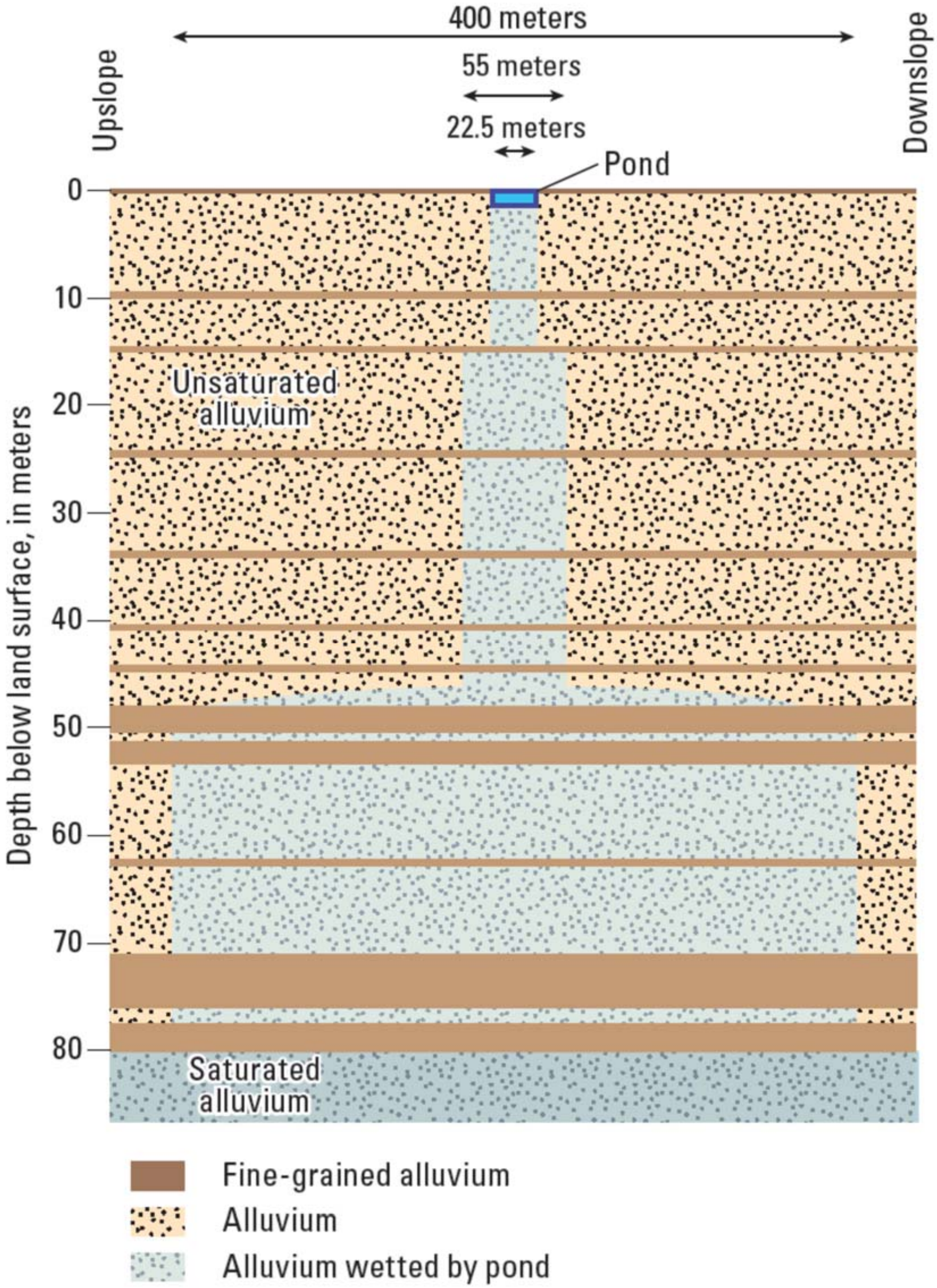


Figure 3.4 Diagram showing the extent of wetting within the unsaturated zone underlying a recharge pond used for *in-situ* removal of arsenic, near Palmdale, California

WATER CHEMISTRY

Arsenic

Arsenic concentrations in samples of groundwater from well 7B1 and infiltrated from the pond ranged from 27 to 30 µg/L, with a median concentration of 29 µg/L (Table 3.1). Arsenic concentrations in samples collected as part of this study within the pond were similar and ranged from 27 to 28.5 µg/L (not included in Table 3.1). Arsenic concentrations in samples of groundwater collected from the water table well adjacent to the recharge pond (8N/14W-7G1) ranged from 5.0 to 6.4 µg/L, with a median concentration of 6.2 µg/L (Table 3.1). Prior to the start of the experiment, the unsaturated zone beneath the pond was dry and most lysimeters did not yield water. The first sample from a lysimeter generally corresponded to the arrival of the wetting front at that depth. The exception was the deepest lysimeters at 76.8 m which yielded water from previously saturated material above the water table at about 79.9 m below land surface. This lysimeter went dry by October 2011 and did not consistently yield water again until the water table rose above the lysimeter in October 2012.

Table 3.1
Field measurements and selected trace-element concentrations in water from well 8N/14W-7B1, suction-cup lysimeters at selected depth within the unsaturated zone, and a water-table monitoring well in an instrumental borehole adjacent to groundwater recharge pond used for in-situ removal of arsenic, Palmdale, California, Dec. 2010 to Jan. 2013.

State well number	USGS ID	Common name	Date	pH	Specific conductance	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
008N014W07B001S	344815118240401	RG-5	05/19/09	7.8	457	-	27	-	-	-	-
			12/03/10	8.1	497	0.52	27	-	-	4.0	8.7
			06/17/11	8.4	456	0.53	28	2.7	0.67	4.1	8.7
			07/22/11	7.8	-	0.55	29	2.6	0.70	4.2	8.4
			11/30/11	7.7	466	0.57	30	2.8	0.68	4.5	9.1
			03/27/12	7.9	470	0.54	29	2.7	0.70	4.4	-
			05/31/12	7.7	492	0.47	29	2.8	0.68	4.2	9.1
			07/16/12	6.8	483	0.52	29	3.0	0.75	4.4	-
008N014W07G002SLYS	344751118241903	Lysimeter at 76.8	01/23/11	8.2	10,500	-	-	-	-	-	-
			02/02/11	8.2	6,290	-	-	-	-	-	-
			02/24/11	8.2	5,050	1.0	6.0	0.74	2.3	0.78	24
			04/01/11	8.2	3,670	-	-	-	-	-	-
			06/15/11	8.3	3,970	0.81	5.5	0.54	1.7	0.68	19
			07/22/11	-	3,200	-	-	-	-	-	-
			10/13/11	-	2,200	-	-	-	-	-	-
			11/29/11	-	2,400	0.43	5.4	0.47	1.6	1.3	24
			10/18/12	7.6	1,200	0.20	5.6	1.20	1.3	0.85	5.4
008N014W07G003SLYS	344751118241911	Lysimeter at 47.5	10/13/11	7.9	170	1.1	2.2	2.8	6.2	6.8	29
			11/29/11	7.5	1,900	1.2	3.4	2.6	10.5	17	13
			01/19/12	7.3	1,600	0.68	3.6	2.7	7.0	23	-
			02/02/12	7.3	1,270	0.12	1.5	0.51	1.3	–	4.6
			03/15/12	7.2	1,200	0.48	2.4	1.9	5.0	24	-
			03/26/12	7.5	1,220	0.43	2.3	2.3	5.2	24	-
			05/30/12	7.7	1,220	0.30	2.1	2.4	4.9	23	4.3
			07/16/12	7.7	1,220	0.28	1.0	<0.07	0.66		4.7
			08/15/12	6.8	1,250	0.31	2.2	2.7	5.2	23	4.4
			10/17/12	7.6	1,190	0.30	2.1	2.0	5	22	4.2
			10/18/12	7.5	1,180	0.28	2.1	3.0	5.5	21	4.2

Note: **pH and specific conductance measured in field, other analysis by U.S. Geological Survey National Water Quality Laboratory in Denver, Colorado. pH in standard units specific conductance in microSiemens per centimeter at 25 degrees Celsius trace element concentrations in micrograms per liter.**

Table 3.1 (Continued)

State well number	USGS ID	Common name	Date	pH	Specific conductance	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
008N014W07G004SLYS	344751118241915	Lysimeter at 33.8	02/24/11	8.3	1,660	1.35	2.8	2.6	4.3	48	26.6
			03/08/11	-	-	0.30	2.5	2.6	2.1	31	8.4
			04/01/11	8.1	608	-	-	-	-	-	-
			06/15/11	8.5	740	0.26	2.2	0.59	1.6	25	4.1
			07/22/11	-	-	0.18	2.1	1.8	5.1	44	6.7
			10/13/11	7.9	680	0.16	2.4	0.57	1.1	14	4.8
			11/29/11	8.3	-	0.30	6.3	1.4	1.1	9.3	11
			01/19/12	7.1	497	0.35	4.2	1.3	0.75	4.4	-
			02/02/12	7.5	465	0.18	3.2	1.6	0.66	3.8	5.5
			03/15/12	7.4	470	0.16	3.0	1.0	0.70	4.7	-
			03/26/12	7.6	473	0.15	3.1	2.1	0.68	6.6	-
			05/18/12	-	440	0.14	3.3	0.8	0.67	7.3	4.6
			05/30/12	7.6	479	0.14	3.6	2.0	0.54	8.2	4.7
			07/16/12	7.7	468	0.26	2.5	<0.07	0.90	1.8	4.7
			08/15/12	7.0	486	0.14	3.4	1.1	0.59	9.2	4.2
			10/17/12	7.6	462	0.13	3.6	0.84	0.56	8.1	4.4
			10/18/12	7.5	484	0.13	3.5	2.3	0.60	8.3	4.4
008N014W07G005SLYS	344751118241921	Lysimeter at 14	02/02/11	8.1	5,980	6.0	36	28	4.2	51	49
			02/24/11	8.1	3,720	3.5	21	16	2.4	41	22
			03/08/11	-	-	2.6	19	12	4.0	54	16
			04/01/11	8.9	2,900	1.9	13	7.6	2.7	35	13
			06/15/11	8.3	4,880	2.8	22	15	3.4	66	17
			07/22/11	-	-	2.6	18	9.7	2.5	53	17
			10/13/11	7.5	2,440	2.1	17	6.7	2.8	45	15
			11/29/11	7.8	1,080	2.1	21	6.6	1.5	18	15
			01/19/12	7.6	1,110	1.9	21	4.8	1.4	14	15
			02/02/12	7.5	1,000	1.9	19	6.8	1.5	13	13
			03/15/12	7.5	856	1.6	19	5.5	1.4	12	-
			03/26/12	7.9	879	1.5	18	5.8	1.5	13	11
			05/18/12	8.2	820	1.4	17	4.6	1.3	12	10
			05/30/12	7.9	819	1.0	17	4.3	1.5	12	8.9

(continued)

Table 3.1 (Continued)

State well number	USGS ID	Common name	Date	pH	Specific conductance	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
008N014W07G005SLYS	344751118241921	Lysimeter at 14	07/16/12	7.6	751	0.9	16	2.5	1.6	13	8.3
			08/15/12	-	-	1.5	16	4.1	1.4	12	9.5
			10/17/12	7.9	558	1.7	16	3.9	1.2	12	9.5
			10/18/12	7.9	924	1.4	17	6.2	1.3	12	10
008N014W07G006SLYS	344751118241925	Lysimeter at 7.9	01/23/11	8.0	755	-	-	-	-	-	-
			02/02/11	8.4	1,030	0.27	5.6	2.2	0.74	3.0	10
			02/24/11	8.2	1,490	0.59	3.0	1.4	6.0	12	8.8
			03/08/11	-	-	0.38	4.2	0.98	1.0	5.3	7.0
			04/01/11	8.7	941	0.56	5.1	1.6	3.5	16	6.7
			06/15/11	8.8	2,270	1.0	5.7	1.6	8.4	25	11
			07/22/11	-	-	0.71	6.1	1.0	1.4	5.4	8.9
			10/13/11	7.9	526	0.47	7.2	1.8	0.66	5.8	10
			11/29/11	8.3	99	0.92	9.8	3.3	1.3	8.6	12
			01/19/12	7.9	635	0.59	7.7	2.5	1.0	7.1	7.3
			02/02/12	7.4	535	0.33	5.6	2.4	0.77	6.0	4.9
			03/15/12	7.8	532	0.26	5.1	2.7	0.75	5.7	4.4
			03/26/12	8.2	524	0.29	5.7	2.4	0.72	5.8	4.3
			05/18/12	8.2	510	0.27	5.3	2.4	0.52	5.3	3.9
			05/30/12	7.9	552	0.27	6.4	2.1	0.71	5.5	4.5
			07/16/12	7.7	540	0.96	4.8	0.08	0.67	8.0	4.9
			08/15/12	7.1	562	0.35	7.4	2.1	0.94	5.3	6.0
			10/17/12	7.9	558	0.40	7.4	2.0	0.79	5.6	6.0
			10/18/12	-	-	0.67	7.7	2.3	0.69	6.7	7.4
008N014W07G001S	344751118241901	water-table well	10/14/10	7.6	454	0.20	5.0	-	-	2.4	4.6
			07/21/11	7.7	446	0.22	6.2	3.1	0.95	2.2	6.0
			11/30/11	7.7	405	0.20	6.4	3.3	1.0	2.4	6.7
			05/30/12	7.6	463	0.21	5.9	2.8	1.1	2.2	6.2
			10/17/12	7.8	460	0.17	6.0	2.9	1.0	2.4	6.4

As water from the pond moved downward through the unsaturated zone, arsenic concentrations decreased (Figure 3.5). By the end of the experiment, arsenic concentrations in the lysimeters at 33.8 and 47.5 m below land surface were 3.6 and 2.1 µg/L, respectively. It was not possible to determine the arsenic concentration of water infiltrated from the pond as it reached the water table using data collected from the deepest lysimeter at 76.8 m below land surface, or in the water table well screened from 79.2 to 82.3 m below land surface, because the water table rose above these instruments as a result of nearby groundwater recharge and samples from the lysimeter and well near the end of the experiment were native groundwater.

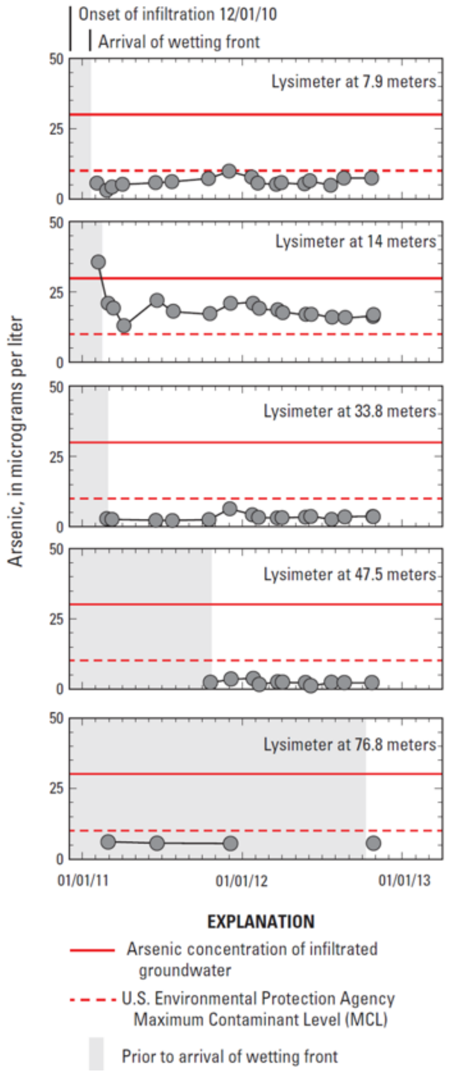


Figure 3.5 Arsenic concentrations in water from suction-cup lysimeters at selected depths within the unsaturated zone adjacent to a groundwater recharge pond used for *in-situ* removal of arsenic, near Palmdale, California, December 2010 to January 2013

Arsenic concentrations in water from the lysimeter at 14 m were initially as high as 36 µg/L (Figure 3.5)—higher than concentrations in groundwater pumped into the pond. High arsenic concentrations in the unsaturated zone at this depth coincided with specific conductance values as high as 5,980 microSiemens per centimeter. High arsenic and specific conductance in low-permeability layers at this depth are believed to result from accumulation of dissolved solids, arsenic, and other trace elements as a result of infiltration of irrigation-return water from past agricultural activity at this site. Arsenic was mobilized from this depth during the experiment, and concentrations decreased to 16.3 µg/L by the end of the experiment. If recharge continued at this site arsenic would continue to be mobilized from this layer. Arsenic mobilized from this layer was sorbed, along with arsenic in groundwater infiltrated from the pond, before reaching the lysimeter 33.8 m below land surface (Figure 3.5). Leaching of arsenic from salt-affected materials similar to those present at 14 m below land surface would pose a serious limitation if the unsaturated zone was thin and the water table were close to this depth.

Arsenic concentrations in the shallowest lysimeter at 7.9 m below land surface ranged from 3 to 9.8 µg/L (Figure 3.5). Arsenic concentrations in this lysimeter initially decreased, and later increased with breakthrough of concentrations approaching the MCL of 10 µg/L apparent by November 2011—presumably as sorption sites within the overlying material became saturated. However as infiltration continued, arsenic concentrations once again decreased to concentrations as low as 4.8 µg/L, before increasing again to concentrations greater than 7 µg/L. Changing arsenic concentrations may be related to several different factors including the development of an organic layer on the pond bottom and subsequent changes in infiltration rates and redox chemistry, or sequester of arsenic within more crystalized iron and aluminum minerals on the surfaces of mineral grains with time.

Other Trace Elements

Antimony, chromium, selenium, uranium, and vanadium concentrations also were measured during the experiment. These trace elements were present in groundwater pumped into the pond from well 7B1 at concentrations below their respective drinking water MCLs (Table 3.1).

Uranium concentrations in groundwater from well 7B1 were about 4 µg/L (Table 3.1). Uranium concentrations in the unsaturated zone were as high as 66 µg/L (Figure 3.6), more than twice the MCL for uranium of 30 µg/L. The highest concentrations were from the lysimeter in the salt-affected clays at 14 m below land surface. However, uranium concentrations above 20 µg/L were measured in all lysimeters, except the deepest lysimeter (and the water table well) where only native groundwater from the shallow aquifer were present. Uranium concentrations declined as the experiment progressed and the wetting front moved deeper (Figure 3.7).

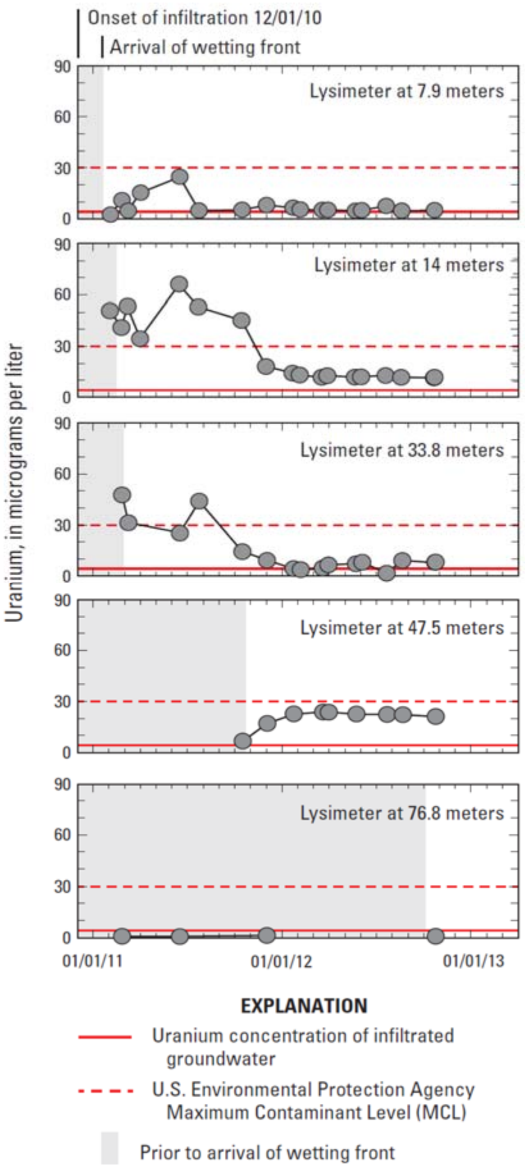


Figure 3.6 Uranium concentrations in suction-cup lysimeters at selected depths within the unsaturated zone adjacent to a groundwater recharge pond used for *in-situ* removal of arsenic, near Palmdale, California, December 2010 to January 2013

Uranium in the unsaturated zone may be related to irrigation-return associated with past agricultural activity at the site. Irrigation-return water is commonly saturated with respect to minerals such as calcite which may precipitate in the unsaturated zone as water infiltrates. As calcite precipitates, uranium may accumulate with calcite and accumulate within the unsaturated zone. Infiltration of water from the pond may have dissolved calcite, or bicarbonate within infiltrated water may have complexed with uranium on exchange sites (Jurgens, et al., 2010) increasing its concentration in infiltrating water, remobilizing uranium. This may be a concern at other sites where former agricultural land is used for groundwater recharge.

Concentrations of other trace elements, antimony, chromium, selenium, and vanadium were greater in the salt-affected clay 14 m below land surface. Although small increases in the concentrations of antimony, selenium, and vanadium were observed at depth within the unsaturated zone as infiltrated water moved toward the water table, concentrations of these constituents were generally low. Chromium concentrations generally decreased at depth within the unsaturated zone (Table 3.1).

SEQUENTIAL EXTRACTION DATA

Sorption of arsenic to iron, aluminum, and manganese oxides on the surfaces of mineral grains within the unsaturated zone may remove arsenic from groundwater infiltrated from the recharge pond. The abundance of these elements was evaluated on the basis of elemental concentrations in the strong acid (4M HNO_3) extractable fraction associated with well-crystalized oxides on mineral surfaces (Table 3.2).

Iron is the most abundant of the three elements. In alluvium greater than 2.5 m deep, iron concentrations in the strong acid extractable fraction ranged from about 1,300 to 3,500 milligrams per kilogram (mg/kg) of alluvium, with a median concentration of 2,000 mg/kg (Figure 3.7). In comparison, aluminum and manganese concentrations ranged from about 650 to 2,300 mg/kg and 10 to 560 mg/kg, with median concentrations of 860 and 14 mg/kg, respectively. These median concentrations are between one and two orders of magnitude lower than concentrations of iron, aluminum, and manganese in bulk continental crust of 56,000, 82,000, and 950 mg/kg, respectively (Reimann and Caritat, 1998). The data are consistent with occurrence of these elements mostly within primary minerals. Iron concentrations in the strong acid extractable fraction were greater in deeper alluvium than shallower alluvium (less than 2.5 m deep) (Figure 3.7). In contrast, aluminum, and manganese concentration in the strong acid extractable fraction were greater in shallow alluvium (less than 2.5 m deep) than in deeper alluvium, with median concentrations of 2,700 and 2,400 mg/kg, respectively (Figure 3.7). The greater concentrations of aluminum and manganese at shallow depths results from weathering during soil development, and accumulation of these elements within the soil profile as they are released from primary minerals.

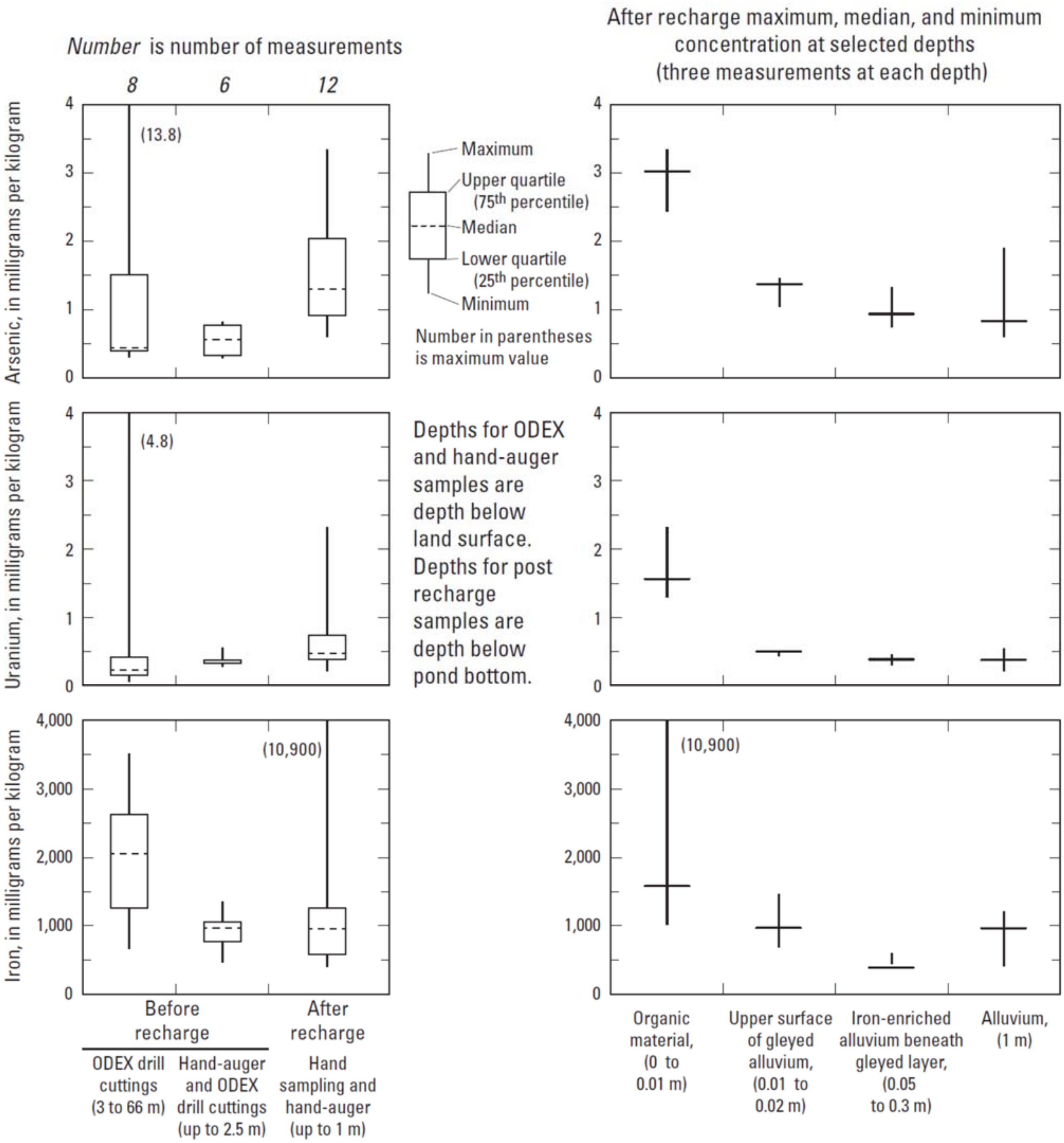


Figure 3.7 Arsenic, uranium, and iron concentrations, expressed as mg/kg of alluvium, in the strong acid extractable fraction from selected samples of alluvium before and after infiltration from a recharge pond used for *in-situ* removal of arsenic from groundwater, near Palmdale, California.

Table 3.2
Selected trace-element concentrations in sequential extracts from ODEX (Overburden Drilling Exploration) drill cuttings from unsaturated zone monitoring site 8N/14W-7G1 (AVUZ-4) adjacent to a groundwater recharge pond used for in-situ removal of arsenic, near Palmdale.

Lithlogy	Depth to top of sample interval, in meters	Depth to bottom of sample interval, in meters	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
			Concentration in micrograms per liter of extract								
			Extraction 1: 0.25 molar potassium chloride (KCl) extraction: non-specifically sorbed fraction								
Slightly Gravelly Sand	3.0	4.6	<85	38	17	<1.4	3.4	<3.0	<1.5	<0.2	<4.0
Silty Clay	8.5	9.8	<85	55	7.2	<1.4	<1.1	<3.0	<1.5	<0.2	<4.0
Sandy Silt	14.6	15.5	<85	<13	39	<1.4	<1.1	<3.0	<1.5	<0.2	<4.0
Slightly Gravelly Red Sand	20.7	22.3	<85	<13	10	<1.4	<1.1	<3.0	<1.5	<0.2	<4.0
Slightly Gravelly Tan Sand	25.3	25.9	<85	<13	145	<1.4	1.4	<3.0	<1.5	<0.2	<4.0
Bright Yellow Sand	40.2	40.5	<85	29	102	<1.4	4.1	<3.0	<1.5	<0.2	<4.0
Red Clay	49.4	50.0	<85	<13	78	<1.4	4.3	<3.0	<1.5	<0.2	<4.0
Fine White Sand	65.2	65.8	<85	<13	1,500	<1.4	4.5	<3.0	<1.5	<0.2	<4.0
Fine White Sand (HCl washed)	65.2	65.8	26,100	1,780	588	<1.4	4.0	7.3	<1.5	6.7	<4.0
			Extraction 2: 0.05 molar ammonium dihydrogen phosphate $((NH_3)H_2PO_4)$, ADP, extraction: specifically-sorbed fraction								
Slightly Gravelly Sand	3.0	4.6	106	21	599	1.2	59	<1.8	<0.9	0.22	14
Silty Clay	8.5	9.8	74	14	31	<0.8	213	<1.8	<0.9	0.57	41
Sandy Silt	14.6	15.5	125	18	179	<0.8	102	<1.8	<0.9	0.70	29
Slightly Gravelly Red Sand	20.7	22.3	137	14	383	<0.8	62	<1.8	<0.9	0.41	17
Slightly Gravelly Tan Sand	25.3	25.9	177	62	859	<0.8	50	<1.8	<0.9	0.30	13
Bright Yellow Sand	40.2	40.5	154	33	164	<0.8	217	<1.8	<0.9	0.47	47
Red Clay	49.4	50.0	66	<10	27	<0.8	270	<1.8	<0.9	0.39	21
Fine White Sand	65.2	65.8	111	29	1,140	<0.8	41	<1.8	<0.9	<0.12	3.9
Fine White Sand (HCl washed)	65.2	65.8	217	43	13	<0.8	12	<1.8	<0.9	<0.12	<2.4

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

Note: **Extraction procedure modified from Chao and Sanzalone (1989) and Wenzel et al., (2001). Extracting done sequentially using materials from previous extraction, except extraction 6 done on material from extraction 2. Water analyzed at U.S. Geological Survey National Quality Laboratory (NWQL) in Denver, Colorado. Laboratory results rounded for reporting purposes. Sample depth in meters below land surfaces. <,less then**

Table 3.2 (Continued)

Lithlogy	Depth to top of sample interval, in meters	Depth to bottom of sample interval, in meters	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
			Concentration in micrograms per liter of extract								
			Extraction 3: 0.2 Molar ammonium acetate ($(NH_4)_2C_2O_4{\cdot}H_2O$): amorphorous and poorly-crystalline hydrous iron and aluminum oxide fraction								
Slightly Gravelly Sand	3.0	4.6	13,800	25,100	2,020	<5.4	27	39	<6.0	9.5	27
Silty Clay	8.5	9.8	15,300	7,680	5,560	<5.4	53	<12	<6.0	31	84
Sandy Silt	14.6	15.5	25,400	23,800	4,590	<5.4	78	14	<6.0	44	120
Slightly Gravelly Red Sand	20.7	22.3	16,000	17,400	9,310	<5.4	42	24	<6.0	19	55
Slightly Gravelly Tan Sand	25.3	25.9	15,900	17,800	2,590	<5.4	31	24	<6.0	16	58
Bright Yellow Sand	40.2	40.5	11,400	11,900	1,440	<5.4	50	<12	<6.0	9.6	79
Red Clay	49.4	50.0	13,700	2,780	2,580	<5.4	62	<12	<6.0	46	57
Fine White Sand	65.2	65.8	12,900	17,800	2,690	<5.4	21	25	<6.0	5.6	34
Fine White Sand (HCl washed)	65.2	65.8	3,250	16,400	<26.0	<5.4	<4.4	<12	<6.0	1.1	<16.0
			Extraction 4: 0.2 molar ammonium acetate ($(NH_4)_2C_2O_4{\cdot}H_2O$) and 0.1 molar ascorbic acid ($C_6H_8O_6$)--well-crystalliized hydrous oxides of iron and aluminum								
Slightly Gravelly Sand	3.0	4.6	8,190	131,000	4,330	5.2	150	86	<4.5	7.4	198
Silty Clay	8.5	9.8	18,500	209,000	47,600	22	596	87	<4.5	35	1,070
Sandy Silt	14.6	15.5	15,200	242,000	6,310	20	366	72	<4.5	35	946
Slightly Gravelly Red Sand	20.7	22.3	6,150	55,600	15,000	5.0	137	64	<4.5	13	158
Slightly Gravelly Tan Sand	25.3	25.9	5,000	31,400	1,730	<4	104	42	<4.5	11	102
Bright Yellow Sand	40.2	40.5	10,900	172,000	2,730	8.1	476	26	<4.5	9.6	393
Red Clay	49.4	50.0	17,700	63,200	80,000	16	247	29	<4.5	38	563
Fine White Sand	65.2	65.8	5,720	60,200	2,480	<4	90	60	<4.5	6.8	100
Fine White Sand (HCl washed)	65.2	65.8	3,500	63,300	59.5	<4	51	21	<4.5	1.1	70.3

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

(continued)

Table 3.2 (Continued)

Lithlogy	Depth to top of sample interval, in meters	Depth to bottom of sample interval, in meters	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
			Concentration in micrograms per liter of extract								
			Extraction 5: 4 normal Nitric acid (HNO_3) extraction--well-crystallized hydrous oxides of iron and								
Slightly Gravelly Sand	3.0	4.6	204,000	613,000	7,800	<14	99.8	139	<15	35	403
Silty Clay	8.5	9.8	636,000	754,000	31,700	<14	341	616	<15	166	1,830
Sandy Silt	14.6	15.5	353,000	803,000	11,100	<14	162	201	<15	75	936
Slightly Gravelly Red Sand	20.7	22.3	132,000	293,000	10,300	<14	118	163	<15	63	296
Slightly Gravelly Tan Sand	25.3	25.9	111,000	310,000	4,420	<14	102	88	<15	33	237
Bright Yellow Sand	40.2	40.5	129,000	375,000	5,360	<14	230	71	<15	43	502
Red Clay	49.4	50.0	634,000	899,000	30,000	<14	327	534	<15	167	1,140
Fine White Sand	65.2	65.8	89,700	219,000	4,890	<14	68	110	<15	54	179
Fine White Sand (HCl washed)	65.2	65.8	24,900	57,600	246	<14	15	<30.0	<15	5.1	51
			Extraction 6 (done on material from extraction 2): 4 normal HNO3--well-crystallized hydrous								
Slightly Gravelly Sand	3.0	4.6	288,000	450,000	5,140	<14	59	129	32	<15	325
Silty Clay	8.5	9.8	130,000	621,000	112,000	26	2,750	3540	968	27	5,100
Sandy Silt	14.6	15.5	462,000	527,000	5,830	<14	86	194	74	<15	463
Slightly Gravelly Red Sand	20.7	22.3	172,000	255,000	2,740	<14	83	178	52	<15	176
Slightly Gravelly Tan Sand	25.3	25.9	174,000	336,000	2,240	<14	66	95	38	<15	201
Bright Yellow Sand	40.2	40.5	135,000	410,000	2,110	<14	205	85	30	<15	307
Red Clay	49.4	50.0	388,000	704,000	22,700	15	588	370	85	<15	791
Fine White Sand	65.2	65.8	81,100	253,000	1,600	<14	86	69	114	<15	177
Fine White Sand (HCl washed)	65.2	65.8	36,000	136,000	411	<14	35	33	13	<15	117

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

Table 3.3
Selected trace-element concentration of sequential extracts from soil and alluvium before and after infiltration from a pond used for in-situ removal of arsenic, near Palmdale, California

Site location latitude/longitude ddmmss dddmmss	Type of sample	Type of material	Depth of sample interval, in cm	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
				Concentrations, in micrograms per liter of extract								
				Extraction 1: 0.25M potassium chloride [KCl] extraction: non-specifically sorbed fraction								
344753 1182418	Before infiltration	Soil	5	13,200	81	11,200	<1.4	4.1	3.9	<1.5	0.57	6.3
344753 1182417	Before infiltration	Soil	5	17,600	213	12,500	<1.4	6.6	5.2	<1.5	1.1	8.4
344753 1182416	Before infiltration	Soil	5	<110	<13	1,140	<1.4	3.7	<3.5	<1.5	0.22	4.5
344751 1182419	Before infiltration	Alluvium	183	<110	<13	27	<1.4	2.5	<3.5	<1.5	0.33	6.5
344751 1182419	Before infiltration	Alluvium	213	<110	<13	51	<1.4	3.7	<3.5	<1.5	0.34	5.4
344751 1182419	Before infiltration	Alluvium	244	<110	<3.2	25	<1.4	4.2	<3.5	<1.5	0.32	5.3
3447521 182419	After infiltration	Organic	0-1	<110	16	1,000	2.6	20	4.0	4.1	4.2	22
344751 1182418	After infiltration	Organic	0-1	<110	21	776	1.7	17	<3.5	3.3	2.5	18
344752 1182419	After infiltration	Organic	0-1	<110	22	3,850	1.7	15	3.5	3.2	13	16
344752 1182419	After infiltration	Alluvium	1-2	<110	<13	178	<1.4	13	<3.5	<1.5	0.48	7.4
344751 1182418	After infiltration	Alluvium	1-2	<110	<13	119	<1.4	7.0	<3.5	<1.5	0.64	7.5
344752 1182419	After infiltration	Alluvium	1-2	<110	<13	331	<1.4	11	<3.5	<1.5	0.73	7.6
344752 1182419	After infiltration	Alluvium	5-30	<110	<13	20	<1.4	9.1	<3.5	<1.5	0.47	<4
344751 1182418	After infiltration	Alluvium	5-30	<110	<13	16	<1.4	7.5	<3.5	<1.5	0.57	<4
344752 1182419	After infiltration	Alluvium	5-30	<110	<13	47	<1.4	10	<3.5	<1.5	0.42	<4
344752 1182419	After infiltration	Alluvium	100	<110	<13	16	<1.4	3.1	<3.5	<1.5	<0.2	<4
344751 1182418	After infiltration	Alluvium	100	<110	16	9.4	<1.4	6.7	<3.5	<1.5	0.76	6.0
344752 1182419	After infiltration	Alluvium	100	12,800	40	1,530	<1.4	2.6	<3.5	<1.5	1.4	<4

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

Note: **Extraction procedure modified from Chao and Sanzalone (1989) and Wenzel et al., (2001). Extracting done sequentially using materials from previous extraction. Extraction 5, Table 2, was not done on these samples. Water samples were analyzed at U.S. Geological Survey National Quality Laboratory (NWQL) in Denver, Colorado. Laboratory results rounded for reporting purposes. Latitude longitude in degrees (dd or ddd), minutes (mm), seconds (ss); cm, centimeters; M, molar; <, less than**

Table 3.3 (Continued)

Site location latitude/longitude ddmmss dddmmss	Type of sample	Type of material	Depth of sample interval, in cm	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
				Concentrations, in micrograms per liter of extract								
				Extraction 2: 0.05M ammonium dihydrogen phosphate (ADP) [(NH3)H2PO4] extraction: specifically-sorbed fraction								
344753 1182418	Before infiltration	Soil	5	2,070	196	1,500	<0.8	18	<2	<0.9	2.1	16
344753 1182417	Before infiltration	Soil	5	2,950	336	1,520	<0.8	15	3.2	<0.9	2.7	21
344753 1182416	Before infiltration	Soil	5	249	89	828	<0.8	26	<2	<0.9	1.6	18
344751 1182419	Before infiltration	Alluvium	183	<66	18	254	1.2	49	<2	<0.9	0.29	35
344751 1182419	Before infiltration	Alluvium	213	<66	13	323	0.93	79	<2	<0.9	0.33	35
344751 1182419	Before infiltration	Alluvium	244	<66	14	385	<0.8	70	<2	<0.9	0.37	31
3447521 182419	After infiltration	Organic	0-1	<66	17	833	2.8	427	<2	2.6	0.17	176
344751 1182418	After infiltration	Organic	0-1	<66	12	1,100	2.9	362	<2	2.2	0.23	149
344752 1182419	After infiltration	Organic	0-1	<66	13	960	2.5	602	2.1	4.6	0.12	142
344752 1182419	After infiltration	Alluvium	1-2	<66	16	1,230	<0.8	215	<2	<0.9	0.15	58
344751 1182418	After infiltration	Alluvium	1-2	<66	<9.6	627	1.2	182	<2	1.4	0.14	71
344752 1182419	After infiltration	Alluvium	1-2	<66	<9.6	1,410	1.2	297	<2	1.8	<0.12	72
344752 1182419	After infiltration	Alluvium	5-30	<66	22	298	<0.8	215	<2	<0.9	0.29	34
344751 1182418	After infiltration	Alluvium	5-30	<66	<9.6	155	<0.8	150	<2	<0.9	0.21	44
344752 1182419	After infiltration	Alluvium	5-30	<66	17	231	<0.8	184	<2	<0.9	0.16	33
344752 1182419	After infiltration	Alluvium	100	217	25	247	<0.8	75	<2	<0.9	0.60	20
344751 1182418	After infiltration	Alluvium	100	<66	<9.6	61	<0.8	234	<2	<0.9	0.20	60
344752 1182419	After infiltration	Alluvium	100	865	69	219	<0.8	60	<2	<0.9	0.48	7.6

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

(continued)

Table 3.3 (Continued)

Site location latitude/longitude ddmmss dddmmss	Type of sample	Type of material	Depth of sample interval, in cm	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
				Concentrations, in micrograms per liter of extract								
				Extraction 3: 0.2M ammonium-oxalate $[(NH_4)_2C_2O_4 \cdot H_2O]$: amorphorous and poorly-crystalline hydrous iron and aluminum oxide fraction								
344753 1182418	Before infiltration	Soil	5	52,100	36,300	4,820	<5.4	26	51	<6	20	158
344753 1182417	Before infiltration	Soil	5	52,500	43,300	4,060	<5.4	30	60	<6	24	172
344753 1182416	Before infiltration	Soil	5	11,300	9,470	7,070	<5.4	18	36	<6	24	110
344751 1182419	Before infiltration	Alluvium	183	6,370	8,070	1,060	<0.8	21	20	<0.9	11	16
344751 1182419	Before infiltration	Alluvium	213	12,900	10,800	1,930	<5.4	53	36	<6	25	28
344751 1182419	Before infiltration	Alluvium	244	13,600	16,100	2,420	<5.4	41	36	<6	19	36
3447521 182419	After infiltration	Organic	0-1	12,000	4,900	4,880	5.5	201	81	<6	108	305
344751 1182418	After infiltration	Organic	0-1	12,400	7,300	5,050	<5.4	137	70	<6	82	201
344752 1182419	After infiltration	Organic	0-1	32,100	8,840	5,360	6.2	259	94	<6	78	322
344752 1182419	After infiltration	Alluvium	1-2	16,400	15,600	3,960	<5.4	101	35	<6	19	37
344751 1182418	After infiltration	Alluvium	1-2	10,500	7,620	2,110	<5.4	88	35	<6	33	56
344752 1182419	After infiltration	Alluvium	1-2	25,300	20,000	4,850	<5.4	157	46	<6	19	54
344752 1182419	After infiltration	Alluvium	5-30	9,430	8,340	1,540	<5.4	55	29	<6	15	43
344751 1182418	After infiltration	Alluvium	5-30	5,260	1,650	414	<5.4	37	34	<6	30	25
344752 1182419	After infiltration	Alluvium	5-30	12,200	6,560	1,020	<5.4	56	30	<6	12	33
344752 1182419	After infiltration	Alluvium	100	9,950	13,900	1,980	<5.4	30	32	<6	15	41
344751 1182418	After infiltration	Alluvium	100	3,480	871	215	<5.4	135	38	<6	36	50
344752 1182419	After infiltration	Alluvium	100	30,500	28,500	1,050	<5.4	55	38	<6	16	66

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

(continued)

Table 3.3 (Continued)

Site location latitude/longitude ddmmss dddmmss	Type of sample	Type of material	Depth of sample interval, in cm	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
				Concentrations, in micrograms per liter of extract								
				Extraction 4: 0.2M ammonium-acetate [$(NH_4)_2C_2O_4{\cdot}H_2O$] and 0.1M ascorbic acid [$C_6H_8O_6$]. well-crystalliized hydrous oxides of iron and aluminum								
344753 1182418	Before infiltration	Soil	5	18300	238000	5970	6.5	86	80	<4.5	19	458
344753 1182417	Before infiltration	Soil	5	17,200	165,000	5,700	6.7	107	86	<4.5	22	459
344753 1182416	Before infiltration	Soil	5	12,600	85,400	7,520	<4	93	63	<4.5	30	373
344751 1182419	Before infiltration	Alluvium	183	26,700	176,000	22,600	11	221	136	<6.0	22	672
344751 1182419	Before infiltration	Alluvium	213	27,400	205,000	22,700	14	323	172	<6.0	33	749
344751 1182419	Before infiltration	Alluvium	244	11,400	131,000	11,100	6.6	164	83	<4.5	14	308
3447521 182419	After infiltration	Organic	0-1	250,000	211,000	19,800	13	356	279	<4.5	40	1,380
344751 1182418	After infiltration	Organic	0-1	96,800	196,000	11,900	9.3	229	168	<4.5	27	1,040
344752 1182419	After infiltration	Organic	0-1	249,000	308,000	15,200	12	563	1,610	<4.5	40	1,320
344752 1182419	After infiltration	Alluvium	1-2	18,300	122,000	15,900	4.8	200	54	<4.5	16	459
344751 1182418	After infiltration	Alluvium	1-2	31,700	186,000	20,000	9.1	201	74	<4.5	21	713
344752 1182419	After infiltration	Alluvium	1-2	39,100	273,000	17,800	11	382	138	<4.5	27	920
344752 1182419	After infiltration	Alluvium	5-30	13,300	111,000	15,600	4.6	200	42	<4.5	11	366
344751 1182418	After infiltration	Alluvium	5-30	23,400	87,400	22,800	5.5	117	43	<4.5	12	463
344752 1182419	After infiltration	Alluvium	5-30	17,400	111,000	20,100	<4	182	41	<4.5	10	410
344752 1182419	After infiltration	Alluvium	100	5,870	68,600	5,030	<4	123	41	<4.5	8.1	166
344751 1182418	After infiltration	Alluvium	100	32,100	242,000	20,400	17	491	114	<4.5	25	1,010
344752 1182419	After infiltration	Alluvium	100	12,000	164,000	7,100	7.0	212	67	<4.5	10	377

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

(continued)

Table 3.3 (Continued)

Site location latitude/longitude ddmmss dddmmss	Type of sample	Type of material	Depth of sample interval, in cm	Aluminum	Iron	Manganese	Antimony	Arsenic	Chromium	Selenium	Uranium	Vanadium
				Concentrations, in micrograms per liter of extract								
				Extraction 6 (done on material from extraction 2): 4M nitric acid [HNO_3] extraction: well-crystallized hydrous oxides of iron and aluminum								
344753 1182418	Before infiltration	Soil	5	664,000	904,000	24,700	<14	59	576	<15	76	1,610
344753 1182417	Before infiltration	Soil	5	552,000	794,000	19,900	<14	58	506	<15	65	1,410
344753 1182416	Before infiltration	Soil	5	424,000	452,000	27,000	<14	88	337	<15	112	1,070
344751 1182419	Before infiltration	Alluvium	183	590,000	1,250,000	28,900	<14	155	398	<15	74	1,290
344751 1182419	Before infiltration	Alluvium	213	505,000	703,000	22,100	<14	165	—	<15	74	1,010
344751 1182419	Before infiltration	Alluvium	244	324,000	486,000	15,200	<14	148	202	<15	57	685
3447521 182419	After infiltration	Organic	0-1	225,000	2,180,000	96,200	<14	488	3,020	19	313	5,990
344751 1182418	After infiltration	Organic	0-1	272,000	2,310,000	157,000	<14	669	4,840	31	464	9,570
344752 1182419	After infiltration	Organic	0-1	3,360,000	2,170,000	87,800	<14	604	3,000	16	260	5,820
344752 1182419	After infiltration	Alluvium	1-2	820,000	1,070,000	46,300	<14	291	592	<15	88	1,780
344751 1182418	After infiltration	Alluvium	1-2	1,150,000	1,470,000	48,400	<14	208	869	<15	103	2,390
344752 1182419	After infiltration	Alluvium	1-2	1,030,000	1,380,000	49,600	<14	275	1,030	<15	101	2,470
344752 1182419	After infiltration	Alluvium	5-30	548,000	652,000	31,500	<14	266	305	<15	78	1,160
344751 1182418	After infiltration	Alluvium	5-30	660,000	1,200,000	35,300	<14	149	405	<15	93	1,370
344752 1182419	After infiltration	Alluvium	5-30	526,000	1,060,000	27,900	<14	187	332	<15	60	1,110
344752 1182419	After infiltration	Alluvium	100	189,000	291,000	7,060	<14	119	113	<15	44	393
344751 1182418	After infiltration	Alluvium	100	973,000	1,200,000	29,900	<14	380	643	<15	110	1,970
344752 1182419	After infiltration	Alluvium	100	466,000	716,000	16,100	<14	167	303	<15	76	1,020

NOTE: Values in paper discussed in milligrams per kilogram of alluvium.

In alluvium greater than 2.5 m deep, arsenic concentrations in the strong acid extractable fraction ranged from 0.3 to 13.8 mg/kg of alluvium, with a median concentration of 0.4 mg/kg (Figure 3.7). Although the range of arsenic measured in the shallow alluvial deposits was less than the range measured in deeper deposits, the median concentration was not statistically different from the median arsenic concentration in deeper alluvium. The median arsenic concentration was lower than the range of arsenic concentrations reported for the bulk continental crust of 1 to 1.8 mg/kg (Reimann and Caritat, 1998). This suggests that although most arsenic is still within primary minerals there has been preferential release of arsenic during weathering of primary minerals compared to iron, aluminum, and manganese.

Arsenic concentrations in the strong acid extractable fraction after recharge ranged from 0.6 to 3.3 mg/kg, with a median concentration of 1.3 mg/kg (Figure 3.7). The median concentration was statistically different from the median arsenic concentration in deep and shallow alluvium prior to recharge. Examination of the data show the highest arsenic concentrations, about 3 mg/kg, were in the organic layer within the upper 0.01 m of the profile. Arsenic accumulated within this layer represents about 2 percent of the arsenic in water infiltrated through the pond—the remaining arsenic was sorbed at greater depth beneath the pond. Much of this sorbed arsenic was in the KH2PO4 extractable, or surface sorbed fraction, and is only weakly held on exchange sites within the unsaturated zone (Figure 3.8).

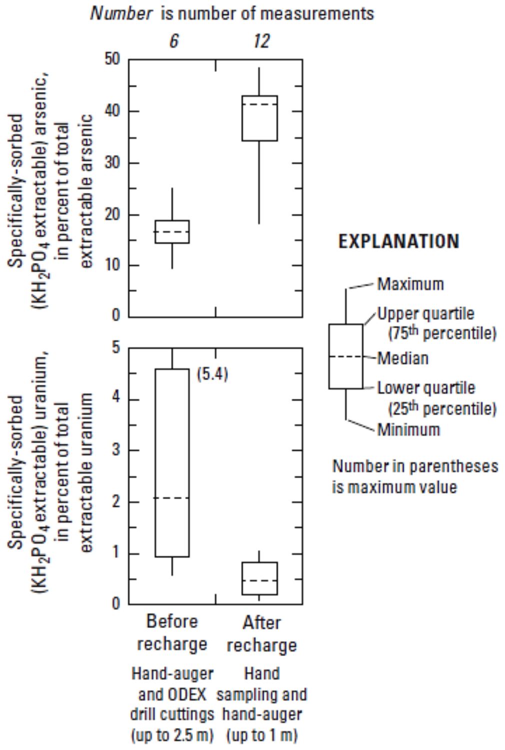


Figure 3.8 Exchangeable arsenic and uranium in percent of total extractable arsenic and uranium in shallow alluvium before and after infiltration through a pond used for *in-situ* removal of arsenic, near Palmdale, California, December 2010 to January 2013

Toxicity Characteristic Leaching Procedure (TCLP) data on samples collected from the organic mat, within gleyed alluvium immediately beneath the organic mat, within iron-enriched alluvium beneath the gleyed layer, and at one-meter depth from three locations within the pond show arsenic concentrations to be below the reporting level of 0.5 µg/L in the TCLP extract and below hazardous levels beneath the pond after infiltration. Control samples collected from alluvium collected adjacent to the pond and beneath the pond prior to infiltration also were below reporting levels for TCLP.

Uranium, chromium, and vanadium were distributed similar to arsenic in deeper and shallow alluvium. Concentrations of these elements increased accumulated in organic material at the bottom of the pond (Table 3.3). Approximately 9 percent of uranium, virtually all the chromium, and almost 80 percent of the vanadium in deep groundwater pumped from well 7B1 was present within the organic material accumulated at the bottom of the pond. In contrast to arsenic, KH2PO4 extractable uranium as a percent of total extractable uranium decreased in the shallow alluvium as a result of infiltration through the pond (Figure 3.8). This decrease is consistent with the mobilization of uranium during infiltration from the pond (Figure 3.6). Deeper alluvial deposits collected during test drilling had low KH2PO4 extractable uranium concentration (0.002 milligram per kilograms or 0.4 percent of the total extractable uranium) and were able to resorb uranium from shallower depths before it reached the water table.

ARSENIC-73 DATA

Prior to the experiment there was concern from regulatory agencies that arsenic sorbed within the unsaturated zone would be exchangeable, and potentially mobile if overlying land use and the chemistry of infiltrating water changed. This concern is reasonable given mobilization of arsenic from unsaturated zones beneath recharge ponds in other areas, and the high fraction of surface sorbed arsenic (KH2PO4 extractable fraction) after infiltration (Figure 3.8). Batch experiments, using arsenic-73 (a man-made radioisotope of arsenic having a half-life of 80.3 days), were used to determine if arsenic remains within the surface sorbed fraction and is readily exchangeable or if arsenic may become increasingly mineralized and potentially less mobile with time. During the experiment one complete set of microcosms was harvested at each of four predetermined time-steps: 0 days, 1 month, 6 months, and 12 months (Table 3.4).

Table 3.4

Arsenic 73 activity for sequential extractions from batch microcosms harvested at selected times for alluvium from selected depths within the unsaturated zone adjacent to a pond used for in-situ removal of arsenic, near Palmdale, California.

Lithology	Depth to top of sample interval, in meters	Depth to bottom of sample interval, in meters	Arsenic-73 activity in each extraction and operational fraction, as a percent of total arsenic-73 activity						
				0.25M KCl	0.05M ammonium dihydrogen phosphate (ADP)	0.2M ammonium oxalate	0.2M ammonium oxalate and 0.1M ascorbic acid	4M Nitric acid	Residual
			Aqueous phase	Non-specifically sorbed	Specifically-sorbed	Amorphous and poorly-crystaline fraction	Well-crystallized hydrous oxides	Well-crystallized hydrous oxides	Residual
						time = 0			
Slightly Gravelly Sand	3.0	4.6	12	1.6	42	22	14	--	8.8
Silty Clay	8.5	9.8	0.5	0.1	28	17	17	--	38
Sandy Silt	14.6	15.5	2.5	0.3	41	24	20	--	12
Slightly Gravelly Red Sand	20.7	22.3	4.6	0.6	43	25	16	--	10
Slightly Gravelly Tan Sand	25.3	25.9	6.9	0.6	38	28	18	--	9.2
Bright Yellow Sand	40.2	40.5	0.7	0.2	39	25	14	--	21
Red Clay	49.4	50.0	1.1	0.2	30	15	15	--	39
Fine White Sand	65.2	65.8	4.6	0.6	39	29	18	--	8.6
Fine White Sand (HCL washed)	65.2	65.8	8.2	2.7	35	31	16	--	7.4
						time = 1 month			
Slightly Gravelly Sand	3.0	4.6	1.2	0.6	29	32	21	8.6	7.4
Silty Clay	8.5	9.8	0.1	0.1	22	23	18	14	22
Sandy Silt	14.6	15.5	0.5	0.2	31	27	24	9.2	8.7
Slightly Gravelly Red Sand	20.7	22.3	0.7	0.3	30	29	24	9.0	8.1
Slightly Gravelly Tan Sand	25.3	25.9	0.8	0.3	28	30	26	9.0	6.4
Bright Yellow Sand	40.2	40.5	0.3	0.3	26	26	19	17	11
Red Clay	49.4	50.0	0.2	0.1	25	25	18	12	20
Fine White Sand	65.2	65.8	1.2	0.4	28	30	26	8.9	5.3
Fine White Sand (HCL washed)	65.2	65.8	0.7	0.6	20	32	31	11	5.6

Note: Sequential extractions modified from Wenzel et al., 2001, and Chao and Sanzolone, 1989. Arsenic 73 activity in percent of total arsenic 73 activity for each microcosm at each time step. Activity is average of two measurements. Activity rounded from measured laboratory activity.--, no data

Table 3.4 (Continued)

Lithology	Depth to top of sample interval, in meters	Depth to bottom of sample interval, in meters	Arsenic-73 activity in each extraction and operational fraction, as a percent of total arsenic-73 activity						
				0.25M KCl	0.05M ammonium dihydrogen phosphate (ADP)	0.2M ammonium oxalate	0.2M ammonium oxalate and 0.1M ascorbic acid	4M Nitric acid	Residual
			Aqueous phase	Non-specifically sorbed	Specifically-sorbed	Amorphous and poorly-crystaline fraction	Well-crystallized hydrous oxides	Well-crystallized hydrous oxides	Residual
					time = 6 months				
Slightly Gravelly Sand	3.0	4.6	0.9	0.5	16	29	29	13	11
Silty Clay	8.5	9.8	0.1	0.0	10	16	18	16	40
Sandy Silt	14.6	15.5	0.2	0.2	16	26	31	13	12
Slightly Gravelly Red Sand	20.7	22.3	0.5	0.2	20	26	29	13	12
Slightly Gravelly Tan Sand	25.3	25.9	0.5	0.2	18	27	32	14	9.4
Bright Yellow Sand	40.2	40.5	0.2	0.2	17	24	20	22	15
Red Clay	49.4	50.0	0.1	0.1	12	15	20	21	33
Fine White Sand	65.2	65.8	1.1	0.4	17	26	34	13	7.2
Fine White Sand (HCL washed)	65.2	65.8	0.5	0.5	9.0	16	44	20	9.8
					time = 12 months				
Slightly Gravelly Sand	3.0	4.6	0.9	0.4	16	25	29	15	13
Silty Clay	8.5	9.8	0.1	0.1	12	16	19	19	33
Sandy Silt	14.6	15.5	0.2	0.2	12	18	34	20	16
Slightly Gravelly Red Sand	20.7	22.3	0.4	0.2	11	19	35	18	17
Slightly Gravelly Tan Sand	25.3	25.9	0.3	0.3	9.5	19	37	19	15
Bright Yellow Sand	40.2	40.5	0.2	0.2	14	20	22	25	19
Red Clay	49.4	50.0	0.2	0.1	14	16	20	19	31
Fine White Sand	65.2	65.8	0.8	0.4	8.9	24	39	17	10
Fine White Sand (HCL washed)	65.2	65.8	1.6	1.0	7.5	14	42	22	12

Initially (time = 0), 28 to 43 percent of the arsenic-73 added to the microcosms was in the KH2PO4 extractable (surface sorbed) fraction, with a median of 39 percent (Figure 3.9). This is similar to the percent exchangeable arsenic measured in samples beneath the pond after recharge. Smaller percentages of surface specifically-sorbed arsenic, between 28 and 30 percent, were extracted from clay-rich samples at 8.5 to 9 m and 49.4 and 50 m below land surface (Table 3.4). These samples had about 39 percent of the arsenic-73 within the residual material remaining after centrifugation. This greater sequestration of arsenic within the residual material for fine-textured alluvium is consistent with sorption to positively charged edge-structures on clay minerals (Manning and Goldberg, 1996; Ma and Pierre, 1999). By the end of the 1 year experiment, slightly more than half of the arsenic-73 in the clay-rich samples was within the residual fraction.

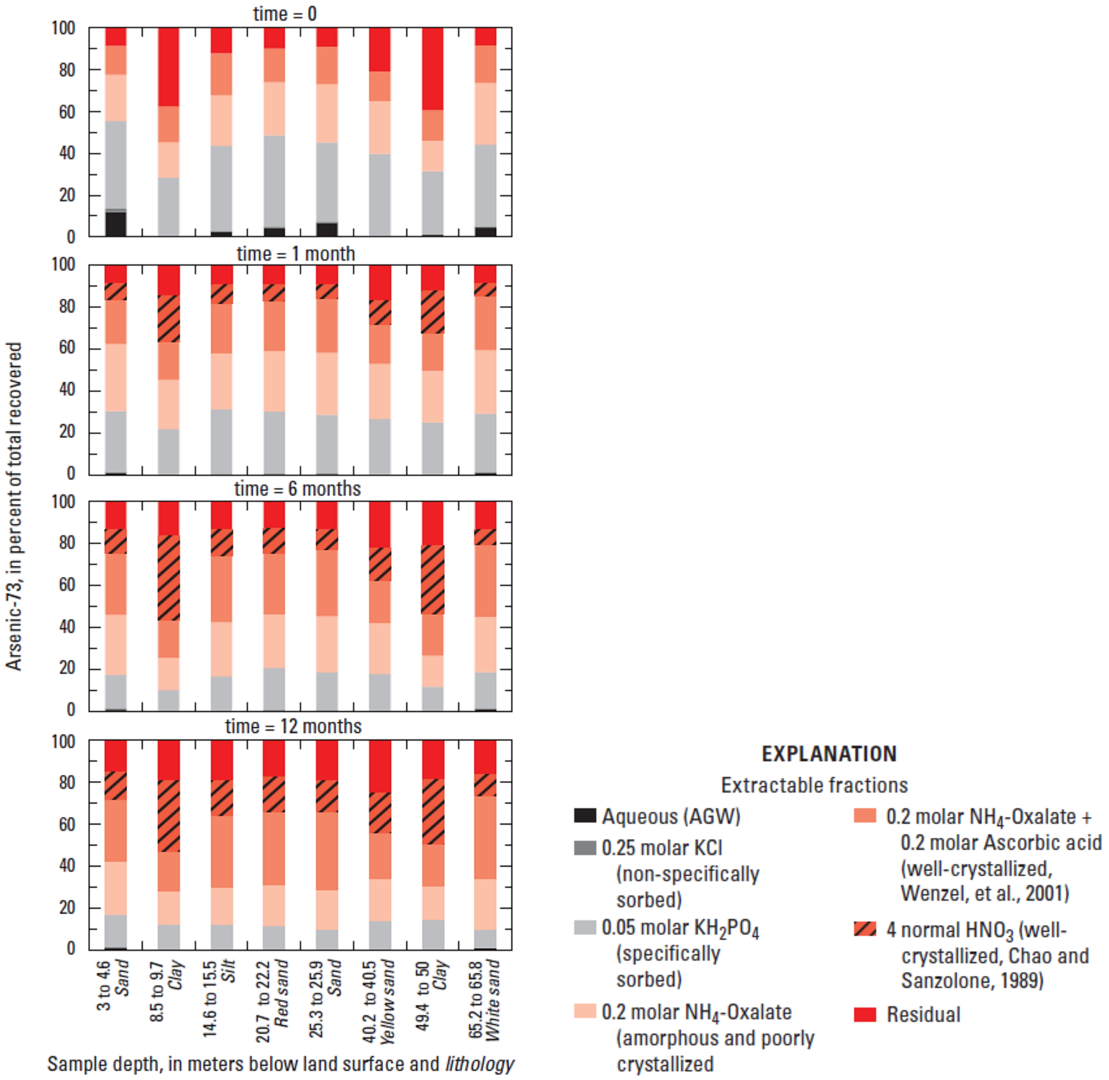


Figure 3.9 Arsenic-73 in percent of total recovered at selected times during batch microcosm experiments from operationally defined sites on the surfaces of mineral grains within selected unsaturated materials beneath a recharge pond used for *in-situ* removal of arsenic from groundwater, near Palmdale, California

With time, arsenic-73 was incorporated into progressively more refractory (less reactive) sites as surface specifically-sorbed arsenic was first incorporated into amorphous (NH4-Oxcalate fraction) and then into crystalline minerals (HNO3 and residual fractions) on the surfaces of primary mineral grains (Figure 3.10). By the end of the one year experiment, only about 12 percent of the arsenic-73 remained within the surface sorbed fraction. The NH4-Oxalate + Ascorbic acid extraction was the largest reservoir of extractable arsenic-73, containing from 19 to 39 percent of the arsenic-3, with a median of 32 percent (Figure 3.10). The experiment could only be run for one year because of the relatively short half-life of arsenic-73. Although the conversion from exchangeable to crystalline forms appears largely complete after about 12 months, the amorphous arsenic (about 20 percent of the total extractable arsenic-73) may continue to become increasingly crystalline with time until the amorphous fraction approaches background levels (about 10 percent of the total extractable arsenic).

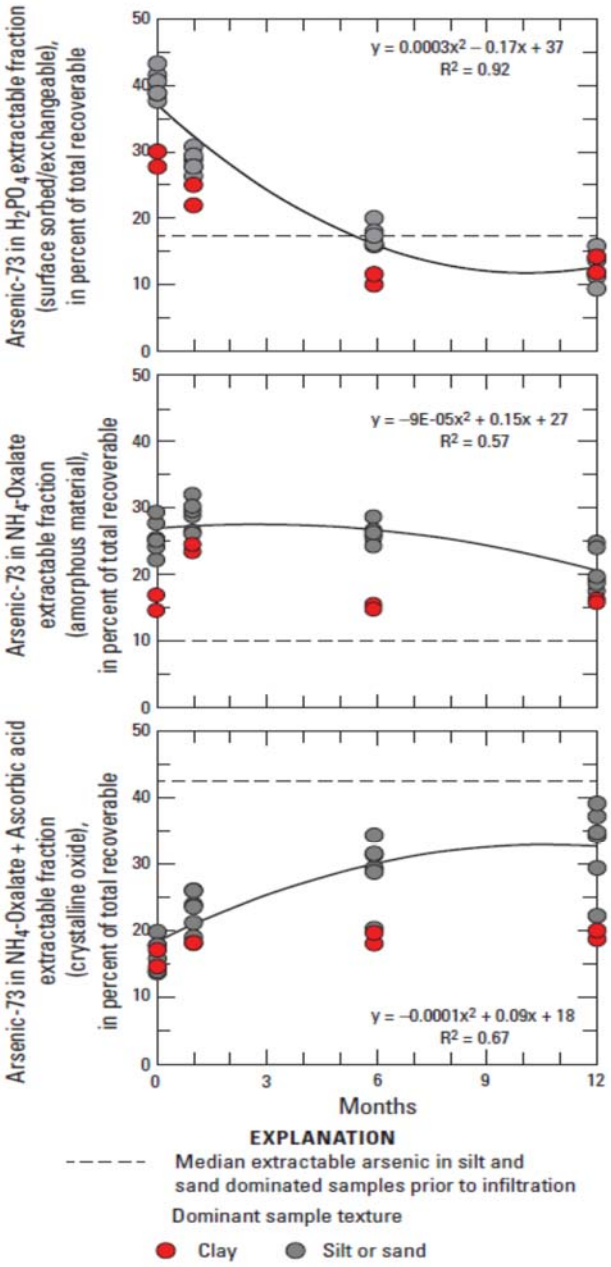


Figure 3.10 Arsenic-73 in the H_2PO_4 (surface sorbed/exchangeable), NH_4-Oxalate (amorphous), and NH_4- Oxalate + Ascorbic acid (crystalline oxide) fractions as a function of time during microcosm experiments for selected unsaturated materials beneath a recharge pond used for *in-situ* removal of arsenic from groundwater, near Palmdale, California

COLUMN EXPERIMENTS

Bromide breakthrough in columns at concentrations in the test solutions occurred between 1 to 1.5 pore volumes. This is consistent with piston-flow of a conservative tracer in a properly packed column. In contrast, arsenic did not breakthrough at concentrations in the test solutions

(30 and 300 µg/L), or at concentrations in excess to the MCL for arsenic of 10 µg/L, in any of the columns at either pH 6 or pH 8 (Figure 3.11)

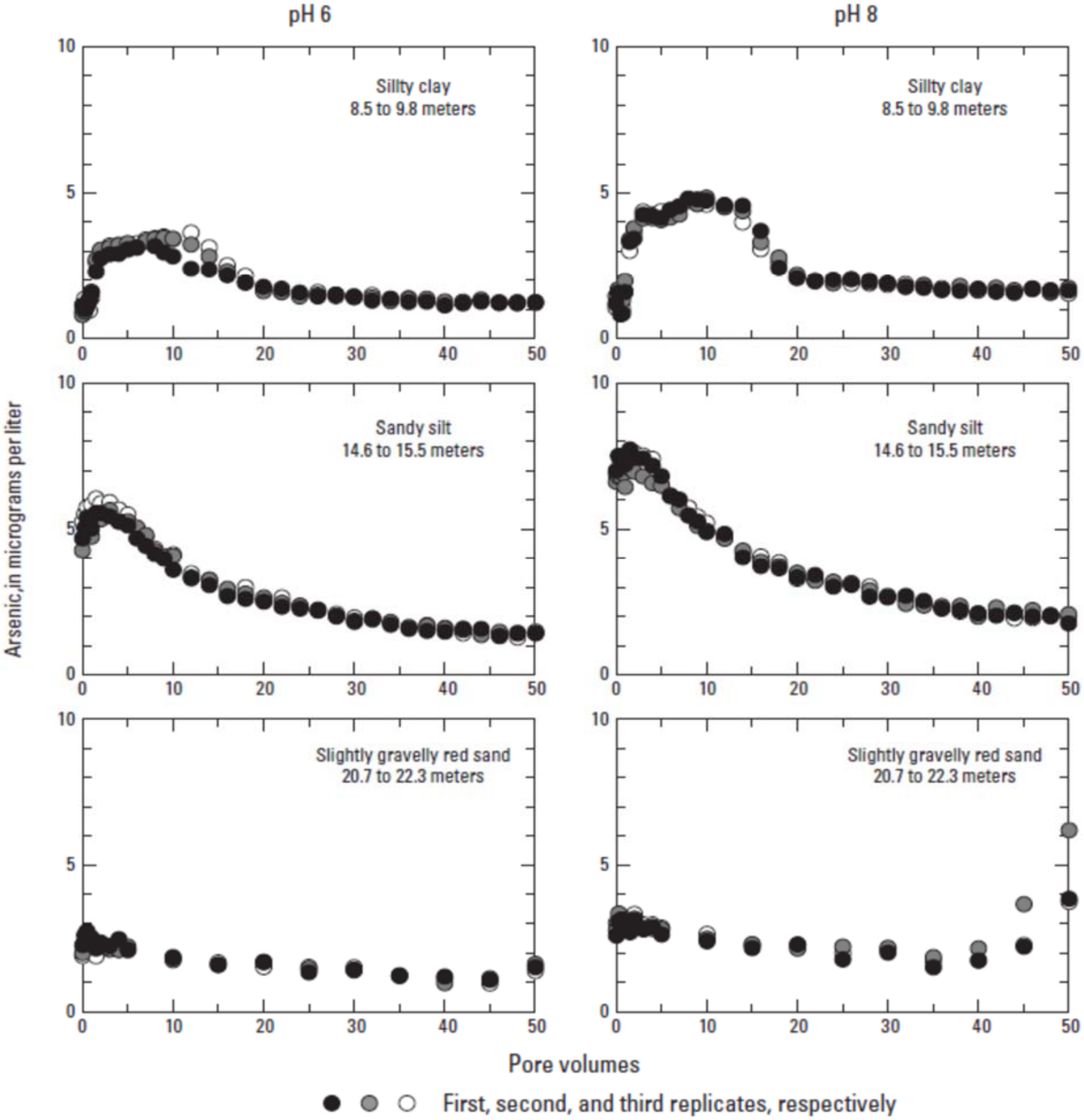


Figure 3.11 Arsenic concentrations in column effluents for alluvium from selected depths adjacent to a groundwater recharge pond used for *in-situ* removal of arsenic, near Palmdale, California (Influent arsenic concentration, 300 µg/L. Results for influent arsenic concentrations of 30 µg/L not shown.)

The column experiments are consistent with the results of the field-scale experiment that show arsenic retention within the alluvium. During the experiments, effluents from most columns reached a constant arsenic concentration of about 1 to 2 µg/L. This is similar to the arsenic concentration measured as part of the field-scale experiment in the lysimeter at 47.5 meters below land surface. Only one set of columns, containing alluvium from 20.7 to 22.3 meters below land surface, having influent arsenic concentrations of 300 g/L and a pH of 8 showed increases in arsenic concentrations during the latter part of the experiment consistent with the onset of arsenic breakthrough (Figure 3.11).

Column experiments were up to 6 months in duration. Arsenic-73 experiments show this is sufficiently long for arsenic retention, which is initially dominated by sorption to exchange sites, shifting to retention by amorphous iron and aluminum hydrous oxides and then to incorporation within more crystalline iron and aluminum minerals (Figure 3.10). Shorter duration experiments using higher flow rates, even though they may pass the same amount of water through the column, may not yield the same results if sorption is dominated by exchangeable or amorphous oxides during the time of the study. Increasing incorporation of arsenic into crystalline oxides on the surface of mineral grains may explain why arsenic concentrations increased to near the MCL of 10 μg/L and then decreased in the lysimeter at 7.9 meters below land surface (Figure 3.5). Comparison of extractable (KH2PO4) iron and aluminum in the slightly gravelly red sand from 20.7 to 22.3 meters below land surface (Table 3.2) shows almost 4-fold less iron sorbent and 2- to 3-fold less aluminum sorbent in this material than material from 8.5 to 9.8 and 14.6 to 15.5 meters below land surface (Table 3.2).

Column experiment results show higher arsenic retention than the field-scale results. This may be attributed, in part, because the materials selected for the column experiments were expected to have greater sorptive capacity. In addition, although ODEX cuttings were not contaminated by drilling fluids, they were disturbed by drilling. Naturally occurring aggregates, layering, and cementation that contribute to fine-scale heterogeneity within the undisturbed alluvium were not preserved in the cuttings. In addition, the columns were loosely-packed to bulk densities less than those found in alluvial material within the Mojave Desert. This may have resulted in greater contact between material within the columns and the test solutions than may occur between alluvium and water infiltrated from the pond. Furthermore, column studies cannot duplicate the large-scale heterogeneity present within thick alluvial deposits as a result of layering and subsurface geology present at the site that were important during the field-scale experiment. Use of column experiment data to assess the suitability of a site for in-situ arsenic treatment would likely overestimate the sorptive capacity of the site.

CHAPTER 4: DISCUSSION AND CONCLUSIONS

About 121,500 m^3 of groundwater having arsenic concentrations of about 30 µg/L was pumped from a deep aquifer between December 2010 and July 2012 and infiltrated from a 0.11 ha (1,100 m^2) pond to recharge the underlying water table aquifer. Infiltration rates from the pond ranged from 0.4 to less than 0.2 m/d. Arsenic concentrations in the water decreased from 30 to 2 µg/L as water infiltrated through the 80 m thick unsaturated zone underlying the pond and recharged the water table aquifer.

During the experiment, infiltrated water spread laterally above low-permeability layers within the unsaturated zone (Figure 3.4). Most spreading occurred above fine-grained layers about 50 m below land surface and the rate of downward movement decreased from 25 cm/d to 5 cm/d below that depth. By the time water reached the water table in January 2013, the wetted footprint from the pond was about 13 ha. Approximately 4.5 x 10^6 m^3 of alluvium was wetted by water from the pond.

Although data show breakthrough of arsenic was beginning to occur in the shallowest lysimeter at 7.9 m below land surface, arsenic concentrations in water from this lysimeter remained below the MCL for arsenic of 10 µg/L. Of the estimated 3.6 kg of arsenic present in water infiltrated through the pond, almost 3 kg of arsenic was retained within the 8,700 m^3 of alluvium above 7.9 m. Arsenic retention within the alluvium was about 0.34 g/m^3 of alluvium. Field data showed an increase in arsenic concentrations in alluvium beneath the pond as a result of arsenic retention during the experiment, although on the basis of Toxicity Characterization Leaching Procedure (TCLP) data collected as part of this study, arsenic concentrations on alluvial material beneath the pond were below concentrations considered to be hazardous.

On the basis of these data, unsaturated alluvium wetted by the pond could retain as much as 1,500 kg of arsenic. The experimental pond built for this study has the capacity to treat 60 x 10^6 m^3 of groundwater having an arsenic concentration of 30 µg/L to less than the MCL of 10 µg/L. Assuming an average infiltration rate of 0.3 m/d, the unsaturated zone beneath the experimental pond would function to retain arsenic for more than 500 years. This estimate is conservative, and does not account for the greater sorptive capacity of fine-grained materials within the subsurface.

In contrast to the field data, column experiment results show arsenic retention within alluvium of 4.3 to 7.9 g/m^3 without breakthrough of arsenic. These values are 10 to 20 times higher than arsenic retention estimated from field data. Greater retention of arsenic within columns occurred in part because materials selected for the column experiments were expected to have greater sorptive capacity on the basis of their fine-grained texture (greater surface area and therefore greater abundance of iron and aluminum oxide sorbents) and color (more extensive paleosol development and therefore greater abundance of iron and aluminum oxide sorbents). In addition, disturbance of the alluvium during sample collection, subsequent packing within the column, and piston-flow through the column also contributed to greater contact between the alluvium and test solutions, and therefore greater retention—compared to the more heterogeneous distribution of alluvium and water flow in field settings. Arsenic retention within the columns was relatively independent of pH (within the range pH 6 to 8), suggesting that *in-situ* treatment may work in more humid environments where unsaturated zones are less alkaline, as long as sufficient sorptive materials are present.

Arsenic-73 data show arsenic retention within the unsaturated zone was initially through sorption to exchange sites associated with iron and aluminum oxide coatings on the surfaces of mineral grains. With the exception of surface soils, manganese oxides were not abundant and did not provide much sorptive capacity. Some sorption appeared to be associated with clay mineral edge structures. With time, exchangeable arsenic was incorporated into amorphous oxides, and after one year most arsenic was incorporated within crystalline surface coatings. These data suggest that once sorbed, after a short time arsenic would not be highly mobile and would be unlikely to be mobilized solely by water passing through the unsaturated zone. Future changes in land use that result in increased infiltration of water from lawn watering or changing irrigation practices would not be likely to mobilize sorbed arsenic. However, sorbed arsenic would potentially be mobilized by changes in redox conditions that may occur as a result of future changes in land use. These include use of the pond to recharge stormflow runoff having a high dissolved organic carbon concentration, recharge through flooded agricultural fields where organic matter accumulates, dairy or confined animal feeding operations, or unsewered residential land uses. It also is possible that applications of phosphate fertilizer associated with agricultural land use may desorb arsenic. It may be appropriate to retain some natural sorptive capacity within the unsaturated zone as a protective buffer to guard against unforeseeable changes in future land use and minimize the need for permanent land use restrictions on sites used for *in-situ* treatment of high-arsenic water.

The cost of arsenic treatment and recharging the shallow aquifer was the cost of pumping the water from the deeper aquifer, about \$120 per 1,000 m3. This compares favorably with the cost of arsenic treatment using sorbent resins (neglecting construction cost), about \$490 to \$650 per 1,000 m3 (U.S. Environmental Protection Agency, 2000 and 2003).

CHAPTER 5: GUIDANCE FOR UTILITIES

Hydrogeologic conditions that make *in-situ* treatment of high-arsenic water feasible include a deeper aquifer having high-arsenic groundwater that is otherwise potable, and a shallower aquifer used as a source of public supply. This situation is common in the southwestern United States, the Central Valley of California, and in other areas. The unsaturated zone overlying the aquifer needs to be contain sufficient naturally-occurring iron and aluminum oxides (which are ubiquitous on the surfaces of mineral grains) to provide for an economically viable treatment site.

In-situ arsenic removal provides cost benefits related to capital expenditures and operation and maintenance compared to more conventional forms of arsenic removal without the generation of hazardous waste. Pumping of high-arsenic groundwater from deeper aquifers that are no longer suitable as sources of public supply will restore a beneficial use to those aquifers that was lost as a consequence of regulatory changes. Furthermore, pumping from deeper aquifers will lower water levels in those aquifers and reduce vertical pressure gradients (if present) that may allow high-arsenic water from deeper aquifers to migrate upward into shallower aquifers used as a source of public supply. However, implementation of *in-situ* arsenic removal will require careful forethought by water resource managers and, depending on the jurisdiction, compliance with regulatory controls to ensure successful operation during the life of the project. It is possible that there may be additional concerns associated with future land use after the site is no longer used for *in-situ* arsenic removal.

Initial site selection and design, as with other water resource management activities, is often dictated by practical considerations such as 1) land availability, 2) proximity to nearby wells having high-arsenic concentrations, and 3) the location of wells or suitable aquifer material for recovery of treated water. In addition, geologic considerations for site selection include the presence of a sufficiently thick unsaturated zone to allow for extended use of the site. At this point the technology is relatively new, and only general guidance on the range of conditions under which this approach can be used in is available. Although the demonstration site had an 80-m thick unsaturated zone, given the cost of conventional arsenic treatment, thinner unsaturated zones also may provide economic benefits to utilities. Infiltration though the unsaturated zone needs to be sufficiently rapid to allow use of the treated water within a reasonable time—but not so rapid that there is little lateral spreading of the water and minimal contact with unsaturated materials containing naturally-occurring iron and aluminum oxides needed for treatment processes. Site-specific characterization of subsurface geology, hydraulic properties, and naturally-occurring iron oxide sorbent abundance at proposed site (including the presence of low-permeability layers that enhance lateral spreading of infiltrated water within the unsaturated zone and increase contact between water and aquifer sorbent material) may be required before management decisions concerning site suitability can be made and estimates of site performance developed.

This work provides a series of steps used to understand important site characteristics. It is likely that not all the characterization done at this site would need to be done at every site. However, the ability to monitor arsenic concentrations at the water table and within the unsaturated zone is critical to demonstrating *in-situ* treatment is effective. Similarly monitoring arsenic concentrations on unsaturated materials before and during the life of a project (which may be many decades) will be critical to ensuring sorptive capacity of the materials has not been exhausted and the materials are not approaching hazardous levels.

Once a site has been selected, and ponds and other infrastructure constructed, management of the *in-situ* treatment process is comparatively simple. Specific considerations for pond management by individual utilities involve both water supply and pond maintenance. If water is supplied to the pond by pumping deeper groundwater the pumping rate should not exceed pond capacity. Wells intended to supply water directly for consumption may need to meet peak seasonal or daily demands. In contrast, smaller wells equipped with smaller pumps can be used to supply water to a treatment pond, Water supply costs may be reduced further for local utilities by pumping during off-peak demand periods having lower electricity costs. Pond maintenance will be required to ensure infiltration rates remain sufficiently high to meet project goals. The test pond used in this study required cleaning and removal of algal material that accumulated on the pond bottom once every 4 to 6 months. Less frequent cleaning may be required in cooler climates having slower algal growth rates. More frequent cleaning may be required if the groundwater is high in nutrients that increase algal growth, or if the pond sidewalls are subject to erosion creating sedimentation within the pond. Regardless of the specific supply and maintenance activities at an *in-situ* treatment site, documenting applied water, water levels in the pond, groundwater levels, and maintenance activities will help utilities fine-tune operations to ensure the efficient operation of the site.

As algal material accumulates on the pond bottom, some arsenic may be incorporated into algal material. In this study incorporation of arsenic into organic material was not an important arsenic removal mechanism (although almost complete removal of trace elements such as selenium and chromium from infiltrated water occurred in organic material accumulated on the pond bottom). However, accumulation of organic material may change redox conditions in the pond bottom. The effects of changing redox were not fully investigated in this study, but may include reduction of As (V) to As (III). As (III) is less strongly sorbed than As (V), and if arsenic is present as As (III), treatment efficiency through sorption within the unsaturated zone may be reduced. Furthermore, although the MCL is for total arsenic As (III) is more toxic than As (V). On the basis of data from this study, there is potential for reductive dissolution of iron (and associated trace elements) beneath the pond bottom if reducing conditions develop, and also the potential for methlyization and increased mobility of arsenic under reduced conditions. In ponds overlying sufficiently thick unsaturated zones that allow reoxygenation of the infiltrated water, the iron would subsequently precipitate as oxic conditions are reestablished; thereby removing iron and trace elements such as arsenic. These processes would mimic conventional arsenic removal through coprecipitation with iron (U.S. Environmental Protection Agency, 2000).

One concern is the possible need for permanent land-use restrictions after a site used for *in-situ* treatment of arsenic is removed from service. Arsenic-73 experiments done as part of this work show arsenic becomes incorporated within crystalline iron and aluminum oxide mineral structures and less mobile with time. As a consequence, simply passing water of similar quality through the unsaturated zone after an *in-situ* treatment site is removed from service will not mobilize sorbed arsenic. However, changes in land use that alter redox conditions within the unsaturated zone may mobilize arsenic. For example, using a pond for infiltration of stormflow runoff water having high organic carbon concentrations may alter the redox conditions within the unsaturated zone and increase the mobility of arsenic. Similarly, unsewered residential or commercial land uses or land uses that include land application of animal wastes may be inappropriate. It may be desirable to maintain some sorptive capacity in the unsaturated zone after *in-situ* treatment is stopped to allow for unforeseen changes in land use that could mobilize arsenic in the future. For example, if site characterization suggests that there may be sorbent capacity to operate a site for 100 years, it may be desirable to cease operation after 50 years and leave half the treatment capacity as a buffer to allow for unforeseen changes in land use.

Although not addressed in this report, it may be possible to increase the sorptive capacity of a proposed or active *in-situ* treatment site through addition of iron (in either the oxide or metallic form) to the pond. This may extend pond life in areas having a thin unsaturated zone and consequently less available naturally-occurring sorbent on the surfaces of mineral grains, or in areas where the natural sorptive capacity of the site is nearing exhaustion. From a regulatory standpoint management of a treatment pond would allow recovery of arsenic sorbed on materials added to the near-surface, thereby eliminating concerns over adverse effects associated with future changes in land use. Careful management of these materials may minimize disposal costs if amendments are removed before concentrations become hazardous.

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ABBREVIATIONS

ADP	ammonium dihydrogen phosphate
AGI	Advanced Geosciences Inc.
As (III)	reduced form of arsenic, arsenite
As (V)	oxidized form pf arsenic, arsenate
AVEK	Antelope Valley East Kern
DC	direct current
EM	electromagnetic
HNO_3	nitric acid
ICP-MS	Inductively coupled plasma mass spectrometry
KC1	potassium chloride
LACDPW	Los Angeles County Department of Public Works
MCL	maximum contaminant level
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
ODEX	Overburden Drilling EXploration
PVC	polyvinyl chloride
redox	reduction-oxidation
TCLP	toxicity characteristic leaching procedure
USDA	U.S. Department of Agriculture