

Prepared in cooperation with the U.S. Army Corps of Engineers

Geochemistry and Microbiology of Groundwater and Solids from Extraction and Monitoring Wells and Their Relation to Well Efficiency at a Federally Operated Confined Disposal Facility, East Chicago, Indiana



Scientific Investigations Report 2018–5073

Cover. Photograph of groundwater-quality sampling equipment at well EW-14A. Photograph taken on October 8, 2014, by Patrick C. Mills, U.S. Geological Survey (retired).

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By E. Randall Bayless, Travis R. Cole, David C. Lampe, Rebecca E. Travis,
Marjorie S. Schulz, and Paul M. Buszka

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Patrick C. Mills, USGS, assisted with sample collection. Sara Peek, USGS, analyzed solids from CDF wells for carbon and sulfur isotopes. Kate Campbell, USGS, provided semi-quantitative X-ray diffraction analysis of solids collected from CDF wells. John Fitzpatrick, USGS, provided inductively coupled plasma mass spectrometry analyses of chemically digested solids from CDF wells. James Landmeyer, USGS, provided a chromatograph to determine the presence of hydrocarbons in a scraping taken from a pump at the CDF.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m ²)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm ²)
acre	0.004047	square kilometer (km ²)
square mile (mi ²)	259.0	hectare (ha)
square mile (mi ²)	2.590	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
Flow rate		
foot per day (ft/d)	0.3048	meter per day (m/d)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m ³ /s)
Mass		
ounce, avoirdupois (oz)	28.35	gram (g)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8.$$

Datums

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29) or North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L) and micrograms per liter ($\mu\text{g}/\text{L}$). Chemical concentrations and water temperature are given in metric units.

A milligram per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. For water with dissolved-solids concentrations less than 7,000 mg/L, the numerical value for milligrams per liter is the same as for concentrations in parts per million.

A concentration of 1,000 $\mu\text{g}/\text{L}$ is equivalent to 1 mg/L. For water with dissolved-solids concentrations less than 7,000 mg/L, the numerical value for micrograms per liter is the same as for concentrations in parts per billion.

The mole ratio of two substances expresses the amount of chemical constituents in solution as the weight of a chemical substance, in milligrams (10^{-3} g), in a liter of water, divided by the atomic weight of one atom or molecule of its composition elements, in grams (one mole), divided by the amount of a second substance, also expressed in moles.

One mole is equivalent to 1,000 millimoles.

One atmosphere (atm) of pressure is equivalent to 760 millimeters of mercury.

δ (delta), as used in this report, refers to the stable isotope ratio $\delta x = [(R_x/R_{\text{STD}}) - 1] \times 1,000$, where R_x and R_{STD} are the $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$ values of the sample and reference standard. The value of δ is generally expressed in parts per thousand (‰, or per mil).

Abbreviations

atm	atmosphere
BSE	backscatter electrons
CDF	confined disposal facility
CFU/mL	colony forming units per milliliter
EDS	energy dispersive spectroscopy
MRL	minimum reporting limit
NAVD 88	North American Vertical Datum of 1988
NBS	National Bureau of Standards
NWQL	National Water Quality Laboratory
NTU	nephelometric turbidity units
RPD	relative percent difference
SEM	scanning electron microscopy
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
XRD	X-ray diffraction

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Abstract

In cooperation with the U.S. Army Corps of Engineers, Chicago District, the U.S. Geological Survey investigated the processes affecting water quality, geochemistry, and microbiology in representative extraction and monitoring wells at a confined disposal facility (CDF) in East Chicago, Indiana. The CDF is a 140-acre Federally-managed facility that was the former location of an oil refinery and is now used for the long-term disposal and storage of dredge material from the Indiana Harbor and Indiana Harbor Canal. Residual petroleum hydrocarbons and leachate from the CDF are contained within the facility by use of a groundwater cutoff wall. The wall consists of a soil-bentonite slurry and a gradient control system made up of an automated network of 96 extraction wells, 42 monitoring wells, and 2 ultrasonic sensors that maintain an inward hydraulic gradient at the site. The pumps in the extraction wells require vigilant maintenance and must be replaced when unable to withdraw water at a rate sufficient to maintain the required inward gradient. The wells are screened in the Calumet aquifer, a coarse-grained sand and gravel unit that extends approximately 35 feet below the land surface and is not utilized for drinking-water supply at the CDF or in the surrounding area. This study was initiated to identify the cause of decreased pump discharges and to identify potential mitigation strategies.

For this study, the U.S. Geological Survey collected groundwater and solids from monitoring and extraction wells. Groundwater samples were collected during June 2014 for precautionary health screening and on four occasions during September 2014 through November 2014. Groundwater samples collected from two extraction wells during June 2014 were analyzed for concentrations of anthropogenic organic constituents. During September through November 2014, groundwater samples were collected from one additional extraction well, and samples from three monitoring wells were analyzed for concentrations of inorganic and organic constituents, dissolved gases, and bacterial abundance and

diversity. Solid samples were collected during April 2014, during September 2014 through November 2014, and during November 2016. Solid samples were collected from the exterior of extraction-well pumps and as flocculent from water samples. Solid samples were collected from 10 wells, including 1 extraction well and 3 monitoring wells sampled for water quality. Solid samples were analyzed for mineralogy, solid-phase habit, geochemistry, and organic composition.

The following is a list of observations that were made during this study: (1) the water quality is substantially variable among the six well locations sampled as part of this study—lower (more negative) redox values and higher concentrations of many constituents (including calcium, magnesium, sodium, and sulfate) and properties (including dissolved solids, hardness, and turbidity) were detected in sampled wells located near the extraction wells with the highest frequency of failure; (2) water-level drawdown is variable between extraction wells—wells with the greatest drawdown may pull deeper groundwater into the borehole; (3) dissolved gas results indicate reducing oxidation-reduction processes in the aquifer material that can feasibly contribute iron, carbon dioxide, and other byproducts from hydrocarbon degradation to precipitates and solids that accumulate on and impair pump operation; (4) crystalline and amorphous solid-phase minerals are precipitating in the borehole; (5) several types of bacteria are present in water pumped from extraction wells and are likely responsible for bonding mineral and microbiologic matter to the pump (and other well components); and (6) bacteria may create microenvironments that facilitate precipitation of solids or inhibit dissolution of unstable minerals once the bacteria adhere to biofilm attached to the pump. Results of the study indicate that bacteria may be accumulating and entrapping solid material on the exterior of pumps. This accumulation reduces heat transfer and water discharge from the pump and may lead to decreased efficiency or mechanical failure. Observations could not be made on the well screen, gravel pack, or surrounding geologic formation; therefore, mitigating measures in the borehole may not solve well-productivity issues.

Remedies for the pump fouling problems were derived from the review and interpretation of data collected during this study and from information documented in other sources about groundwater well fouling. Potential remedies to problems associated with pump fouling at the CDF may include the following: (1) reducing attractiveness of the extraction wells for microbiological growth by modifying the chemical or physical environment of the well, (2) modifying the pump exterior to decrease microbiological adherence, (3) changing the pumping regime to control the chemistry of water entering the well from the surrounding aquifer material, (4) modifying the pumps to be less physically and thermally attractive, and (5) removing hydrocarbons from groundwater and the aquifer material surrounding the wells or adding surfactants to make them more mobile. Pilot scale testing may be necessary to identify the most effective treatment or combination of treatments.

Introduction

The U.S. Geological Survey (USGS), in cooperation with the U.S. Army Corps of Engineers (USACE), led a study during June 2014 through November 2014 to specifically identify the hydrologic, chemical, and microbiologic processes affecting declining pump efficiency and frequent pump failure at a confined disposal facility (CDF) in East Chicago, Ind. (fig. 1). A decline in groundwater pump efficiency through time is common and can be attributed to biofouling (Sterrett, 2007). To better understand the causes behind declining pump efficiency, data were collected to describe the geochemistry and microbiology of groundwater and solids collected from extraction and monitoring wells at the CDF.

Site History

The efficiency of groundwater-extraction wells used to maintain an inward hydraulic gradient at the CDF site near East Chicago, Ind., is of necessary operational concern for the site operator, the USACE, Chicago District. The inward hydraulic gradient is maintained by use of a network of monitoring and extraction wells (fig. 2).

The site was formerly the home of oil-refining operations. In 1981, the property owner filed for bankruptcy; therefore, all aboveground materials and structures related to refinery operations were removed, and the site was covered with a layer of clean soil. Groundwater monitoring began in 1991 following the detection of hydrocarbon contamination, and a groundwater-recovery system was installed in 1992 along the southern boundary of the CDF property on the north side of the Lake George Branch (fig. 1). Organic compounds have been identified in soil and water samples since monitoring began and were observed during installation of the extraction and monitoring wells that currently regulate water levels at the CDF (Cohen and others, 2002) (fig. 3). Hydrocarbon seepage along

the south margin of the property and into the Lake George Branch also was described in Cohen and others (2002). The location of hydrocarbons at the site differs through time.

The Lake George Branch is a segment of the Indiana Harbor Canal (fig. 1). The Lake George Branch and Indiana Harbor Canal are connected to Lake Michigan (fig. 1) and water levels in the Indiana Harbor Canal vary continually in response to water levels in Lake Michigan and discharges from the Grand Calumet River (fig. 1), another tributary of the Indiana Harbor Canal. The gradient-control system at the CDF automatically responds to changing water levels in groundwater adjacent to the Indiana Harbor Canal.

The study area is underlain by the Calumet aquifer and wells at the CDF are completed in that geologic unit. The Calumet aquifer is a coarse-grained sand and gravel unit that extends approximately 35 feet (ft) below the land surface. The Calumet aquifer is not utilized for drinking-water supply at the CDF or in the surrounding area and for purposes of this study, is referred to as “aquifer material”.

Maintenance of inward, horizontal hydraulic gradients on all sides of the CDF is a critical operating feature of the site that enables isolation and control of residual hydrocarbons and leachate from the dredged sediment as well as control of existing site issues. The 22 nests of 4 extraction wells were installed in the permeable aquifer material, surficial sand and gravel deposits inside a groundwater cutoff wall. The groundwater cutoff wall consists of an impermeable bentonite slurry that extends from land surface to at least 3 ft below the interface between the fine-grained deposit and the surficial aquifer material. An additional eight extraction wells were added to three well nests along the southern perimeter of the CDF in 2015. Two monitoring wells are collocated with each nest of extraction wells. One monitoring well is located inside the slurry wall, and one monitoring well is outside the slurry wall. Pumps within the extraction wells are periodically activated to maintain an inward gradient between the monitoring wells. Extraction wells are about 30 ft with 5-ft screens at their base to limit the possibility for drawdown to reach the well screen. The wells were screened below occasional residual petroleum contamination from prior site activities.

A strong hydraulic connection between wells and aquifer materials surrounding the well screen is necessary to allow accurate monitoring of water levels in the subsurface and to maintain withdrawal rates required to establish the inward gradient. A poor connection between the well and the surrounding materials can increase drawdown in the extraction well and delay water-level responses outside the well to changes in water levels inside the well. During 2012, fouling became evident in some extraction wells at the CDF by the accumulation of a black gelatinous matter that formed on the pump intakes. Pump efficiency progressively decreased and eventually required pump replacement (fig. 4). Fouling of the well screen, gravel pack surrounding the screen, and adjacent aquifer material was possible but was not observed nor indicated by withdrawal rates when new pumps were installed.

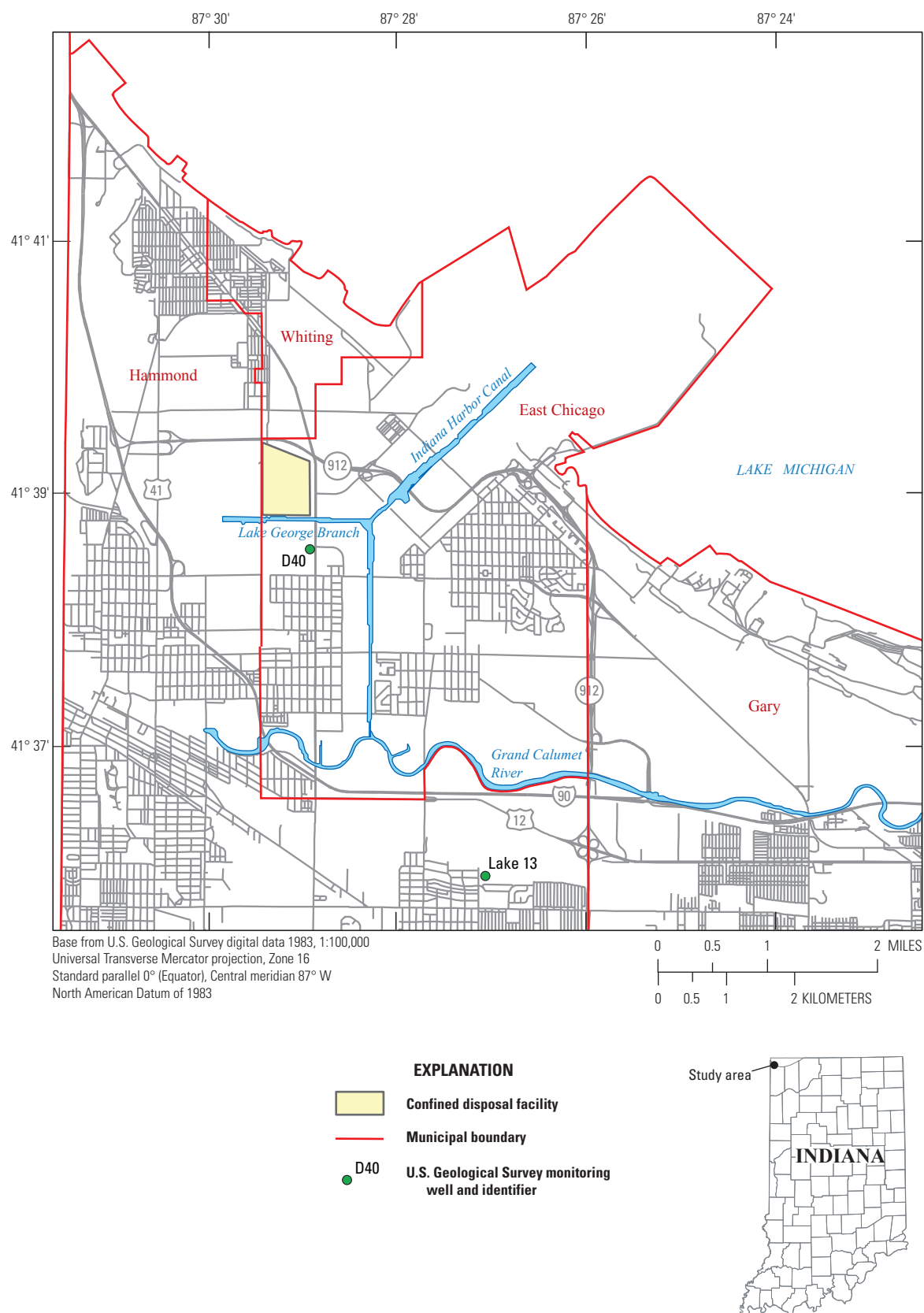


Figure 1. Location of the confined disposal facility at East Chicago, Indiana.



Figure 2. Locations of monitoring and extraction wells at the confined disposal facility.

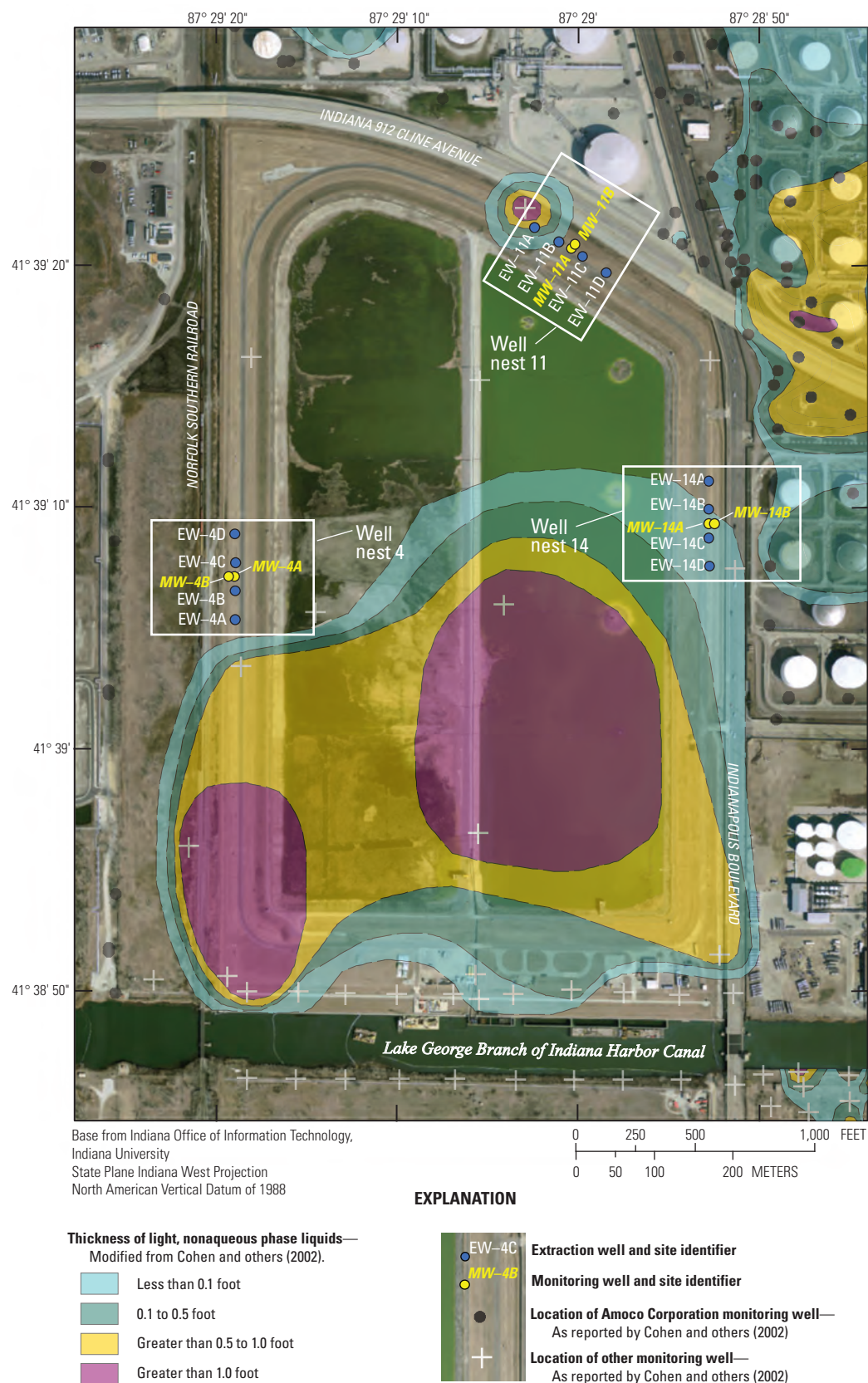


Figure 3. Estimated thickness of light, nonaqueous phase liquids on groundwater near the confined disposal facility and Indiana Harbor Canal, East Chicago, Indiana (modified from Cohen and others, 2002). Data represented on the figure were collected before 1998.

Of the affected extraction wells, fouling was more frequently evident in some wells than in other wells (fig. 5).

Assessing changes in water-level recovery and water-withdrawal characteristics of extraction and monitoring wells and determining the physical, chemical, and microbiological causes of decreased well yield are a necessary part of well-efficiency evaluation at the CDF. In 2014, the USGS, in cooperation with the USACE, led an investigation to identify the source of the unknown material causing the pump fouling and to describe the subsurface conditions that may control the presence or absence of the material on the CDF property. The first phase of the investigation used (1) single-well aquifer tests of extraction wells to characterize water-level drawdown and recovery characteristics relative to the volume of water produced during a normal cycle of operation and (2) single-well slug tests of monitoring wells to measure monitoring well characteristics. The tests were done at three sets of extraction and monitoring wells and were repeated 6 months later to measure changes in well properties through time. The results of that investigation were documented in Lampe and Unthank (2016) and applied to the data interpretation for this study.



Figure 4. Solid material adhered to a pump removed from extraction well EW-4B on May 8, 2014.

A second phase of the investigation described in this report analyzed for possible chemical, microbiological, and geochemical processes in the borehole that could explain pump fouling. Groundwater samples were collected in the same three sets of paired wells on four occasions, and solid-phase samples were collected from four of those wells and six additional wells. Paired well sets included an extraction well and a nearby monitoring well. Water samples were collected during four pumping regimes to determine if the pumping schedule affected the water chemistry. The four pumping regimes were as follows: (1) normal pumping intensity and duration, (2) no pumping for 8–16 hours before sample collection, (3) 2 weeks after resuming normal pumping conditions, and (4) 4 weeks after resuming normal pumping conditions. Samples were analyzed for bulk water properties, inorganic aqueous constituents, and dissolved gases. Discrete solid-phase samples were analyzed for chemical composition, carbon and sulfur isotopes, mineralogy, solid-phase morphology, and bacterial activity.

The information developed from this study addresses aspects of the USGS water science goals and objectives to clarify the linkage between human water use (engineered hydrology) and the water cycle (natural hydrology) (Evenson and others, 2012). The USACE and its partners benefit by having an improved understanding of the causes of pump fouling at the CDF and actions that might be undertaken to inhibit those processes.

The USGS, in cooperation with Federal and State partners, has published numerous reports on the groundwater, surface-water, and water-quality conditions in northwestern Indiana. The interaction of surface-water and groundwater levels near the Grand Calumet River and Indiana Harbor Canal were analyzed by Fenelon and Watson (1993) and Greeman (1995). The distribution of hydraulic conductivity in the Calumet aquifer and streambed sediments was analyzed by Kay and others (1996) and Duwelius and others (1996). The hydrology and geochemistry of slag affected aquifers and groundwater in northwestern Indiana were analyzed by Bayless and others (1998). Isotopic analyses were used to identify sources of groundwater, groundwater flowpaths and rates, to assess aquifer vulnerability in the Calumet aquifer in northwestern Indiana (Kay and others, 2002). These studies provided information and data to describe conditions in the area surrounding the CDF.

Review of Well and Pump Biofouling

Well fouling is a common issue. In about 80 percent of well-fouling occurrences, the well is fouled because of microbiological processes (Vance, 1998; Sterrett, 2007; Hackett, 1987). The symptoms of a fouled well screen often include increased drawdown during pumping, prolonged recovery following pumping, and poorer water quality relative to background conditions. The most notable degradation of water quality includes elevated iron or manganese concentrations and larger bacteria populations relative to background or

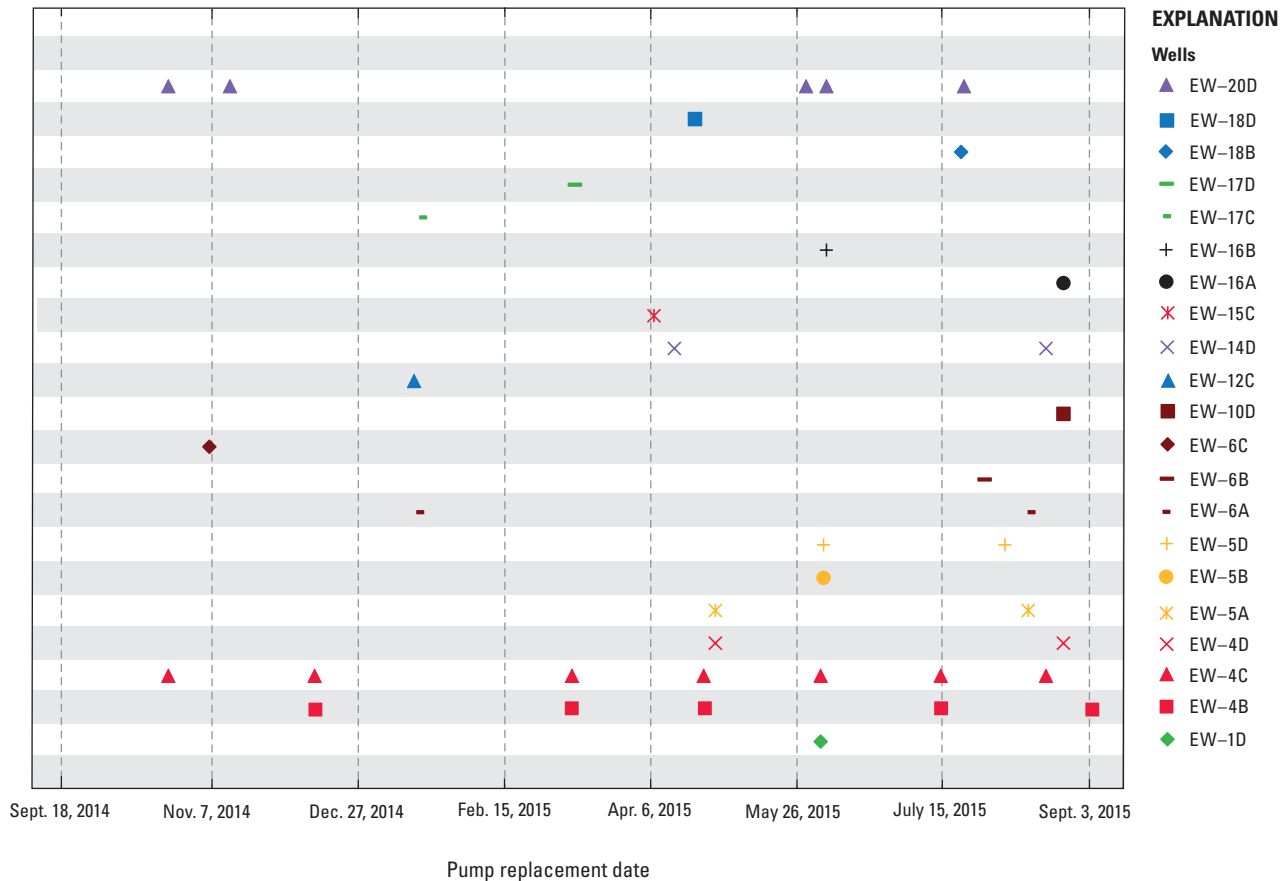


Figure 5. Pump replacement frequency data for October 2014 through September 2015.

nonpumped conditions (Vance, 1998). Biofouling is the term generally applied to the process of accumulating biofilms on well screens that become a nuisance (Characklis and Cooksey, 1983; Cullimore, 1999). Nuisance biofilms can impede the flow of heat across the surface of the pump, increase the fluid frictional resistance at the surface, and increase the rate of corrosion of the surface resulting in equipment stress and inefficiency (Characklis and Cooksey, 1983).

Biofilms are bacterial products that adhere to well components. More specifically, biofilms are a complex mixture of active microbial cells, extracellular polymeric substances, polysaccharides, and other matter that attaches to submerged surfaces. Commonly, extracellular polymeric substances extend from the cells and form a tangled mass of fibers (Characklis and Cooksey, 1983). These stringy fibers are primarily composed of polysaccharides but may also contain glycoproteins, proteins, and nucleic acids (Characklis and Cooksey, 1983). Polysaccharides are long chains of sugars created by the bonding of many monosaccharide molecules. Polysaccharides possess high molecular weight and act as carbohydrate storage for active cells. Extracellular polymeric substances may also serve the microbial cells by providing cohesive forces, adsorbing nutrients, binding particulates, and providing protection from rapid environmental changes including

biocides (Smith, 1992). The active bacteria cells represent a minor component of the total biomass (Vance, 1998). Biofilms can be beneficial to the environment by removing organic and inorganic substances from stream water and are the basis for trickle filters in wastewater treatment systems.

Mechanisms of biofouling that result in impaired wells include the following: (1) the physical presence of extracellular slimes that are excreted by the bacteria and aid attachment to surfaces within the borehole and surrounding geologic materials, (2) the accumulation of entrained solids and precipitated minerals within those slime layers; some minerals are scavenged from the ambient fluid by extracellular chemicals that are excreted by bacteria for that specific purpose, (3) the occlusion by gases that are generated by active bacteria, and (4) the corrosion of well components by hydrogen sulfide or organic acids that are generated by the microbiological activity (Vance, 1998). Biofouling can be complex and can be caused by a variety of bacteria (Vance, 1998). Black slime is the result of sulfur-reducing bacteria that cause precipitation of black sulfides, whereas white or clear slimes have not accumulated any precipitated minerals (Vance, 1998). Gray slime has accumulated some solids but is not totally dominated by sulfur-reducing bacteria (Vance, 1998). Orange, red, pink, or brown slimes are present where conditions are significantly

or borderline aerobic; the coloration in these slimes is from the accumulation of precipitated iron or manganese oxides or hydroxides (Vance, 1998).

Redox conditions affect the formation of biofilms. A schematic diagram (fig. 6) conceptually shows how meta-stable redox domains may form in concentric halos around a pump located at the center of a borehole (Vance, 1998). The maximum level of microbiological activity commonly occurs where redox values range from -50 to +150 millivolts (Vance, 1998).

Other factors affecting biofilm formation are surface roughness and borehole turbulence. Well components with

rough surfaces create more opportunities for microbial cell attachment and provide greater shelter from shear forces during pumping (Characklis and Cooksey, 1983). Studies additionally indicate that film density increases with increasing borehole turbulence (Characklis and Cooksey, 1983).

The following four broad treatment approaches for improving the functionality of biofouled wells were suggested by Vance (1998): (1) mechanical agitation of the borehole by surging, water jetting, scrubbing, or air sparging the borehole; (2) acidification to solubilize minerals and the polysaccharide portion of the bacteria; (3) flushing to remove soluble debris dislodged by the mechanical agitation; (4) introduction

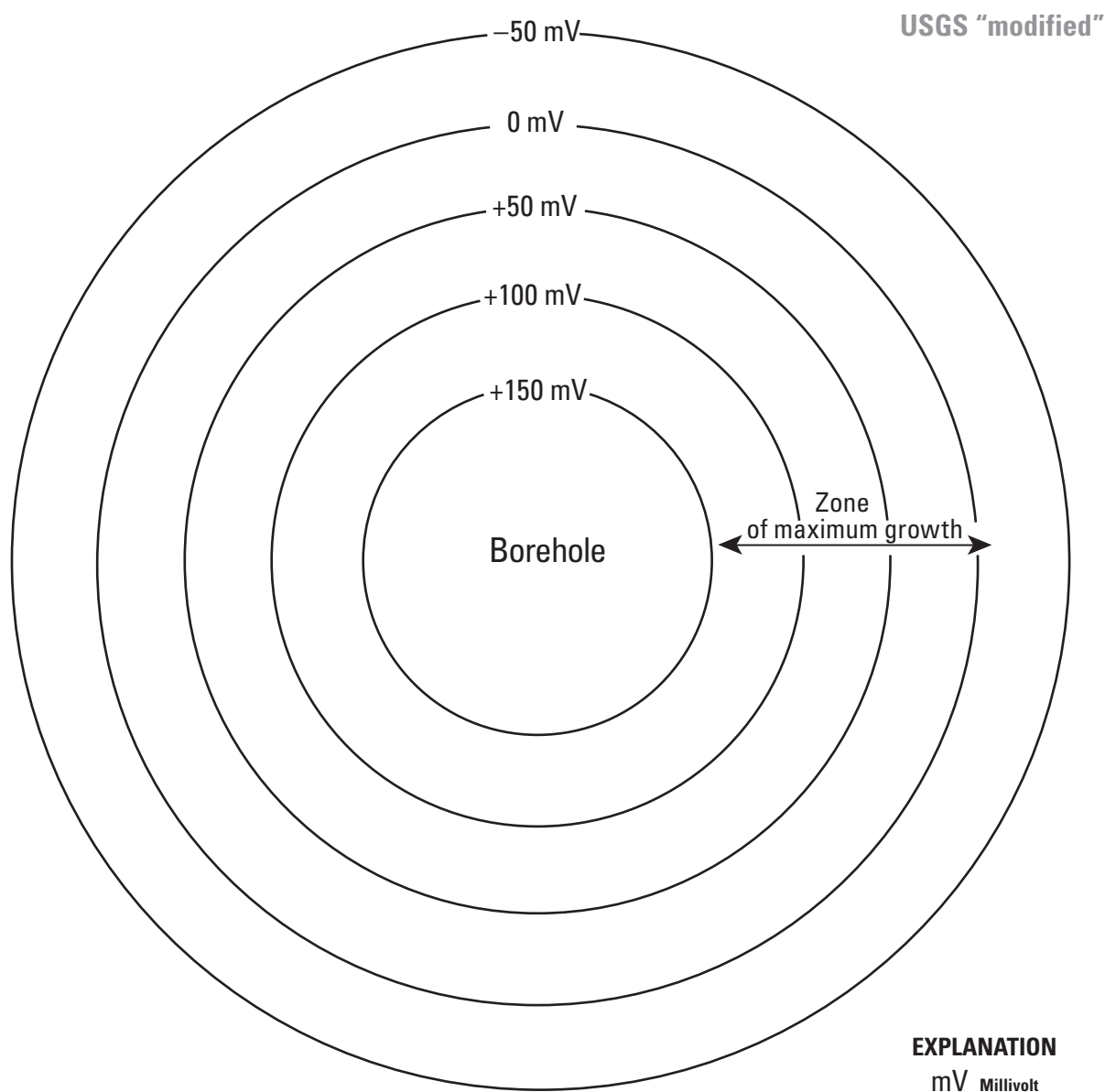


Figure 6. Schematic diagram showing redox environments near a borehole. Diagram modified from Vance (1998).

of bactericides to suppress bacteria populations. The most common acids used in well improvement operations include hydrochloric acid, sulfamic acid, and hydroxyacetic acid. Some acids and well additives may destroy well components, and the selection and concentration of acid should be intentionally selected (Vance, 1998).

A USGS investigation of well fouling in Suffolk County, New York (not shown), identified biofouling as the primary cause of reduced well yields (Brown and others, 1999). The investigation determined that multiple bacteria were present in biofilms. The bacteria included biofilms of aerobic bacteria that encapsulated thicker biofilms of anaerobic bacteria, which were primarily responsible for producing the biofilms. Fouling was not limited to the pump but also included the well screen and surrounding aquifer material. The investigation in Suffolk County determined that much of the pump encrusting material consisted of extracellular bacteria filaments, and the remaining material primarily consisted of amorphous ferric hydroxide with lesser amounts of goethite, hematite, other iron oxides, and silica. Groundwater samples from biofouled wells generally contained median concentrations of total and dissolved iron and manganese, total phosphate, and dissolved sulfate that were higher than those measured in background wells. Lower median concentrations of dissolved oxygen and alkalinity and lower pH were also observed in biofouled wells (Brown and others, 1999). Bacterial growth was determined to be the result of introducing oxygen into an anaerobic aquifer through creation of the well and creating redox gradients that were favorable for growth.

Rorabaugh (1953) defined “well efficiency” as the ratio of the theoretical computed drawdown induced by pumping, assuming no turbulence, to the actual drawdown in the well. Walton (1959) defined “well efficiency” as the ratio of the theoretical specific capacity to the actual specific capacity of the well. During well pumping, the water level in the well is expected to decline by an amount that is related to the decline in water level in the aquifer material surrounding the well. If the drawdown in the well declines disproportionately to the decline in the aquifer material, the well efficiency is less than 100 percent. Well efficiency may be affected by non-optimal screen placement relative to the vertical position of the aquifer, screen type, screen length, open area of the screen, hydraulic conductivity of the gravel pack, and incomplete development of the well. A decline in well efficiency may result from encrustation and bacterial clogging of the well screen, gravel pack, and aquifer material adjacent to the well screen, or other factors that create resistance to flow from the aquifer material into the borehole (Bierschenk, 1963).

Well efficiency was investigated at six monitoring wells and at three extraction wells on the CDF property during an earlier phase of this study (Lampe and Unthank, 2016). Single-well aquifer tests were completed once in August–September 2014 and again in March–May 2015 to evaluate changes in well efficiency through time. Air-slug test results for monitoring wells indicate that with each test in a given well, the hydraulic connection between the well and the

aquifer was increased by the surging of water through the well screen. Hydraulic conductivity results from a monitoring well located approximately 0.25 mile south of the CDF are substantially higher than hydraulic conductivity results from wells on the CDF property. The higher values indicate that (1) the offsite well was completed in a part of the aquifer with higher hydraulic conductivity or (2) a process may be affecting the connectivity of the wells on the CDF property to the Calumet aquifer. Between the tests completed in 2014 and again in 2015, the well and aquifer properties determined from the step drawdown and recovery aquifer tests from three extraction wells on the CDF property remained relatively similar (Lampe and Unthank, 2016). Derived hydraulic conductivity values were relatively similar in EW-4B and EW-14A; values for EW-11C were substantially lower. Specific-capacity estimates derived from the single-well aquifer tests in the tested extraction wells were compared to well development data that were collected in 2008 to evaluate change in well efficiency since well installation. Specific-capacity estimates for EW-4B, EW-11C, and EW-14A are substantially lower than those calculated from initial well development data.

Purpose and Scope

The purpose of this report is to describe (1) the results of groundwater, solids, and microbiological analyses for samples collected at the site, (2) the physiochemical processes that may be active near each well, and (3) the potential applications of those findings to mitigate pump fouling in CDF extraction wells.

This report describes results of water-quality, geochemistry, and microbiological sample collection at the CDF, which encompasses 1.87 square miles in East Chicago, Ind. Groundwater samples were collected from three extraction wells and three monitoring wells located along the perimeter of the CDF, representing three different hydrogeologic and geochemical settings (well nests 4, 11, and 14). Additional data used in this analysis included historic water-quality measurements from two offsite wells and solid samples collected from five other wells at the CDF.

Description of the Study Area

Urban development in the late 1800s and early 1900s brought about notable changes in the area surrounding the CDF. Changes included the draining of marshes in low-lying areas and the digging of the Indiana Harbor Canal to connect the Grand Calumet River to Lake Michigan, causing a change in direction of flow to the river (Moore and Trusty, 1977). Slag, a byproduct of the steel making industry, was used extensively as fill material in depressions and marshy areas in the region (Kay and others, 1996) and in limited quantities at the CDF.

The CDF property is in East Chicago, Ind., and is approximately 1.5 miles south of Lake Michigan. The CDF

site is approximately 140 acres and is bounded by Indianapolis Boulevard to the east, Indiana 912 (Cline Avenue) to the north, Norfolk Southern Railroad to the west, and the Lake George Branch of the Indiana Harbor Canal, to the south (fig. 2).

Beginning in 1918, the CDF property was the location of a petroleum refinery with peak production of about 140,000 barrels of refinery products per day. Products included gasoline, fuel oil, kerosene, lubricating oils, grease, asphalt, propane, liquefied petroleum gas, phenols, paraffin wax, and, for a brief period during the 1940s, insecticides (Geraghty & Miller Environmental Services, 1993). In 1981, the property owner filed for bankruptcy; therefore, all aboveground materials and structures related to refinery operations were removed and the site was covered with a 3-ft thick layer of compacted clay (U.S. Army Corps of Engineers, 2000). Groundwater monitoring began in 1991 following the detection of hydrocarbon contamination, and a groundwater recovery system was installed in 1992 along the southern boundary of the CDF property on the north side of the Lake George Branch. Other groups of inorganic and organic compounds have been identified in soil and water samples collected before 1998 (Cohen and others, 2002).

The USACE took possession of the property and began construction of the CDF in 2002 as the final repository of dredging wastes, including those from the Indiana Harbor and Indiana Harbor Canal. Railroad tracks and buried infrastructure were removed where they conflicted with the installation of the groundwater cutoff wall and well arrays. A steel sheet-pile groundwater cutoff wall and slurry-barrier groundwater cutoff wall seal the border with the Indiana Harbor Canal on the south side. The slurry-barrier and sheet-pile groundwater cutoff walls were installed to connect with a lower confining unit, a silty clay to clay deposit. This groundwater cutoff wall system was intended to meet the permeability requirements of 2.83×10^{-4} foot per day (1.0×10^{-7} centimeter per second) for the CDF perimeter (U.S. Army Corps of Engineers, 2000). Inside the groundwater cutoff wall and outside on the landward sides of the site, aquifer materials are capped with a 3-ft thick layer of compacted clay. The intention of capping the site was to use a relatively impermeable material that would inhibit the infiltration of precipitation and force water to move laterally as overland flow into the ponds where dredge spoils would be deposited.

Within the groundwater cutoff wall, a gradient control system was installed to maintain an inward groundwater gradient at the site. The gradient control system, at the time of the study, consisted of 22 nests. Each nest consisted of four extraction wells installed within the groundwater cutoff wall and a pair of monitoring wells, one well inside and one well outside of the wall. Extraction and monitoring wells were installed during 2008. Eight additional extraction wells were added to three well nests along the southern perimeter of the CDF in 2015. Monitoring wells along the southern perimeter of the CDF use the water levels of the Lake George Branch as the exterior reference for water altitude. An automated system uses continuous water-level data collected from the monitoring

wells and the Lake George Branch to control the operation of the extraction wells within each nest. When the difference in water level between the inner and outer monitoring wells reaches a threshold, pumps in the extraction wells are activated to lower the water table. Lowering the water level in the extraction wells effectively increases the gradient inward toward the CDF across the groundwater cutoff wall. Groundwater from the extraction wells is pumped from the aquifer inside of the groundwater cutoff wall into the water-collection system. The groundwater then discharges into the unlined disposal cells in the center of the CDF before treatment by the onsite wastewater treatment plant and offsite discharge. The monitoring and extraction wells are approximately 30 ft with 5-ft screens at their base to limit drawdown from reaching the well screen and to be screened below residual petroleum contamination. Pumps are not installed within the monitoring wells on the CDF property, and these wells were not routinely pumped or redeveloped. The detection of hydrocarbons during extraction well installation was noted on well-drillers' records. Anecdotal observations indicated that the distribution of petroleum hydrocarbons varies spatially with time. Hydrocarbons were measured in two groundwater samples collected on June 19, 2014, to determine the level of personal protective equipment required by the staff for this study (table 1).

Beginning in 2012, specific extraction wells at the CDF site began to show evidence of fouling. A precipitate formed on the intake of some of the extraction-well pumps causing them to overheat and become inoperable, ultimately requiring site personnel to pull the equipment from the well and replace each inoperable pump. Of the affected extraction wells, fouling was more frequently evident in some wells than in other wells.

Hydrogeologic Setting

The CDF is in Lake County in northwestern Indiana and is in the Calumet Lacustrine Plain physiographic province (Schneider, 1966). The province is made up of several distinct dune-beach complexes formed in the Pleistocene and Holocene Epochs when Lake Michigan was at higher levels than it is today (2017) (Leverett and Taylor, 1915; Bretz, 1951; Hansel and others, 1985). The dune, beach, and lacustrine silts, sands, and gravels that were deposited form a thin but laterally extensive surficial aquifer (referred to herein as the Calumet aquifer). In the area of the CDF, the Calumet aquifer extends approximately 35 ft below the land surface based on driller's well logs from the extraction wells installed on site (U.S. Army Corps of Engineers, written commun., 2014). Glacial till and lacustrine clay immediately underlie the Calumet aquifer. The thickness of the clay unit ranges from 50 to 140 ft in the area surrounding the CDF and forms a confining unit between the Calumet aquifer and the underlying carbonate bedrock aquifer (Fenelon and Watson, 1993).

Table 1. Hydrocarbons measured in groundwater samples collected June 19, 2014, at the confined disposal facility.

[All groundwater samples were analyzed for unfiltered, recoverable compounds in micrograms per liter; --, no data; <, less than; E, estimated]

Station name	1,2-Dibromo-ethene	1,2-Dichloro-ethane	1,2-Dichloro-propane	1,3-Dichloro-propene	1,4-Dichloro-benzene	2,4,5-Trichloro-phenol	2,4,6-Trichloro-phenol	2,4-Dichloro-phenol	2,4-Dimethyl-phenol	2-Methyl-4,6-dinitrophenol
EW-4B	--	--	--	--	<2.20	--	<4.98	<3.60	<8.0	--
EW-14A	--	--	--	--	<2.20	--	<3.40	<3.60	44.3	--
Station name	4-Chloro-3-methylphenol	4-Chloroaniline	4-Nitrophenol	Aldrin	alpha-Endo-sulfan	alpha-HCH	beta-Endosulfan	beta-HCH	Bromomethane	Carbon disulfide
EW-4B	<5.40	--	<5.34	<0.013	<0.012	--	--	--	--	--
EW-14A	<5.40	--	<5.20	<0.013	<0.012	--	--	--	--	--
Station name	Chlordane (technical)	cis-1,3-Dichloropropene	cis-Chlordane	delta-HCH	Dieldrin	Endosulfan sulfate	Endrin aldehyde	Endrin ketone	Endrin	gamma-Chlordane
EW-4B	<0.1	--	--	--	<0.008	--	--	--	<0.012	--
EW-14A	<0.1	--	--	--	<0.008	--	--	--	<0.012	--
Station name	Heptachlor epoxide	Heptachlor	Hexachloro-benzene	Lindane	Mirex	o-Cresol	p,p'-DDD	p,p'-DDE	p,p'-DDT	p,p'-Methoxy-chlor
EW-4B	<0.009	<0.008	<3.00	<0.014	<0.0060	--	<0.016	<0.014	<0.010	<0.002
EW-14A	1.17	<0.008	<3.00	0.007	<0.0060	--	<0.016	<0.014	<0.010	<0.002
Station name	p-Cresol	Pentachloro-phenol	Toxaphene	trans-1,3-Dichloropropene	Aroclor 1016	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
EW-4B	--	--	<1	--	--	--	--	--	--	--
EW-14A	--	--	<1	--	--	--	--	--	--	--
Station name	PCBs	1,1,1-Trichloro-ethane	1,1,2,2-Tetrachloroethane	1,1,2-Trichloro-ethane	1,1-Dichloro-ethane	1,1-Dichloro-ethene	1,2,4-Trichloro-benzene	1,2-Dichloro-benzene	1,2-Dichloro-ethene (cis & trans)	1,2-Diphenylhydrazine
EW-4B	<0.1	--	--	--	--	--	<2.60	<2.0	--	<3.00
EW-14A	1.4	--	--	--	--	--	<2.60	<2.0	--	<3.00
Station name	1,3-Dichloro-benzene	2,4-Dinitrophenol	2,4-Dinitrotoluene	2,6-Dinitrotoluene	2-Chloroethyl vinyl ether	2-Chloronaphthalene	2-Chlorophenol	2-Methylnaphthalene	2-Nitroaniline	2-Nitrophenol
EW-4B	<2.20	--	<5.60	<4.0	--	<2.40	<2.60	--	--	<5.3
EW-14A	<2.20	--	<5.60	<4.0	--	<2.40	<2.90	--	--	<4.0
Station name	3,3'-Dichlorobenzidine	3-Nitroaniline	4-Bromophenyl phenyl ether	4-Chlorophenyl phenyl ether	4-Nitroaniline	9H-Fluorene	Acenaphthene	Acenaphthylene	Acetone	Anthracene
EW-4B	<4.20	--	<2.40	<3.40	--	E1.46	<2.80	<3.00	--	<3.80
EW-14A	<4.20	--	<2.40	<3.40	--	E0.47	E0.46	<3.00	--	<3.80
Station name	Benzene	Benzo[a]anthracene	Benzo[a]pyrene	Benzo[b]fluoranthene	Benzo[ghi]perylene	Benzo[k]fluoranthene	Benzyl n-butyl phthalate	Bis(2-chloroethoxy)methane	Bis(2-chloroethyl) ether	Bis(2-chloroisopropyl) ether
EW-4B	16.7	E0.18	E0.13	E0.08	E0.07	<3.00	<18	<2.40	<3.00	<1.40
EW-14A	2,780	<2.60	<3.20	<3.00	<3.80	<3.00	<18	<2.40	<3.00	<2.00

Methods of Investigation

The methods selected for this investigation were intended to characterize the microbiology, aqueous chemistry, geochemistry, and mineralogy in select wells at the CDF. This section describes the different methods used to sample each well type and to prevent cross contamination of wells. Uncommonly high concentrations of solids in the samples required modifications of some standard procedures.

Well Selection

Groundwater and microbiological properties were measured in water from six wells at three locations (table 2). The three locations contained the same wells tested for hydrologic properties by Lampe and Unthank (2016); these well clusters were previously observed to have different rates of pump fouling. The historic water-quality data from two offsite wells were added to the dataset to represent background water-quality conditions; new samples were not collected from those wells. Ten wells were sampled for solid-phase properties, and

four of those wells were within nests of wells sampled for water-quality and microbiological properties; however, none of the wells sampled for solid phases were sampled for water-quality and microbiological properties (table 2). The well nests sampled for groundwater and microbiological properties included extraction well EW-4B and monitoring well MW-4A (well nest 4), on the west side of the property; EW-11B and MW-11A (well nest 11) on the north side; and EW-14A and MW-14A (well nest 14) on the east side. Monitoring wells tested as part of this investigation were located within the perimeter of the CDF slurry wall.

Well nest 4 had high levels of fouling, well nest 14 was experiencing well fouling to a lesser extent than well nest 4, and well nest 11 was experiencing little to no well fouling. The extraction wells are equipped with pumps that need to be serviced or replaced whenever fouling causes a significant decline in productivity. The extraction wells are also equipped with transducers for measuring groundwater levels. The monitoring wells are located near the extraction wells and may provide some indication of conditions in the subsurface that are not geochemically perturbed by pumping. Monitoring wells are equipped with transducers for measuring groundwa-

Table 2. Number and type of analyses on groundwater and solids collected from wells at the confined disposal facility.

[Scanning electron microscopy analyses by the U.S. Geological Survey (USGS) Rock Kinetics Laboratory, Menlo Park, California; semi-quantitative X-ray diffraction analyses by the Biogeochemistry and Mineralogy of Redox-Active Environmental Systems Lab, Boulder, Colorado; inductively coupled plasma chromatography by the USGS Metal and Metalloid Isotope Research Laboratory, Menlo Park, Calif.; carbon and sulfur isotope analyses by the USGS Stable Isotopes Laboratory; semi-quantitative chromatography for hydrocarbon evaluation by the USGS South Atlantic Water Science Center Studies Unit, Columbia, South Carolina; dissolved gas analyses by the USGS Dissolved Gas Laboratory, Reston, Virginia; bacteria type and approximate population by the USGS Ohio-Kentucky-Indiana Water Science Center, Indianapolis, Indiana; and water-quality analyses by the USGS National Water Quality Laboratory, Arvada, Colo. Number does not include quality-assurance samples. --, no sample]

Well name	Analyses on solid-phase samples					Analyses on aqueous-phase samples		
	Scanning electron microscopy	X-ray diffraction	Inductively coupled plasma chromatography	Carbon and sulfur isotopes	Petroleum hydrocarbons scan	Dissolved gases	Bacteria	Water quality
EW-4B	--	--	2	--	1	5	16	¹ 26
EW-4C	1	1	1	1	--	--	--	--
EW-4D	6	1	1	1	--	--	--	--
EW-6C	1	--	1	1	--	--	--	--
EW-11B	--	--	--	--	--	4	16	4
EW-11D	1	1	1	1	--	--	--	--
EW-14A	--	--	--	--	--	4	16	¹ 5
EW-20D	2	3	3	3	--	--	--	--
MW-4A	--	--	2	--	--	5	16	² 5
MW-4B-1	8	2	2	1	--	--	--	--
MW-4B-2	--	--	--	1	--	--	--	--
MW-11A	--	--	2	--	--	4	16	4
MW-14A	--	--	2	--	--	4	16	4

¹The sample count at this well includes the precautionary health screening samples collected June 19, 2014.

²The sample count at this well includes a second sample collected November 5–6, 2014.

ter levels and are not regularly developed. Water-level data in wells at the CDF were provided to the USGS for the purposes of this study by a contractor of the USACE and are not publicly available.

Wells were installed at the CDF using the hollow-stem auger method during June and July 2008 (U.S. Army Corps of Engineers, 2008a). Monitoring wells were constructed with 2-inch inner diameter fiberglass reinforced epoxy riser and 5-ft long, 0.010-slot screens (table 3). The annulus surrounding the screens was filled with #5 sand and with bentonite pellets above the screen. Extraction wells were constructed with 6-inch inner diameter fiberglass-reinforced epoxy riser and completed with a 5-ft Johnson Type 316 stainless steel 0.010-slot screen. The annular space surrounding the extraction well screens was filled with #7 sand and with bentonite pellets above the screen. Drillers' records at the site describe the generalized geology as clay, overlain by 30 ft of sand with occasional gravel stringers, overlain by 3 ft of clay-rich fill (appendix 1). Wells were instrumented with submersible, impeller-driven pumps constructed from stainless steel and rubber parts.

Water-Sample Collection and Laboratory Analysis

Groundwater samples were collected during September 10, 2014, through November 6, 2014, from the six CDF wells (fig. 7A). Historic water-quality data from two offsite wells representing background conditions were retrieved from the USGS National Water Information System (NWIS) to use in comparisons (U.S. Geological Survey, 2016b).

The weather during water-sample collection included multiple rain events (fig. 7B). At the nearby Gary Airport, three events exceeded 1 inch of rainfall in 24 hours. With the exception of a notable rainfall event during September 2014, the rain fell at least a few days before sampling.

Groundwater sampling was done during a variety of established pumping conditions to represent the full range of conditions that might occur in wells at the site (table 4). Four sets of samples were collected. The first set of samples was collected during normal pumping conditions with the pumps running almost continuously or for an extended period. The second set of samples was collected after the pumps in the extraction wells had been off for 8–16 hours and water levels had mostly recovered. The third set of samples was collected 2 weeks after the resumption of pumping. The fourth set of samples was collected 4 weeks after the resumption of pumping.

Extraction wells and monitoring wells were sampled using different pumps. Samples were collected from the extraction wells using the submersible, stainless-steel pumps that are installed in the wells for gradient control. The pump intakes are 1 ft above the top of the well screen. Water from the pump is routed to a hydrant through a series of smaller diameter stainless steel, copper, and bronze pipes (fig. 8). Samples

were collected from the monitoring wells using a submersible pump constructed from plastic and stainless steel. The pump was lowered to the bottom of the well and then pulled up and secured to locate the pump intake 14–20 inches above the top of the well screen. Each monitoring well had its own dedicated pump.

Before each sampling event, all lengths of the polyethylene tubing, submersible pumps, and sampling equipment were cleaned by pumping at least 5 gallons of each of the following and in the order of (1) a mixture of 1-part laboratory grade detergent to 50 parts tap water, (2) tap water, and (3) sterile deionized water. All the polyethylene tubing used for water flow from hydrants and plastic pumps was new before sample collection and disposed of after each well was sampled. The water-quality sonde and sonde flow-through cell were fed through a separate line connected to the flow manifold (figs. 9A–9C). A valve allowed for the redirection of flow from the flow-through cell to the sampling line. The same cleaned polyethylene tubing used for sampling was connected from the flow manifold to the flow-through cell. The sondes and flow-through chambers were not cleaned with the same decontamination procedures as the rest of the equipment because the sondes and chambers were not in contact with the flow manifold or used for sample water collection.

Water was pumped through the polyethylene tubing and into USGS standard flow manifolds constructed of stainless steel fittings, polytetrafluoroethylene tubing, and polytetrafluoroethylene valves. Additional polyethylene tubing was used to connect the manifold to a flow-through chamber that supported the multiparameter sonde, the discharge line, and the sample-collection line. Initial health-screening samples collected before the start of the project indicated benzene levels as high as 2.78 milligrams per liter (mg/L) and other petroleum by-products at lesser concentrations (table 1). As a consequence, each well had dedicated sampling equipment. Per the USGS National Field Manual for the Collection of Water-Quality Data section 3.3.10.B, pump tubing was replaced rather than cleaned when concentrations of volatile organic compounds exceeded 700 micrograms per liter (U.S. Geological Survey, variously dated). Some items, such as the stainless steel fittings and the USGS flow manifold, were used for the monitoring and extraction wells in the same cluster because the materials in the fittings and manifold have relatively high resistance to chemical absorption and are readily cleaned with the proper decontamination procedures.

Wells were pumped at a rate of 0.12–0.35 gallons per minute during sample collection. Onsite measurements of pH, specific conductance, redox potential, water temperature, dissolved oxygen, and turbidity were made with a YSI 600XL sonde and were recorded. Redox values measured with a silver chloride reference electrode using 3.5 molar potassium chloride were converted to redox (standard hydrogen electrode) values by an addition of 231 millivolts to the measured value. The general redox category and dominant redox process for each water sample collected at the CDF was estimated using methods described in Jurgens and others (2009). Assignment

Table 3. Characteristics of extraction and monitoring wells used for this study.

[USGS, U.S. Geological Survey; NAVD 88, North American Vertical Datum of 1988; na, not applicable]

USGS site identification number	Well name	Total well depth, in feet	Casing inside diameter, in inches	Screen length, in feet	Land surface elevation, in feet above NAVD 88	Top of sand pack, in feet above NAVD 88	Top of screen elevation, in feet above NAVD 88	Bottom of screen elevation, in feet above NAVD 88	Bottom of borehole, in feet above NAVD 88	Pump altitude, in feet above NAVD 88
413907087291801	EW-4B	28.1	6	5.0	591.0	586.0	567.9	562.9	559.0	568.9
413908087291901	MW-4A	27.5	2	5.0	590.5	571.0	568.0	563.0	562.5	na
413921087290103	EW-11B	29.2	6	5.0	592.2	587.2	568.0	563.0	560.0	569.0
413921087290101	MW-11A	27.3	2	5.0	590.3	571.0	568.0	563.0	562.5	na
413911087285201	EW-14A	27.4	6	5.0	590.4	586.6	568.0	563.0	561.6	569.0
413909087285301	MW-14A	24.5	2	5.0	587.5	571.3	568.0	563.0	562.5	na
413941087292600	D21	20.0	2	5.5	584.4	na	569.9	564.4	561.4	na
413835087245101	D40	6.9	2	4.0	584.2	na	581.3	577.3	575.2	na

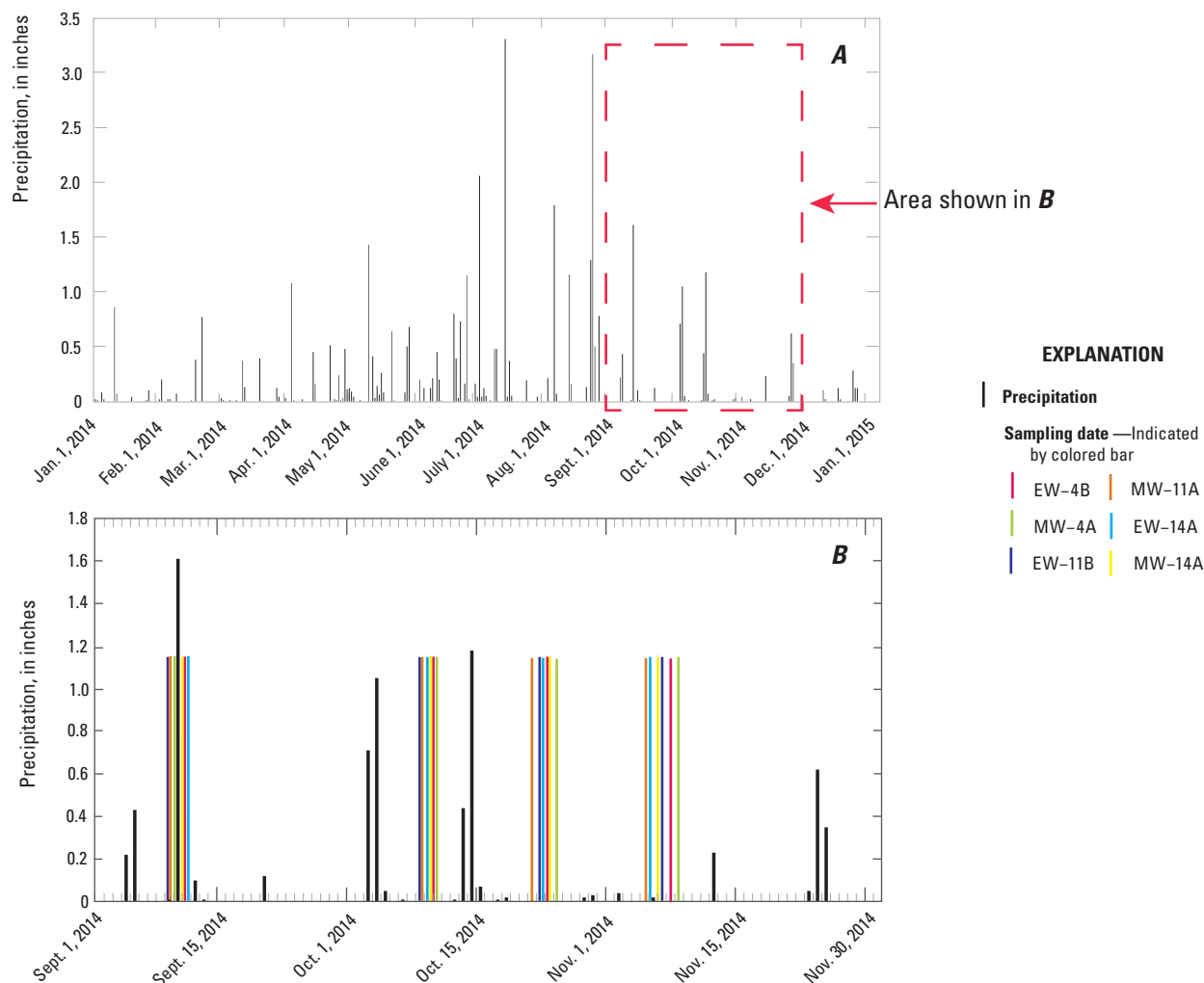


Figure 7. A, dates of water-quality sample collection and precipitation and B, precipitation record at Gary Airport for January 1, 2014, through December 31, 2014.

of redox category and the dominant redox process were made using concentrations of dissolved oxygen, manganese, ferrous iron, sulfate, sulfide, hydrogen sulfide, and dihydrogen sulfide. Data were insufficient to estimate redox condition for offsite wells.

Samples were collected after the well was purged and onsite measurements had stabilized. Stability was determined by multiple sonde readings of temperature, specific conductance, pH, and dissolved oxygen until little to no changes were observed after a specified amount of water was purged from the wells per the USGS National Field Manual for the Collection of Water-Quality Data section 4.2.3 (U.S. Geological Survey, variously dated). Only one well volume was purged before sampling the extraction wells because those wells are almost always continuously pumped. During October 7–9, 2014, at least two well volumes were purged from the extraction wells because the pumps had not been discharging since they were shut off a day before. A minimum of three well

volumes were purged from each monitoring well before sampling per the USGS National Field Manual for the Collection of Water-Quality Data section 4.2.3 (U.S. Geological Survey, variously dated).

Samples could not be filtered at the site using normal procedures because the filters clogged and prohibited discharge of water. All samples were collected unfiltered and sent to the USGS National Water-Quality Laboratory (NWQL) for filtration and analysis. Except for filtration, samples were collected and preserved for water-quality analysis according to guidelines specified by the USGS NWQL and the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). Photometric measurements of dissolved oxygen were done because the membrane of the oxygen sensor on the multiparameter probe was quickly fouled by water during sampling and values could not be reliably used for data interpretation. The clean hands/dirty hands method, as described in the USGS National Field

Table 4. Tested pumping regimes at the confined disposal facility.

[Before, pumping regime began at least 1 month before sample collection date; After, pumping regime ended after November 4, 2014]

Well name	Pumping regime	Pumping conditions	Beginning of pumping regime		End of pumping regime		Water-quality sample collection time and date	
			Time	Date	Time	Date	Time	Date
EW-4B	1	Normal pumping intensity and duration	Before	Before	1500	October 8, 2014	1410	September 11, 2014
EW-11B	1	Normal pumping intensity and duration	Before	Before	1300	October 6, 2014	0930	September 9, 2014
EW-14A	1	Normal pumping intensity and duration	Before	Before	1400	October 7, 2014	1110	September 11, 2014
EW-4B	2	No pumping for 8–16 hours before sample collection	1500	October 8, 2014	1145	October 9, 2014	1410	October 9, 2014
EW-11B	2	No pumping for 8–16 hours before sample collection	1300	October 6, 2014	1115	October 7, 2014	1245	October 7, 2014
EW-14A	2	No pumping for 8–16 hours before sample collection	1400	October 7, 2014	1130	October 8, 2014	1340	October 8, 2014
EW-4B	3	Normal pumping for minimum 2 weeks	1145	October 9, 2014	After	After	1353	October 22, 2014
EW-11B	3	Normal pumping for minimum 2 weeks	1115	October 7, 2014	After	After	0925	October 21, 2014
EW-14A	3	Normal pumping for minimum 2 weeks	1130	October 8, 2014	After	After	1235	October 21, 2014
EW-4B	4	Normal pumping for minimum 4 weeks	1145	October 9, 2014	After	After	1230	November 5, 2014
EW-11B	4	Normal pumping for minimum 4 weeks	1115	October 7, 2014	After	After	0930	November 4, 2014
EW-14A	4	Normal pumping for minimum 4 weeks	1130	October 8, 2014	After	After	1300	November 4, 2014

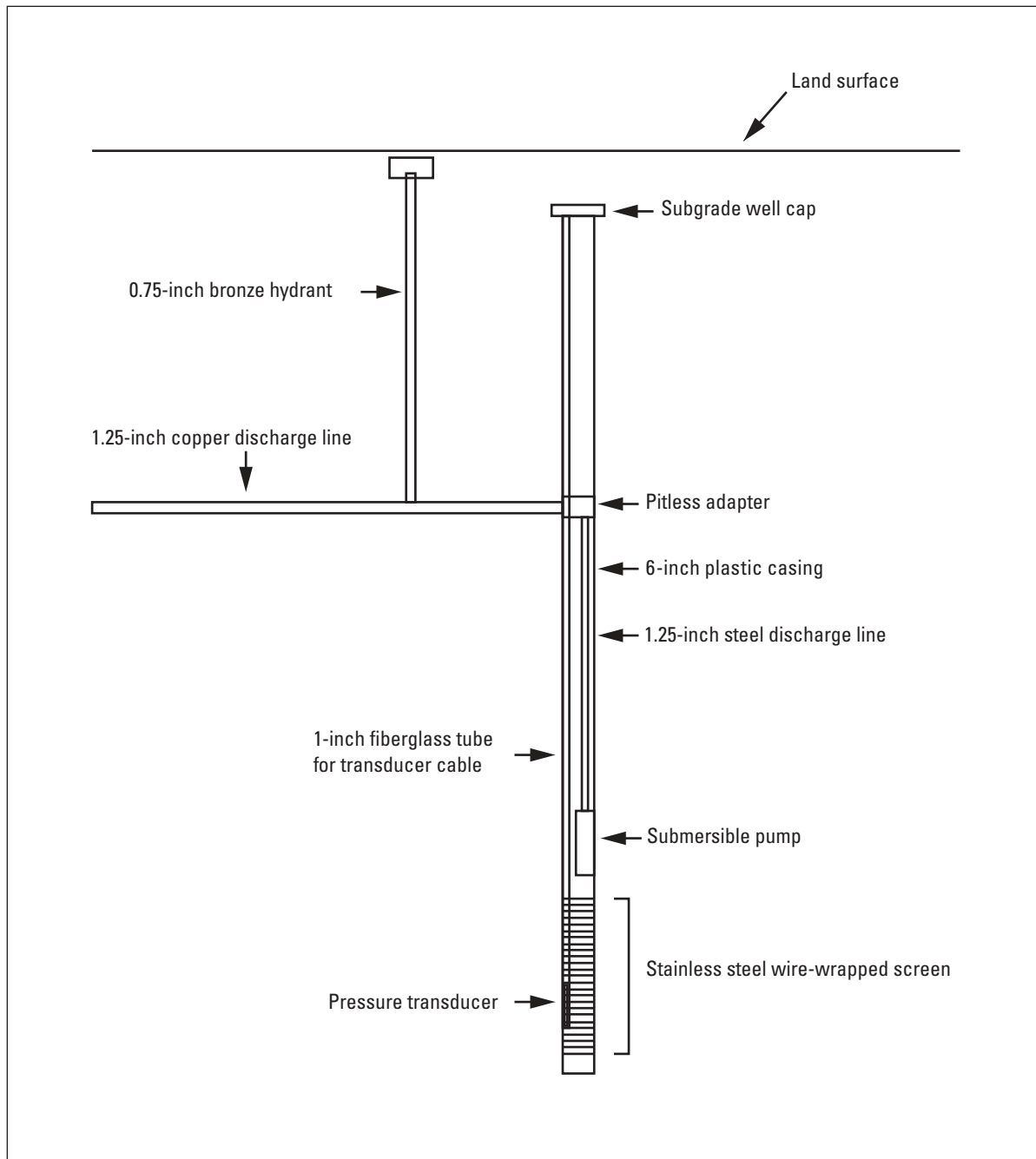


Figure 8. Schematic diagram of the borehole and pump-hydrant system in extraction wells at the confined disposal facility.

Manual for the Collection of Water-Quality Data section 4.0.2, was used inside an enclosed sampling chamber (U.S. Geological Survey, variously dated). Onsite quantification of ferrous iron, sulfide, turbidity, and dissolved oxygen were done using onsite photometric methods (Hach method 8146 [Hach, 2015a], Hack method 8131 [Hach, 2015b], Hack portable turbidimeter 2100P [Hach, 2015c], and CHEMetrics Instrumental Kit K-7503 [CHEMetrics, 2016]). The analytical results for

all environmental samples were placed in the NWIS database (U.S. Geological Survey, 2016b).

Field sampling equipment was cleaned after each well was sampled. The polyethylene tubing was discarded after each sampling. Different cleaning procedures were used for different pieces of equipment. The flow manifold, which consisted of polytetrafluoroethylene valves and tubing and stainless steel fittings, was cleaned with a four-step process. The



Figure 9. Sampling instruments used to collect water-quality samples at the confined disposal facility. *A*, enclosed sampling chamber, manifold, flow-through cell, water-quality sonde, and sampling lines attached to well hydrant; *B*, close-up view of flow-through cell; and *C*, close-up view of sampling manifold.

stainless steel fittings that were removable were cleaned with a six-step process. The submersible plastic pumps were cleaned with a seven-step process. The sonde and flow-through cell were cleaned with three steps to keep the instruments clean of residue and to reduce odor.

The flow manifold and permanently attached stainless steel fittings were cleaned with a brush and fluid consisting of 1-part laboratory grade detergent to 50-parts tap water. The

manifold pieces were then rinsed thoroughly with tap water, methanol, and with sterile deionized water.

The pump and removable stainless steel fittings were cleaned with the same four steps as the flow manifold but were additionally disinfected for bacteria contamination by submergence in alcohol reagent (ethanol 88 to 91 percent), methanol (4.0 to 5.0 volume/volume percent), and isopropyl alcohol (4.5 to 5.5 percent) and by a rinse with sodium thiosulfate.

The submersible pumps were also submerged in the alcohol reagent and sodium thiosulfate and were allowed to continually circulate fluid for 10 minutes while rinsing the outsides of the pumps with the discharge from the pumps. The sodium thiosulfate was used to remove the residuals remaining from disinfection with the alcohol reagent. Lastly, sterile deionized water was used to rinse all the equipment to remove the sodium thiosulfate. The flow-through cells were cleaned with the same laboratory grade detergent and tap water mixture, rinsed with tap water, rinsed with methanol, and rinsed again with tap water.

Dissolved Gas Samples and Quality Assurance

Dissolved gas samples were collected in septum vials that were bottom filled until overflowing. While still bottom filling, the vials were immersed in a volume of groundwater sample and capped underwater to retain gases in the vial. Samples were collected in sequence as an environmental sample and as a replicate sample, with the replicate sample results used to compute quality-assurance statistics. Samples were shipped on ice to the USGS Dissolved Gas Laboratory, Reston, Va. Samples were analyzed by gas chromatography paired with a thermal conductivity detector for concentrations of oxygen, nitrogen, and argon and paired with a flame ionization detector for analyses of carbon dioxide and methane (U.S. Geological Survey, 2016a; Busenberg and others, 1998). Analyses of dissolved gases were also periodically checked at the Dissolved Gas Laboratory by analyzing standard samples prepared at known temperatures in equilibrium with air.

Field quality assurance for dissolved gas samples collected for this project included analysis of quality-assurance samples and data to understand reproducibility of sampling and analysis methods for the dissolved gases. Results from replicate samples were used to understand overall variability of sampling and analysis processes used for this project. Replicate samples were collected in immediate succession to the environmental sample from the same source, using identical handling and analysis methods. Variation between environmental and replicate samples that should be identical in composition was quantified by computing the relative percent difference (RPD) of concentrations of each analyte in each sample type (U.S. Army Corps of Engineers, 2008b).

$$RPD = |(SR-ES)/((SR+ES)/2)| \times 100 \quad (1)$$

where

- RPD* is the relative percent difference,
SR is the concentration in the replicate sample,
 and
ES is the concentration in the environmental sample.

If the RPD of a dissolved gas analysis was within 10 percent, the sample result met the precision objectives of this study. If the RPD was greater than 10 percent, the sample

result was reported, but the concentration for that analysis was flagged with the letter "Q" in data tables to indicate that the concentration is an estimate. This RPD precision objective exceeds that permitted for many environmental analyses (50 percent; U.S. Army Corps of Engineers, 2008b).

Environmental samples for dissolved gases were also evaluated by comparing argon concentrations in environmental samples with hypothetical argon concentrations in equilibrium with air at a range of average monthly air temperatures for the region. Argon was used for this comparison because argon is a noble gas and is not subject to oxidation-reduction related changes to its concentration, as were the other gases (oxygen, nitrogen, carbon dioxide, and methane) analyzed by this study. Dissolved gas solubility in groundwater depends on the average recharge temperature of infiltrating water as it enters the water table and on other properties, which include salinity, the vapor pressure of water at the water table, and barometric pressure. Concentrations of argon may be expected to be in equilibrium with the atmosphere at the prevailing surface pressure and with temperature in water infiltrating below the water table (Heaton and Vogel, 1981). Hypothetical argon concentrations in water in equilibrium with air were computed using a formulation of Henry's law (Ed Busenberg, written commun., August 2016).

The Henry's law equation used to compute argon concentrations in water in equilibrium with air was

$$C = (KH(\text{argon}) \times mf(\text{argon}) \times (BP - VP) \times 39.9480) \quad (2)$$

milligrams of argon per millimole

where

C is concentration of argon in milligrams per liter,
KH (argon) is the Henry's law coefficient for argon,
mf (argon) is 0.0934 is the mole fraction of argon in dry air (reported in Weiss, 1970),

P (barometric pressure, in atmosphere [atm]) is

$$e^{[Water\ table\ altitude\ (feet\ above\ NGVD29) \times 0.3048\ (meters\ per\ foot) / 8,300\ (meters\ per\ atm)]}$$

e is 2.71828183,

VP (vapor pressure of water, in atm) is $e^{(24.4543 - 67.4509(100/T) - 4.8489 \times \ln(T/100) - 0.000544 \times S)}$,

ln is logarithm (natural),

T is water temperature in degrees Kelvin,
 computed as $T = T\ degrees\ Celsius + 273.15$, and

S is water salinity in parts per thousand.

The altitude used to compute the hypothetical argon concentration in equilibrium with water was assumed 578 ft above the National Geodetic Vertical Datum of 1929. The land surface altitude for the three sampled monitoring wells ranged from 587.5 to 590.3 ft above the National Geodetic Vertical Datum of 1929 and the depth to the water table during sampling in monitoring wells sampled for this study was about 11 ft below land surface. Normal monthly mean temperatures during 1981–2010 ranged from -4.1 degrees

Celsius (°C) in January to 22.7 °C in July at a weather station about 20.6 miles east of the site at Indiana Dunes National Lakeshore (Arguez and others, 2010). Because infiltrating precipitation would not be common in months with subfreezing average temperature, a minimum monthly average temperature of 3 °C in March was used to compute argon concentrations for the comparison. The salinity used for the computation was assumed to be 2,000 mg/L, an intermediate value among those measured in groundwater from these sites.

The Henry's law coefficient for argon was computed using the following conventions and data, as modified from Weiss (1970):

$$KH(\text{argon}) = \exp \{A1 + A2 (T/100) + A3 \ln (T/100) + S [B1 + B2 (T/100) + B3 (T/100)^2]\} / 22.414 \quad (3)$$

using the following constants for argon (also from Weiss, 1970):

where

<i>A1</i>	is -55.6578,
<i>A2</i>	is 82.0262,
<i>A3</i>	is 22.5929,
<i>B1</i>	is -0.036267,
<i>B2</i>	is 0.016241,
<i>B3</i>	is -0.0020114, and
22.414	is the volume of 1 millimole of gas at 1 atm pressure and 25 °C.

Microbiological Sample Collection and Laboratory Analysis

Samples to assess microbiological activity were collected from the six wells immediately following collection of the water-quality sample. The four general types of bacteria measured in groundwater samples included heterotrophic aerobic bacteria, slime-forming bacteria, iron-related bacteria, and sulfate-reducing bacteria. Populations of more specific bacteria that comprised these general types were determined if the analytical techniques allowed (table 5). No historical microbiological data were available for groundwater from the two offsite wells.

Microbiological samples required equipment disinfection before sample collection. After all other water-quality samples were collected, the polyethylene sampling line that connected the pump to the manifold was cut to create a new sample-collection point, therefore, eliminating the need to disinfect the manifold between wells. The new sample-collection point for microbiological samples was the polyethylene tubing that was directly connected to either the permanent hydrants of the extraction wells or the removable submersible pumps used for sampling the monitoring wells.

Microbiological samples were analyzed for activity of four types of bacteria using the Hach Biological Activity Reaction Tests (BARTs) (Droycon Bioconcepts, Inc., 2004) (figs. 10A–10C). Microbiological activity was measured by visual assessment of the sample water matrix. The water samples were inspected daily to provide a description for their appearance and then were compared to sterile buffer water. Visual changes depended on the sample type (environmental or quality assurance) and the population of bacteria present in the sample. The largest bacteria populations corresponded to samples with rapid (1–2 days) visual change. Smaller or nonexistent populations corresponded to relatively slow (more than 5 days) visual changes. Numerical populations were assigned based on the rapidity of the culture response to the sample water and utilized a standard table supplied with the test kit. The bacteria subtype was deduced from the color of water and solids in the sample tube.

Solid-Phase Sample Collection and Laboratory Analysis

Solid samples were collected as suspended solids in water and as scrapings from extraction-well pumps. Scrapings were collected when pumps were removed for cleaning or replacement. As a result, scrapings and aqueous samples were not collected simultaneously. The wells where scrapings were collected were EW-4C, EW-4D, EW-6C, EW-11D, EW-20D, and MW-4B. The scrapings were collected between September 11, 2014, and November 6, 2014. Some wells sampled for water quality were not sampled for solids because the pumps did not have accumulations of solids or the pumps had been cleaned or replaced during the preceding weeks. Samples of

Table 5. General and subtypes of bacteria measured in groundwater samples.

[SRB, sulfate-reducing bacteria; na, not applicable]

Heterotrophic aerobic bacteria	Slime-forming bacteria	Iron-related bacteria	Sulfate-reducing bacteria
No subtypes	Slime forming	Iron-related bacteria	Aerobic SRB consortium
na	Pseudomonads and enterics	Enteric	Anaerobic
na	Dense slime	Anaerobic	Dense anaerobic SRB consortium
na	na	Pseudomonads and enterics	na



Figure 10. Microbiological activity reaction tests for *A*, sterile buffer water on day 1; *B*, monitoring well MW-11A positive reactivity on day 2; and *C*, monitoring well MW-4A positive reactivity on day 4.



solids were scraped from pumps immediately after the pump was removed from the extraction well. Samples were sealed in 20-milliliter vials and shipped for analysis. Samples were scraped from pumps in some wells that were not sampled for water-quality analyses but were in the same well cluster and considered potentially useful for improved understanding of processes occurring at the CDF.

An additional scraping was collected from EW-4B on November 3, 2016. That sample was collected using identical methods to earlier scraping samples. The sample collected from EW-4B was submitted to the USGS laboratory in South Carolina and scanned for the presence of petroleum hydrocarbons.

Suspended solids were also collected from wells MW-14A, MW-11A, EW-4B, and MW-4A during November 3–6, 2014. Samples were collected with the pumps used for water-quality sample collection. About 10 gallons of water were collected in two plastic containers. The suspended solids were allowed to settle to the bottom of the containers for 30–60 minutes (most supernatant liquid was decanted) and the sample was sealed and shipped to the USGS laboratory.

Samples of solids were analyzed to determine mineralogy, mineral habit, and solid chemistry. Amorphous solids and biofilms were also identified. Analytical methods included scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS) to describe crystal habit and dominant chemical constituents, SEM/backscatter electrons (BSE) to characterize sample homogeneity, qualitative and quantitative X-ray diffraction (XRD) to determine mineralogy, inductively coupled plasma mass spectrometry on chemically digested samples to determine the chemical composition, and carbon and sulfur isotopes of chemically digested samples to provide information about the formative processes. Sample splits were analyzed by using SEM, XRD, and geochemical digestion for solid chemistry and isotopy.

Solid-phase samples were analyzed at USGS laboratories in Menlo Park, Calif., and Boulder, Colo., and followed the documented procedures established for each lab. One solid split from each scraping was analyzed by SEM. The SEM split was attached to aluminum pins with carbon tape while wet and allowed to dry for several days. Prior to analysis, samples were plasma coated with gold to reduce potential electric-charge buildup that might occur during SEM analysis (Goldstein and others, 2007). A Tescan VEGA-3 SEM was used to image the samples. The magnification of samples ranged from 22,000 to 40,000 times actual size.

In conjunction with the SEM analysis, EDS analysis was done to provide qualitative information about the elemental composition of materials occurring in the SEM samples. EDS analyses were done with an Oxford X-Max Silicon Drift Detector (50 millimeter). About 20 EDS analyses were done on the mostly homogeneous samples. As many as 100 analyses were done on samples displaying some structural variability. The chemical elements detected by EDS in CDF samples included carbon, iron, sulfur, aluminum, silicon, magnesium,

potassium, and sodium. One sample (EW-4B November 5, 2014) also included trace amounts of zinc.

Qualitative and quantitative XRD analyses were done on eight samples of pump scrapings collected from five wells; the wells were EW-4C, EW-4D, EW-11D, EW-20D, and MW-4B. Scraping samples for XRD analyses were collected from wells during pump replacement. The wells were different wells than from where water-quality samples were collected. Although the observations from XRD analyses were generally informative, the observations could not be directly compared to water-quality data to ascertain agreement between the various observations.

Samples were prepared for XRD using a modified method based on Eberl (2003). An homogenized sample of 1 gram was mixed with 20 percent corundum and ground in a McCrone micronizing mill with 4-milliliter ethanol for 5 minutes, generating particle sizes on the order of 10–30 micrometers (mm). After drying at 60 °C, the mixture was transferred to a plastic scintillation vial with three acrylic balls (approximately 1 centimeter in diameter) along with 200–800 microliters Ver-trel solution (DuPont) and shaken for 10 minutes. The powder was passed through a 250-mm sieve to break up larger aggregates and loaded onto an XRD sample holder. Qualitative samples were prepared by sieving the sample to less than 250 mm and packing directly into an XRD sample holder. Samples were analyzed using a Siemens D500 X-ray diffractometer from 5 to 65 degrees two theta using copper-potassium (alpha) X-ray radiation, with a step size of 0.02 degrees and a dwell time of 2 seconds per step. Quantitative mineralogy was calculated using the USGS software, RockJock (Eberl, 2003), which fits XRD intensities of individual mineral standards to the measured diffraction pattern. The raw X-ray diffraction data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018).

Inductively coupled plasma mass spectroscopy was used to measure the concentration of cations in chemically digested samples of pump scrapings and flocculent. Samples for analysis were collected from 10 wells, including EW-4B, EW-4C, EW-4D, MW-4A, MW-4B, EW-6C, EW-11D, MW-11A, MW-14A, and EW-20D. Chemical digestion consisted of mixing solids from the pump scrapings and flocculent with 6 Normal hydrochloric acid and concentrated nitric acid, then evaporated to dryness; this process was repeated three times. The residue following the third repetition of the chemical digestion lastly was mixed with 10 milliliters of 1 Normal nitric acid to form the final solution analyzed by inductively coupled plasma mass spectrometry. Analytes included aluminum, arsenic, barium, boron, cadmium, calcium, cesium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, rubidium, sodium, strontium, phosphorous, potassium, silicon, titanium, uranium, vanadium, and zinc.

Seventeen samples of solids collected from CDF wells were analyzed by inductively coupled plasma mass spectrometry. Approximately 10 milligrams of powdered sample was

weighed into 15-milliliter polytetrafluoroethylene digestion beakers. Deionized water (1 milliliter) was added to each beaker followed by dropwise addition of 6 Normal hydrochloric acid. Effervescence in three samples determined the speed of acid addition. When effervescence ended, additional acid was added totaling 3 milliliters of 6 normal hydrochloric acid and 1 milliliter of concentrated nitric acid. Beakers were capped tightly and allowed to reflux on a 100 °C hotplate for 24 hours. Most of the samples were not completely dissolved after the 24-hour period. Samples were taken to dryness and were subsequently subjected to the same acid digestion procedure for a total of three cycles. The sample digestions reached various degrees of completion as noted. The insoluble residues appeared to be carbon or organic flock but may have also included some refractory mineral phases. The samples were dissolved in 1 normal nitric acid, filtered through membranes with 0.45-mm pore size, and diluted appropriately for analysis. Analyses were made using a Perkin-Elmer Nexion 300Q inductively coupled plasma mass spectrometer. Calibration curves were produced using commercially available multi-element standards. Concentrations are reported as micrograms per gram relative to the original sample weight because the insoluble fraction weight was unknown. Errors were less than 5 percent as determined by multiple inter-run analyses of a quality-control standard.

Carbon and sulfur isotopic composition was analyzed in splits from samples of pump scrapings to provide information about processes contributing to the formation of the solids. Homogenized sample material was weighed into tin capsules along with vanadium pentoxide, an aid to combustion. Samples were analyzed for carbon and sulfur content and isotopic composition by continuous flow isotope ratio mass spectrometry using a Vario ISOTOPE Cube (Elementar) elemental analyzer coupled to a GV Instruments (now Elementar) IsoPrime. Internal standards were used for quantifying carbon and sulfur content and isotopic composition. These standards were calibrated against the National Bureau of Standards (NBS) samples appropriate to each element (NBS 18, NBS 19, and NBS 22 for carbon; NBS 127 and SO-6 for sulfur). The standards were selected to bracket the expected natural sample isotopic composition and were run in a range of sizes based on expected sample concentrations. Carbon isotopic composition was reported in parts per thousand (‰) relative to Vienna Pee Dee belemnite; sulfur isotopic composition was reported in parts per thousand relative to the standard Vienna Canyon Diablo Troilite. The 1-sigma standard deviations for standard materials are plus or minus 0.4‰ for carbon and plus or minus 0.6‰ for sulfur.

The matrix of the CDF samples was an unusual composition that caused some analytical difficulties for sulfur analysis. The matrix material affected sulfur combustion and produced a considerable tail in the chromatograph. A similar effect on carbon combustion was not observed. Carryover from one sample to the next that might be anticipated from the tailing phenomenon was eliminated by running a blank sample

between the CDF samples. During sample analysis, the sulfur pulse was trapped, released, and analyzed as is normal; the subsequent blank sample effectively flushed the remaining sulfur through the system. Blank samples that contained enough carryover sulfur were analyzed, and the analyses determined that $\delta^{34}\text{S}$ ($\{[(^{34}\text{S}/^{32}\text{S})_{\text{sample}}/(^{34}\text{S}/^{32}\text{S})_{\text{standard}}]-1\} * 1000\text{‰}$) values agreed with the sample values within 3‰, indicating limited fractionation. The sulfur carryover implies the $\delta^{34}\text{S}$ values represent a lower bound.

Computed Equilibrium Mineral-Saturation Indices

Mineral-saturation indices were computed using the analyses of groundwater samples collected from wells at the CDF to determine if chemical constituents were present in sufficient concentrations to abiotically precipitate the minerals identified in SEM and X-ray analyses. If mineral precipitation was favored, then an engineered solution to mineral encrustation might include changing the water-quality conditions in the borehole. If the groundwater from CDF wells, however, was determined to be undersaturated with respect to the minerals identified in SEM and X-ray analyses, then the conclusion might be that either (1) the minerals formed during a different water-quality condition than existed when samples were collected and perhaps during pump cycling, (2) the minerals formed in microenvironments possessing different water chemistry than existed throughout most of the borehole and perhaps hosted by the biofilms (Droycon Bioconcepts, Inc., 2006), or (3) the minerals were pulled through the well screen and into the borehole by pumping.

Mineral-saturation indices are theoretical computations that indicate the thermodynamic tendency of a crystalline mineral to dissolve or precipitate based on water-quality conditions and constituent concentrations in a solution (Hem, 1989). The mineral-saturation index is computed as the ratio of the ion activity product to the theoretical or empirically estimated equilibrium solubility product (K_{sp}):

$$SI = \log(IAP/K_{sp}) \quad (4)$$

where

SI is the saturation index,
 IAP is the ion activity product, and
 K_{sp} is the solubility product constant.

The ion activity product is related to the mathematical product of the concentrations of constituents required to form the mineral of interest. The solubility product is the theoretical ion activity product at which mineral precipitation begins. Computed saturation indices greater than zero indicate supersaturation with respect to a certain mineral and a geochemical tendency for the mineral to precipitate from the solution. Computed saturation indices less than zero indicate undersaturation with respect to a certain mineral and a tendency for the mineral to not form or dissolve if it is already present. A

saturation index at or near zero indicates that the mineral and surrounding solution are in geochemical equilibrium.

The computer program PHREEQC (Parkhurst and Appelo, 2013) was used to compute mineral-saturation indices for groundwater samples collected from wells at the CDF. The computer program PHREEQCI (Charlton and Parkhurst, 2002) was used as the graphical user interface to enter and format data for PHREEQC and to execute the program. Input to the PHREEQC computations included the water-quality conditions and concentrations of most chemical elements measured in groundwater samples from the CDF wells (table 6). Iodide and dissolved organic carbon were not included in the input dataset because the concentrations of those elements were relatively small and were not measured in all samples. The sulfide-sulfate redox couple was used to represent the Eh for the solution in the PHREEQC models for this study to alleviate concerns about direct-measurement stability. Sulfide and sulfate were measured in most samples and sulfate was generally the dominant anion. The PHREEQC program contains a large database of mineral solubility products; minerals for saturation index computations were automatically selected by PHREEQC if the necessary chemical constituents of the mineral

were present in the input dataset. An archive of the PHREEQC modeling used in this study is available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018).

The ability of PHREEQC to calculate accurately the tendency for a mineral to precipitate or dissolve is constrained by several factors, including the precision of water-quality analyses, the accuracy of the thermodynamic database, and the kinetics of mineral formation. The water-quality input data must (1) include concentrations for chemical constituents that are present in the most abundant minerals in the system and (2) be analytically accurate. The accuracy of water-quality analyses commonly is assessed by calculating the charge balance of a solution. Poor charge balances may indicate the absence of analytical data for a water-quality constituent having non-trivial concentrations. The charge balances for groundwater samples could not be directly computed because titrations of carbon species could not be done accurately on unstable groundwater samples collected at the CDF. For the saturation index computations, PHREEQC computed concentrations of carbon species from measured concentrations of dissolved inorganic carbon.

Quality-assurance samples analyzed as part of this study

Table 6. Example input file for the PHREEQC program for groundwater chemistry measured in extraction well EW-4B on September 11, 2014.

[°C, degrees Celsius; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; mg/L, milligrams per liter; mg/kgw, milligrams per kilogram of water; µg/L, micrograms per liter; µg/kgm, micrograms per kilogram of water]

Measured constituent or property, reported units of measure	Representation in PHREEQC input file	Concentration or value in PHREEQC	Units of measure in PHREEQC
Temperature, degrees Celsius	temp	16.3	°C
pH, water, unfiltered, onsite, standard units	pH	6.8	standard
Eh (standard hydrogen electrode), millivolts	pE	-5.417	unitless
Carbon, inorganic, water, filtered, as carbon, mg/L	C (+4)	180	mg/kgw
Calcium, water, filtered, mg/L	Ca	276	mg/kgw
Chloride, water, filtered, mg/L	Cl	14.5	mg/kgw
Fluoride, water, filtered, mg/L	F	0.86	mg/kgw
Iron, water, filtered, µg/L	Fe (+2)	5,800	µg/kgm
Potassium, water, filtered, mg/L	K	11.5	mg/kgw
Magnesium, water, filtered, mg/L	Mg	217	mg/kgw
Manganese, water, filtered, µg/L	Mn (+2)	375	µg/kgm
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, mg/L	N (-3)	6.16	mg/kgw
Sodium, water, filtered, mg/L	Na	50.2	mg/kgw
Dissolved oxygen, spectrophotometric, mg/L	O (0)	0.44	mg/kgw
Orthophosphate, water, filtered, mg/L as phosphorus	P	0.583	mg/kgw
Sulfate, water, filtered, mg/L	S (+6)	906	mg/kgw
Silica, water, filtered, mg/L as silica	Si	47.4	mg/kgw

indicate that the field and laboratory analyses produced constituent concentrations and water-quality characteristics that were nearly identical; however, the possibility of a consistent error in sampling methodology is possible. Other potential sources of error in the CDF analyses include, but are not limited to, changes in water quality between sampling and analysis and complexing of cations by organic constituents and colloids (Hem, 1989). Field observations reported that some purge water during well equilibration rapidly changed from clear to black and from transparent to opaque. The extreme and unique water-quality conditions at the CDF made these samples unstable at land surface and required nonstandard methods of preservation and analysis. The kinetics of the precipitation or dissolution reaction may explain the difference between the theoretically indicated reaction and the observed mineralogy. The kinetics of mineral formation describes the rate of reaction as the solid-aqueous system tries to reach thermodynamic equilibrium. For example, a mineral that is not observed but is theoretically predicted to be supersaturated may not be present because the kinetics of formation are limiting the rate of mineral precipitation.

Disagreement between mineral occurrence and the computed saturation index also may be attributed to collection of a sample that represents conditions at the time of groundwater collection that are different from the conditions when the mineral precipitated in the well. Generally, groundwater conditions are assumed to be fairly stable through time, partly as a result of the low velocity and thorough mixing in the subsurface. Pump cycling at the CDF, however, might negate the assumption of geochemical equilibrium in the extraction wells where rapid mixing of water with potentially dissimilar chemistries is possible. The kinetics of mineral dissolution or bacterial encapsulation of microenvironments that are dissimilar from groundwater in most of the borehole may explain the presence of a mineral that is theoretically undersaturated with respect to that mineral.

This study compared computed saturation indices to minerals identified in SEM and X-ray analyses of solids collected at the CDF. Solids were not collected from the same wells where groundwater samples were collected and this may limit definitive correlation between water chemistry and the existence of minerals and amorphous compounds. The solids were collected, however, from wells in the same well cluster and were generally close to the wells where groundwater was sampled.

Quality-Assurance Procedures

Water samples were collected to characterize the quality of the sampling procedure. These quality-assurance samples included a combination of equipment blanks and replicate samples. In total, 10 quality-assurance samples were collected, and 26 environmental samples were collected. Analytical procedures for the laboratories were not assessed by this protocol but are published independently by individual laboratories.

Quality-assurance samples were collected at the CDF during environmental sample collection to evaluate the sampling, cleaning, preservation, and shipping procedures. Replicate samples were collected to evaluate consistency of the sample collection, preservation, and shipping method. Equipment blanks were collected to evaluate the selection and implementation of procedures used to clean the equipment used for sample collection. In addition to internal quality control programs used by the NWQL, the quality of analytical data produced by the NWQL is independently monitored by the USGS Branch of Quality Systems (<https://bqs.usgs.gov/>). The analytical results for quality assurance samples were placed in the NWIS database (U.S. Geological Survey, 2016b).

Equipment blanks were collected by running sterile buffer water through the pump and tubing immediately after cleaning the sampling equipment. The sampling procedure, containers, preservation, shipping, and laboratory analysis were identical to the handling of the environmental samples. The analytical results for these samples were used to characterize the validity of the adapted cleaning/decontamination procedure. Six equipment blanks were collected, including one sample during every sampling event at well MW-4A and one sample during a single sampling event at wells MW-11A and MW-14A.

Replicate samples were collected immediately following collection of the environmental sample without interruption of the flow of water from the well. The sampling procedure, containers, preservation, shipping, and laboratory analysis were identical to the handling of the environmental samples. The analytical results for these samples were used to characterize the homogeneity of groundwater chemistry in the borehole, the impact of shipping and handling, and the consistency of laboratory analyses.

Multiple samples were collected from an extraction well on all four sampling occasions. Replicate samples were collected from three different extraction wells to determine if variations in site chemistry would affect the analytical results. Replicate samples were collected from EW-4B on September 11, 2014, and November 5, 2014; from EW-11B on October 7, 2014; and from EW-14A on October 21, 2014.

A second environmental sample was collected from EW-4B and MW-4A on November 5 and 6, 2014, respectively; however, because those samples were collected more than 30 minutes after the first sample, the second samples were not considered quality-assurance replicate samples.

Geochemistry and Microbiology of Groundwater and Solids from Extraction and Monitoring Wells

The data collected at the CDF were evaluated by comparing data from (1) monitoring and extraction wells, (2) sites with and without pump reliability issues, (3) CDF and

background wells, and (4) different pumping regimes (sampling events 1–4). These comparisons allowed observations that may be used to develop strategies to reduce pump fouling.

Groundwater Levels

Hydrographs of groundwater levels were investigated to provide information about the relation among hydrogeologic condition, climate, and pumping stresses at the site. A nearby monitoring well that is not on CDF property and might represent conditions unaffected by anthropogenic activities, USGS well Lake 13 (USGS site identification number 413559087270301), was also investigated. The hydrograph for USGS well Lake 13 for January 1, 2014, through December 1, 2014, shows a trend of (1) lower groundwater levels during late summer and autumn that correlate to enhanced evapotranspiration and (2) higher groundwater levels during winter and spring that correlate to periods of relatively low evapotranspiration (fig. 11). Groundwater levels at Lake 13 varied from slightly above land surface to about 2.8 ft below land surface during the period displayed. During the period when water samples were collected at the CDF, the depth to water in Lake 13 ranged from 0.98 to 2.37 ft below land surface (U.S. Geological Survey, 2016b).

The hydrograph for representative extraction wells was strongly affected by pumping in the wells (figs. 12A–12C). Groundwater levels in EW-4B during January 1, 2014, through December 31, 2014, varied by more than 20 ft and ranged from 568.33 to 588.73 ft above North American Verti-

cal Datum of 1988 (NAVD 88) (22.67 to 2.27 ft below land surface) (fig. 12A). In comparison, groundwater levels in the nonpumped well, MW-4A, varied by 5.8 ft and ranged from 579.19 to 584.99 ft above NAVD 88 (fig. 12D). Water levels in MW-4A were slightly higher in spring and lower during autumn (fig. 12D). During water-quality sampling, the groundwater levels in EW-4B ranged from 568.41 to 577.43 ft (fig. 13A) and in MW-4A ranged from 579.87 to 584.78 ft above NAVD 88 (fig. 13D).

Groundwater levels in EW-11B during January 1, 2014, through December 31, 2014, varied by more than 13 ft and ranged from 570.17 to 583.97 ft above NAVD 88 (22.03 to 8.23 ft below land surface) (fig. 12B). In comparison, groundwater levels in the nonpumped well, MW-11A, varied by 6.45 ft and ranged from 579.02 to 585.47 ft above NAVD 88 (fig. 12E). Water levels in MW-11A were slightly higher in spring and lower during autumn (fig. 12E). During water-quality sampling, groundwater levels in EW-11B ranged from 570.42 to 580.24 ft above NAVD 88 (fig. 13B) and in MW-11A, groundwater levels ranged from 579.86 to 581.42 ft above NAVD 88 (fig. 13E). Groundwater levels in MW-11A were about 10 ft above groundwater levels in EW-11B during water-quality sampling.

Groundwater levels in EW-14A during January 1, 2014, through December 31, 2014, varied by almost 26 ft and ranged from 567.15 to 593.02 ft above NAVD 88 (23.25 to -0.47 ft below land surface) (fig. 12C). In comparison, groundwater levels in the nonpumped well, MW-14A, varied by 10.8 ft and ranged from 580.32 to 591.15 ft above NAVD 88 (fig. 12F).

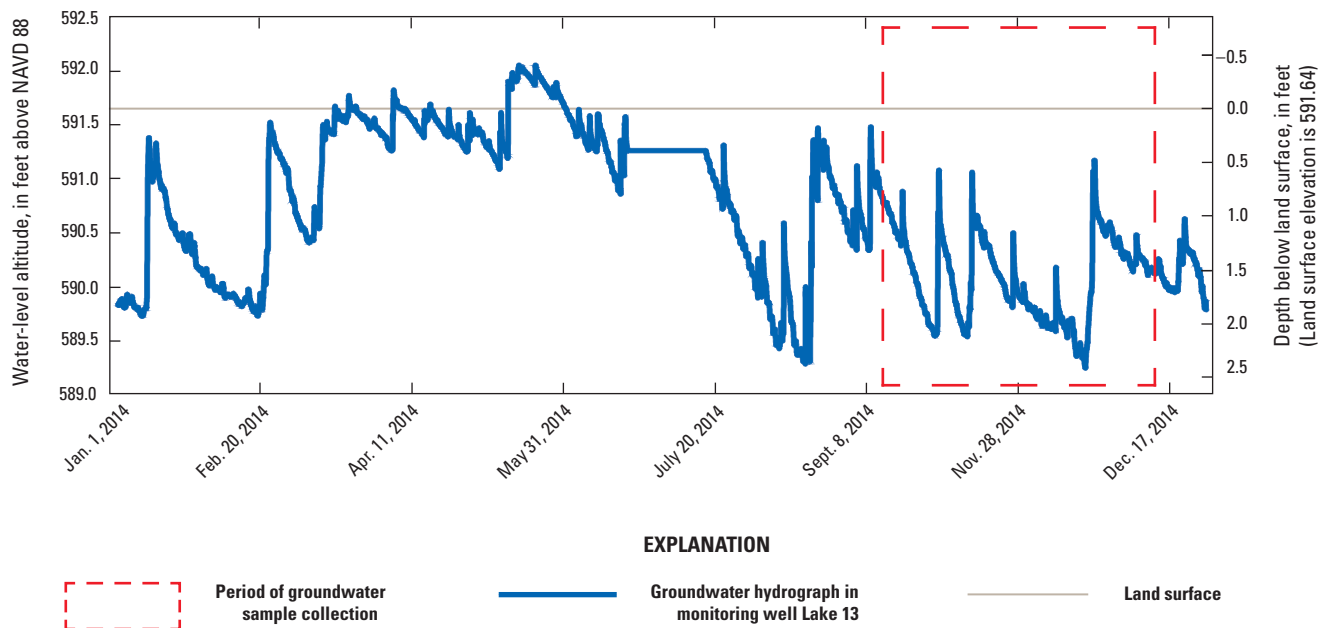
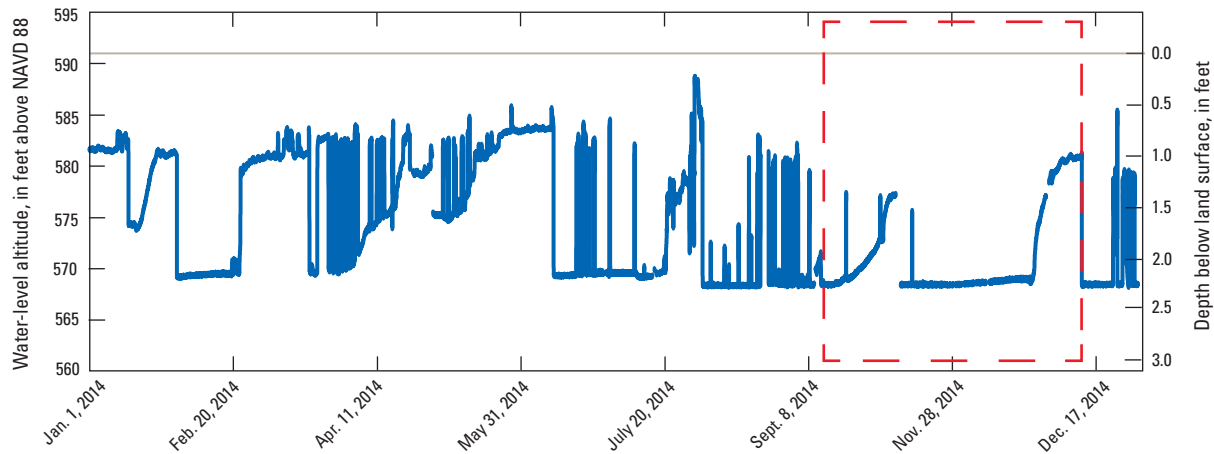
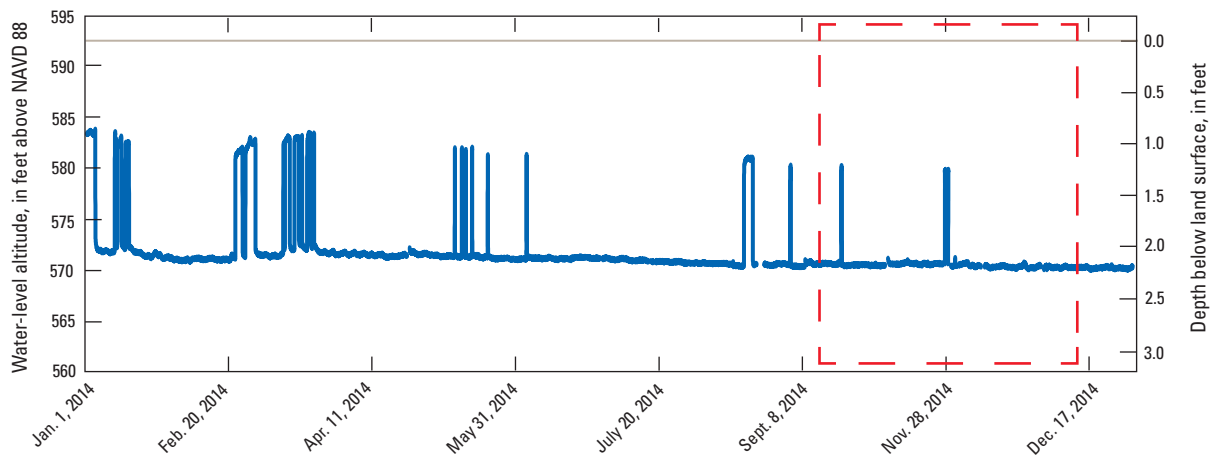


Figure 11. Hydrograph for U.S. Geological Survey monitoring well Lake 13.

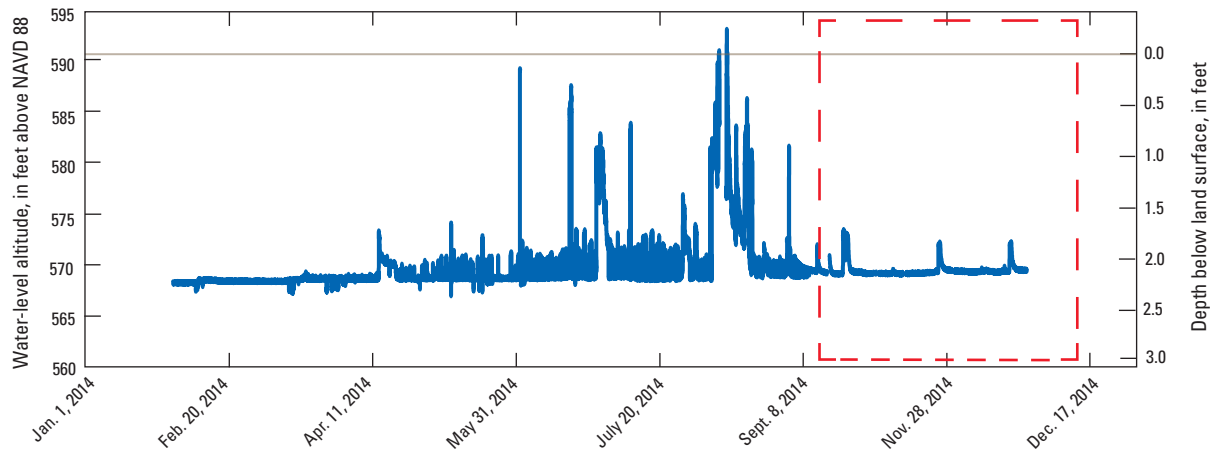
A. Extraction well EW-4B



B. Extraction well EW-11B



C. Extraction well EW-14A



EXPLANATION



Figure 12. Groundwater hydrographs for extraction and monitoring wells at the confined disposal facility during January 1, 2014, through December 31, 2014. A, EW-4B; B, EW-11B; C, EW-14A; D, MW-4A; E, MW-11A; and F, MW-14A.

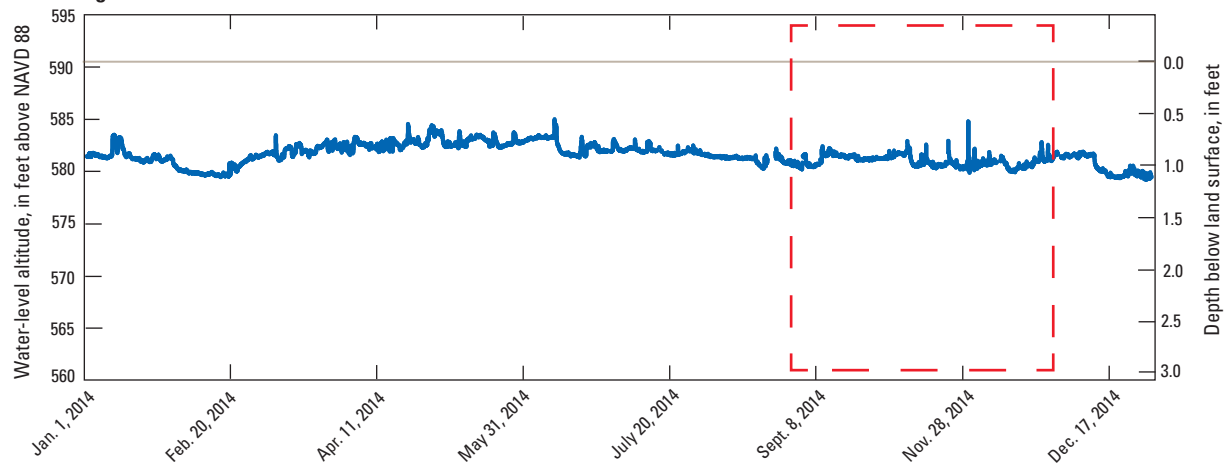
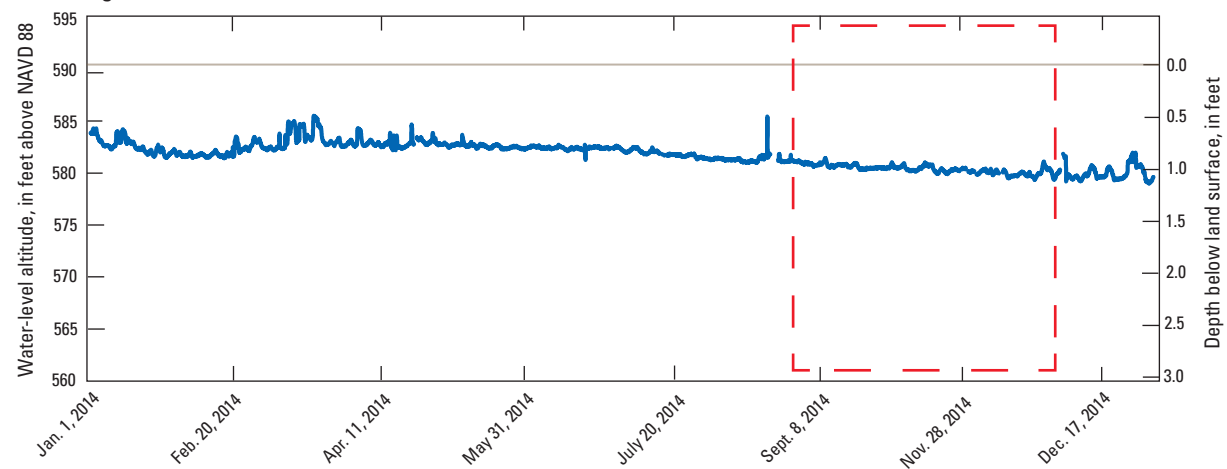
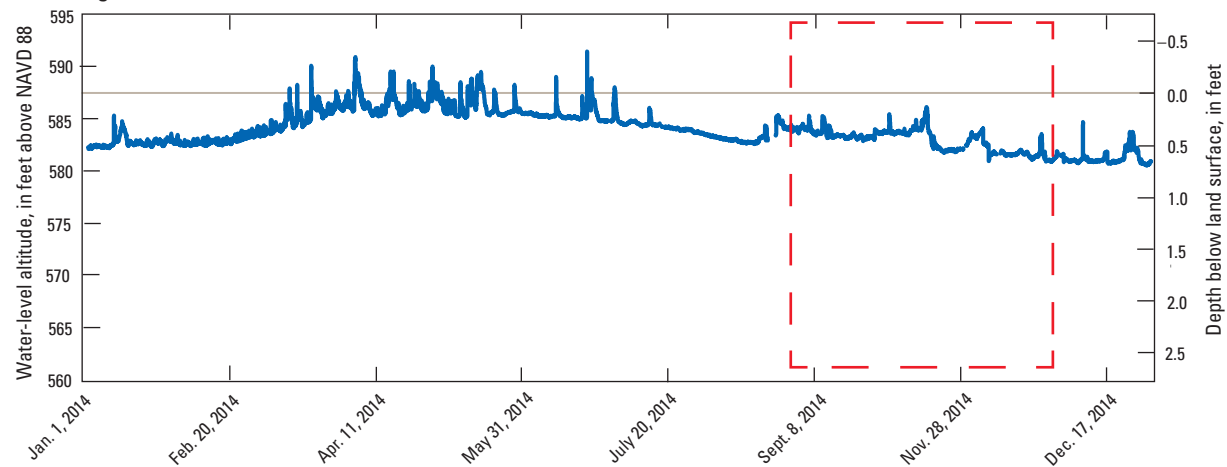
D. Monitoring well MW-4A**E. Monitoring well MW-11A****F. Monitoring well MW-14A****EXPLANATION**

Figure 12. Groundwater hydrographs for extraction and monitoring wells at the confined disposal facility during January 1, 2014, through December 31, 2014. A, EW-4B; B, EW-11B; C, EW-14A; D, MW-4A; E, MW-11A; and F, MW-14A.—Continued

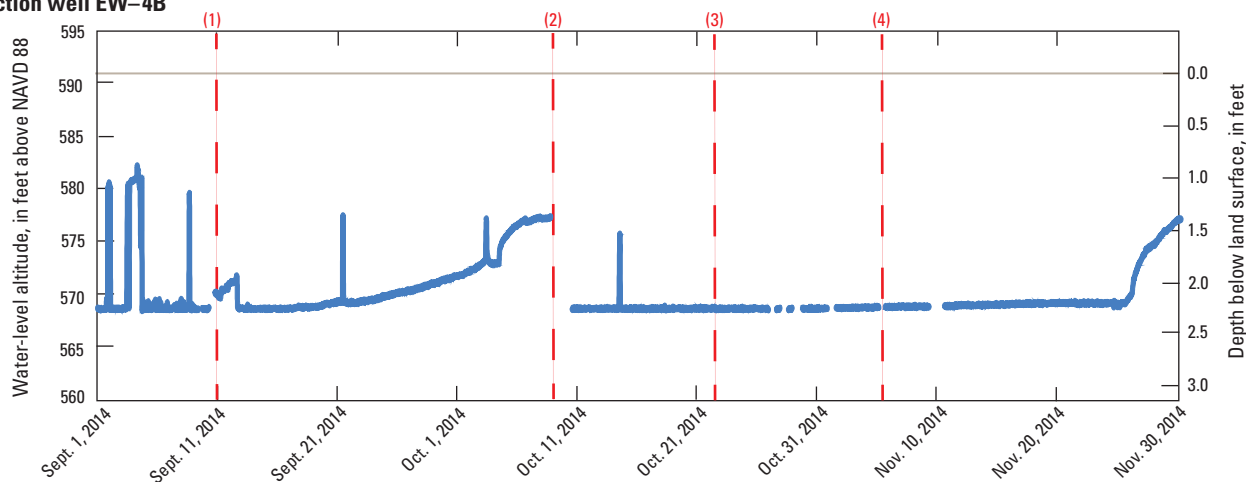
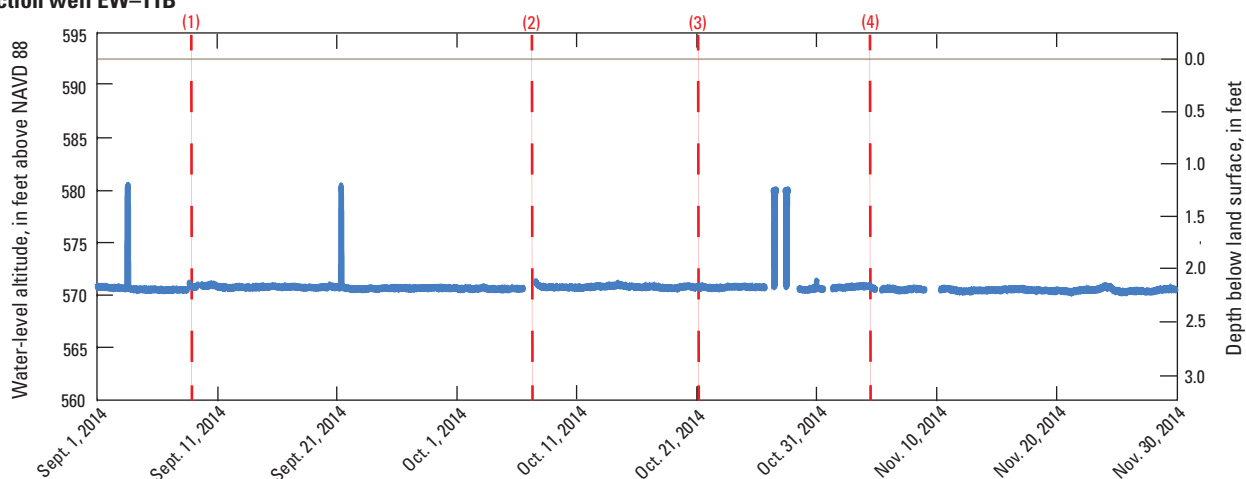
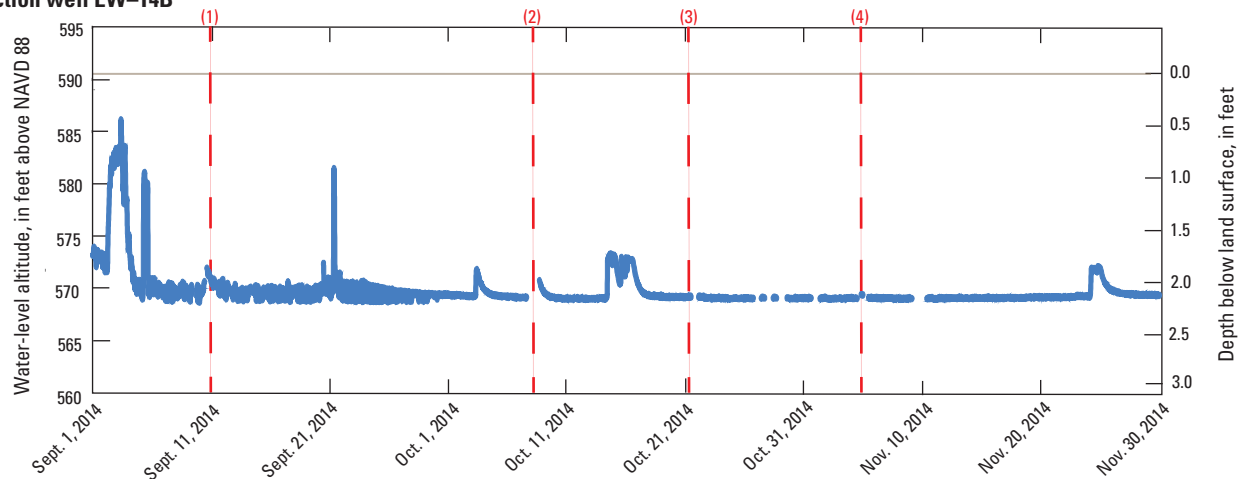
A. Extraction well EW-4B**B. Extraction well EW-11B****C. Extraction well EW-14B****EXPLANATION**

Figure 13. Groundwater hydrographs for extraction and monitoring wells at the confined disposal facility during September 1, 2014, through November 30, 2014. A, EW-4B; B, EW-11B; C, EW-14A; D, MW-4A; E, MW-11A; and F, MW-14A.

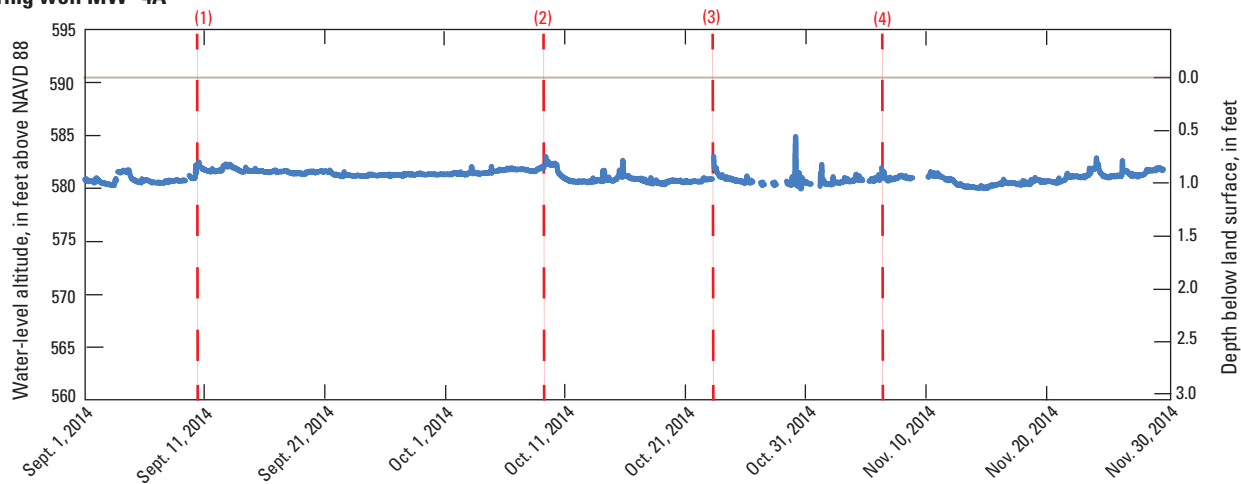
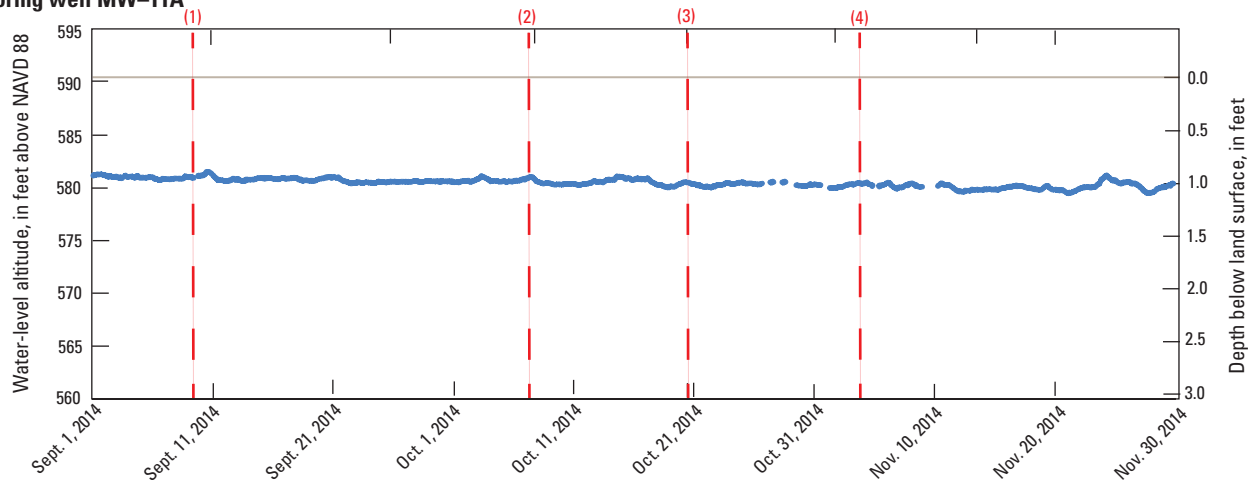
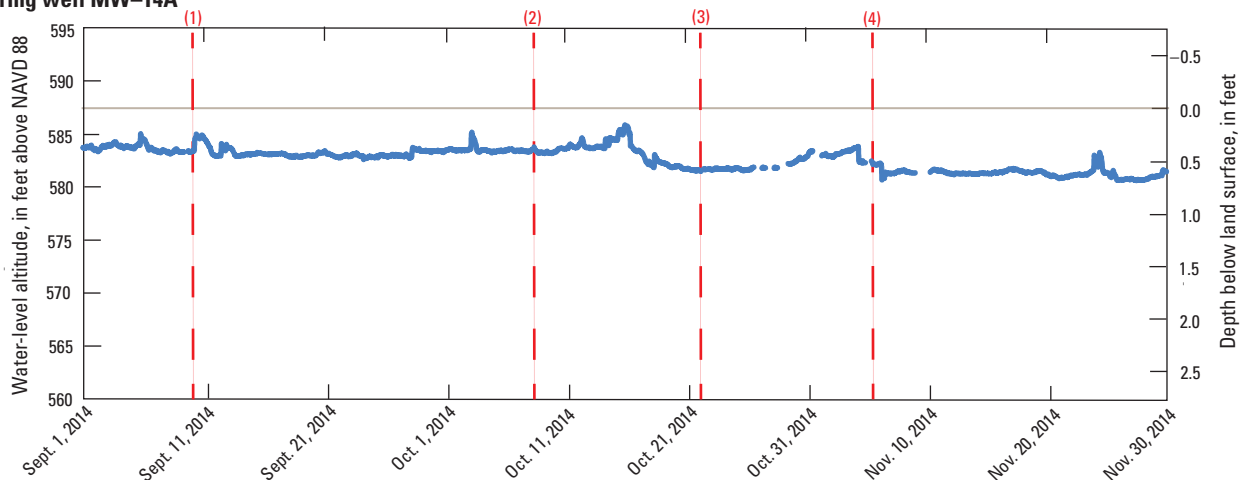
D. Monitoring well MW-4A**E. Monitoring well MW-11A****F. Monitoring well MW-14A****EXPLANATION**

Figure 13. Groundwater hydrographs for extraction and monitoring wells at the confined disposal facility during September 1, 2014, through November 30, 2014. A, EW-4B; B, EW-11B; C, EW-14A; D, MW-4A; E, MW-11A; and F, MW-14A.—Continued

Water levels in MW-14A were slightly higher in spring and lower during autumn (fig. 12F). During water-quality sampling, groundwater levels in EW-14A ranged from 568.78 to 581.35 ft (fig. 13C) and in MW-14A, groundwater levels ranged from 581.57 to 585.87 ft above NAVD 88 (fig. 13F). Groundwater levels in MW-14A were about 10 ft above groundwater levels in EW-14A during water-quality sampling.

Quality-Assurance Data

Measured concentrations of aqueous constituents exceeding the minimum reporting limit (MRL) were detected in 17 of 75 analyses (excluding pH and dissolved solids) from equipment blanks collected at well MW-4A (table 7; Christian, 2018). Ammonia exceeded the MRL in three samples; calcium, magnesium, and organic carbon exceeded the MRL in two samples; and manganese, silica, sulfate, and orthophosphate exceeded the MRL in one sample. Most exceedances were small in comparison to the MRL, but organic carbon and sulfate detections were notable. Organic carbon, inorganic carbon, and ammonia exceeded the MRL in the equipment blank collected October 7, 2014, at well MW-11A. Only the concentration of organic carbon in the equipment blank was greater than 1 percent (2.6 percent) of the concentration measured in the environmental sample. Calcium, magnesium, sulfate, inorganic carbon, iron, organic carbon, and ammonia exceeded the MRL in an equipment blank collected on October 22, 2014, at well MW-14A. The constituent concentrations in the equipment blank were less than 1 percent of the concentrations measured in the environmental sample from well MW-14A, except the concentration of organic carbon was 15 percent of that measured in the environmental sample.

The detected constituent concentrations in the replicate and environmental samples were nearly identical with few exceptions. In 2 of the 4 sets of replicate samples, the concentrations of orthophosphate were about twice as high in the environmental sample as in the replicate sample; although the concentrations were all less than 1 mg/L. On September 11, 2014, the concentration of nitrate plus nitrite at well EW-4B was greater than twice as high in the replicate sample as in the environmental sample; again, the concentrations were near the MRL. A replicate sample was collected on October 7, 2014, from EW-11B about 3 minutes after the environmental sample was collected. The concentrations of most constituents were similar in the replicate and environmental samples. Exceptions were that iodide was approximately twice as high in the replicate sample as in the environmental sample, and orthophosphate was about twice as high in the environmental sample as in the replicate sample. A replicate sample was collected on October 21, 2014, from EW-14A about 3 minutes after the environmental sample was collected. No appreciable differences in constituent concentrations were observed (table 7).

Quality-assurance data results from the analyses made on samples of sterile blank water are listed in tables 7 and 8.

Equipment blanks indicated limited amounts of inorganic, organic, and bacteria carryover; however, these quantities were small in comparison to the magnitudes detected in the environmental samples. In general, results of the quality-assurance data indicated that analyses made on environmental samples should generally be reproducible.

Water Chemistry

Similarities and differences in groundwater chemistry were observed at the six locations (three well nests) during the four sampling regimes. The data were also compared to the groundwater chemistry in two wells (D21 and D40) that are near to the CDF but not located on the site (referred to herein as ‘offsite’ wells) (table 7; fig. 1). The D21 and D40 wells may represent water quality that has not been as significantly impacted by human activities as the CDF wells. The water-quality data for D21 and D40 are for samples collected during 1986–93. Tools used to aid the comparisons included modified boxplots, phase diagrams, x-y plots, and scatter plots. Statistical methods were not used to quantitatively evaluate whether chemical constituents or property values were higher or lower based on a threshold of statistical significance; rather, the following discussions use only relative differences to characterize differences in water chemistry between sites. Modified boxplots were used to show the relative differences in constituent concentrations and parameter values for the four samples at the CDF wells. The terminology ‘modified boxplot’ is used to emphasize that the number of values used to construct the diagrams was smaller than the number that is normally used to construct boxplots. Samples collected for quality-assurance purposes were not included in the following description of environmental samples. The second samples collected in November at EW4B and MW4A also were not included in the analysis.

The depth to water varied considerably between the wells during sample collection. The lowest water levels ranged from 10.5 to 22.5 ft below land surface, with the lowest water levels in EW-4B (22.5 ft; 568.5 ft above the vertical datum) and EW-14A (22.3 ft; 568.1 ft above the vertical datum). The highest water levels ranged from 9.5 to 11.4 ft below land surface. During the study period, water levels fluctuated from 0.7 to 2.4 ft in monitoring wells, compared to 9.7 to 12.3 ft in extraction wells. The depths to water in offsite wells when those wells were sampled, albeit from a different time period, were 0.5 and 2.5 ft.

Dissolved oxygen ranged from 0.18 to 1.64 mg/L (median 0.18 mg/L) in the CDF well waters (hereafter, “well waters” is presented as “wells”), compared to 0.0 to 1.6 mg/L (median 0.4 mg/L) in the offsite wells. In extraction wells, dissolved oxygen ranged from 0.18 to 0.44 mg/L and median concentration was 0.19 mg/L in all three wells (fig. 14). In monitoring wells, dissolved oxygen ranged from 0.18 to 1.64 mg/L and median concentrations ranged from 0.18 to 0.53 mg/L (fig. 14; table 7).

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name			
	D21	D21	D21	D21
	Date sampled			
	July 22, 1987	May 3, 1988	August 4, 1988	June 15, 1993
	Time sampled			
	1600	1645	1015	1635
	Sample type			
	Environ- mental	Environ- mental	Environ- mental	Environ- mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	830	--	--	641
pH, water, unfiltered, laboratory, standard units	7.5	--	--	--
pH, water, unfiltered, onsite, standard units	7.4	7.7	7.4	--
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	983	--	--	--
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	1,330	1,200	1,360	--
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	--	--	-120
Eh (standard hydrogen electrode), millivolts ¹	--	--	--	111
pE	--	--	--	1.95
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	0.00	0.40	0.60	0.10
Temperature, in degrees Celsius	19.0	12.3	19.5	13.3
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	--	--	--
Hardness, water, milligrams per liter as calcium carbonate	580	--	--	--
Calcium, water, filtered, milligrams per liter	160	--	--	120
Magnesium, water, filtered, milligrams per liter	43	--	--	33
Sodium, water, filtered, milligrams per liter	54	--	--	40
Potassium, water, filtered, milligrams per liter	15	--	--	8.5
Sulfate, water, filtered, milligrams per liter	210	--	--	E 187
Chloride, water, filtered, milligrams per liter	78	--	--	E 59.7
Fluoride, water, filtered, milligrams per liter	1.6	--	--	--
Iodide, water, filtered, milligrams per liter	--	--	--	--
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	--	--	--	--
Sulfide, spectrophotometric, milligrams per liter	--	--	--	--
Iron, water, filtered, micrograms per liter	1,600	--	--	--
Ferrous iron, spectrophotometric, milligrams per liter	--	--	--	--
Manganese, water, filtered, micrograms per liter	250	--	--	--
Silica, water, filtered, milligrams per liter as silica	38	--	--	E 36
Organic carbon, water, filtered, milligrams per liter	--	--	--	--
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	--	--	--	--
Ammonia, water, filtered, milligrams per liter as nitrogen	8.5	--	--	--
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	--	--	--	--
Nitrite, water, filtered, milligrams per liter as nitrogen	--	--	--	--
Orthophosphate, water, filtered, milligrams per liter as phosphorus	0.12	--	--	--

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name				
	D40	D40	D40	D40	D40
	Date sampled				
	August 28, 1986	July 16, 1987	May 10, 1988	August 2, 1988	June 14, 1993
	Time sampled				
	950	1318	1000	1845	1705
	Sample type				
	Environ-mental	Environ-mental	Environ-mental	Environ-mental	Environ-mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	--	350	--	--	433
pH, water, unfiltered, laboratory, standard units	--	7.3	--	--	--
pH, water, unfiltered, onsite, standard units	7.1	7.1	7.3	6.9	6.2
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	--	541	--	--	--
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	1,550	550	1,720	2,070	--
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	--	--	--	-85
Eh (standard hydrogen electrode), millivolts ¹	--	--	--	--	146
pE	--	--	--	--	2.58
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	1.60	0.80	0.40	0.90	0.30
Temperature, in degrees Celsius	16.9	18.1	8.7	19.0	12.1
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	--	--	--	--
Hardness, water, milligrams per liter as calcium carbonate	--	240	--	--	--
Calcium, water, filtered, milligrams per liter	--	77	--	--	100
Magnesium, water, filtered, milligrams per liter	--	12	--	--	27
Sodium, water, filtered, milligrams per liter	--	25	--	--	33
Potassium, water, filtered, milligrams per liter	--	1.5	--	--	1.2
Sulfate, water, filtered, milligrams per liter	--	49	--	--	E 5.5
Chloride, water, filtered, milligrams per liter	--	11.0	--	--	29.5
Fluoride, water, filtered, milligrams per liter	--	1	--	--	--
Iodide, water, filtered, milligrams per liter	--	--	--	--	--
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	--	--	--	--	--
Sulfide, spectrophotometric, milligrams per liter	--	--	--	--	--
Iron, water, filtered, micrograms per liter	--	2,800	--	--	--
Ferrous iron, spectrophotometric, milligrams per liter	--	--	--	--	--
Manganese, water, filtered, micrograms per liter	--	690	--	--	--
Silica, water, filtered, milligrams per liter as silica	--	24.0	--	--	E 16.9
Organic carbon, water, filtered, milligrams per liter	--	--	--	--	--
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	--	--	--	--	--
Ammonia, water, filtered, milligrams per liter as nitrogen	--	0.87	--	--	--
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	--	--	--	--	--
Nitrite, water, filtered, milligrams per liter as nitrogen	--	--	--	--	--
Orthophosphate, water, filtered, milligrams per liter as phosphorus	--	0.26	--	--	--

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name							
	MW-4A	MW-4A	MW-4A	MW-4A	MW-4A	MW-4A	MW-4A	MW-4A
	Date sampled							
	September 5, 2014	September 11, 2014	October 23, 2014	November 6, 2014	September 10, 2014	October 9, 2014	October 23, 2014	November 6, 2014
	Time sampled							
	858	915	1300	1335	1600	915	935	848
	Sample type							
	Equipment blank	Equipment blank	Equipment-manifold blank	Equipment-pump blank	Environmental	Environmental	Environmental	Environmental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	<20	<20	<20	<20	2,420	3,450	2,820	3,730
pH, water, unfiltered, laboratory, standard units	6.3	E 6.3	E 6.0	E 6.2	6.8	6.7	6.7	6.7
pH, water, unfiltered, onsite, standard units	--	--	--	--	6.5	6.5	6.6	6.4
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	<5	<5	<5	<5	2,570	3,400	2,890	3,670
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	--	--	--	2,410	3,200	2,740	4,160
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	--	--	--	-116	-201	-186	-255
Eh (standard hydrogen electrode), millivolts ¹	--	--	--	--	115	30	45	-24
pE	--	--	--	--	2.02	0.53	0.79	-0.42
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	--	--	--	0.87	0.18	0.18	1.10
Temperature, in degrees Celsius	--	--	--	--	14.2	12.6	12.4	12.2
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	--	--	--	26	2.4	8.5	60
Hardness, water, milligrams per liter as calcium carbonate	--	--	--	--	1,660	2,360	1,910	2,630
Calcium, water, filtered, milligrams per liter	0.035	<0.022	<0.022	0.028	372	468	466	541
Magnesium, water, filtered, milligrams per liter	<0.011	<0.011	0.026	0.022	178	288	181	311
Sodium, water, filtered, milligrams per liter	<0.06	<0.06	<0.06	<0.06	30.9	45.4	39.8	49.4
Potassium, water, filtered, milligrams per liter	<0.030	<0.004	<0.030	<0.030	25.9	27.6	30.8	27.5
Sulfate, water, filtered, milligrams per liter	<0.02	<0.02	<0.02	0.163	1,300	2,050	1,230	1,730
Chloride, water, filtered, milligrams per liter	<0.02	<0.02	<0.02	<0.02	11.0	11.2	13.9	14.5
Fluoride, water, filtered, milligrams per liter	<0.01	<0.01	<0.01	<0.01	0.54	0.49	0.51	0.51
Iodide, water, filtered, milligrams per liter	<0.001	--	<0.001	<0.001	0.009	0.013	0.008	0.016
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	E 0.4	E 0.3	E 0.5	E 0.3	150	190	140	210
Sulfide, spectrophotometric, milligrams per liter	--	--	--	--	0.481	0.427	0.456	>0.660
Iron, water, filtered, micrograms per liter	<4.0	<4.0	<4.0	<4.0	14,100	11,500	11,100	8,980
Ferrous iron, spectrophotometric, milligrams per liter	--	--	--	--	>3.30	>3.30	>3.30	3.14
Manganese, water, filtered, micrograms per liter	0.211	<0.2	<0.2	<0.2	855	1,040	1,440	1,980
Silica, water, filtered, milligrams per liter as silica	<0.018	<0.018	0.076	<0.018	49.1	55.4	49.3	59.0
Organic carbon, water, filtered, milligrams per liter	15.3	<0.23	<0.23	48.1	29.4	40.0	30.9	48.1
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	<0.05	<0.05	<0.05	<0.05	3.45	3.92	3.14	5.78
Ammonia, water, filtered, milligrams per liter as nitrogen	0.011	0.029	0.013	<0.010	2.28	3.07	1.92	4.12
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	<0.040	<0.040	<0.040	<0.040	<0.040	<0.200	<0.040	<0.040
Nitrite, water, filtered, milligrams per liter as nitrogen	<0.001	<0.001	<0.001	<0.001	0.001	0.003	<0.001	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	<0.004	<0.030	0.007	<0.004	0.069	0.099	0.027	0.077

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name					
	EW-4B	EW-4B	EW-4B	EW-4B	EW-4B	EW-4B
	Date sampled					
	September 11, 2014	November 5, 2014	September 11, 2014	October 9, 2014	October 22, 2014	November 5, 2014
	Time sampled					
	1413	1348	1410	1410	1353	1230
	Sample type					
	Replicate	Replicate	Environ-mental	Environ-mental	Environ-mental	Environ-mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	2,120	1,950	2,100	2,420	2,020	1,960
pH, water, unfiltered, laboratory, standard units	7.0	7.1	7.0	7.1	7.2	7.2
pH, water, unfiltered, onsite, standard units	--	--	6.8	6.9	6.8	6.8
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	2,470	2,320	2,480	2,670	2,320	2,310
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	--	2,430	2,390	2,280	2,210
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	--	-311	-345	-359	-328
Eh (standard hydrogen electrode), millivolts ¹	--	--	-80	-114	-128	-97
pE	--	--	-1.39	-1.98	-2.23	-1.70
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	--	0.44	0.18	0.20	0.18
Temperature, in degrees Celsius	--	--	16.3	16.6	16.3	15.3
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	--	39	5.2	36	28
Hardness, water, milligrams per liter as calcium carbonate	--	--	1,580	1,700	1,430	1,420
Calcium, water, filtered, milligrams per liter	273	237	276	271	245	276
Magnesium, water, filtered, milligrams per liter	218	188	217	249	198	177
Sodium, water, filtered, milligrams per liter	50.1	52.0	50.2	58.2	52.3	48.0
Potassium, water, filtered, milligrams per liter	11.3	11.1	11.5	12.5	12.1	11.9
Sulfate, water, filtered, milligrams per liter	881	860	906	857	806	871
Chloride, water, filtered, milligrams per liter	14.3	15.8	14.5	12.4	15.1	16.4
Fluoride, water, filtered, milligrams per liter	0.825	1.02	0.86	0.75	0.96	0.93
Iodide, water, filtered, milligrams per liter	0.014	--	0.031	0.022	0.042	0.031
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	180	170	180	190	180	180
Sulfide, spectrophotometric, milligrams per liter	--	--	0.660	0.481	>0.660	0.496
Iron, water, filtered, micrograms per liter	5,450	4,870	5,800	7,560	5,060	6,500
Ferrous iron, spectrophotometric, milligrams per liter	--	--	2.93	3.14	>3.30	3.25
Manganese, water, filtered, micrograms per liter	378	426	375	409	396	321
Silica, water, filtered, milligrams per liter as silica	47.6	49.8	47.4	52.1	46.6	46.7
Organic carbon, water, filtered, milligrams per liter	48.1	47.2	45.8	47.9	46.8	45.8
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	6.87	7.88	6.89	7.66	6.82	6.87
Ammonia, water, filtered, milligrams per liter as nitrogen	6.16	6.57	6.16	6.31	6.42	6.07
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	0.078	<0.040	<0.040	<0.200	<0.040	<0.040
Nitrite, water, filtered, milligrams per liter as nitrogen	<0.002	<0.010	<0.005	<0.002	<0.001	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	0.265	0.165	0.583	0.627	0.171	0.158

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name				
	MW-11A	MW-11A	MW-11A	MW-11A	MW-11A
	Date sampled				
	October 7, 2014	September 9, 2014	October 7, 2014	October 20, 2014	November 3, 2014
	Time sampled				
	1445	1225	920	1310	1230
	Sample type				
	Equipment blank	Environ-mental	Environ-mental	Environ-mental	Environ-mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	<20	823	903	912	767
pH, water, unfiltered, laboratory, standard units	E6.3	6.6	6.8	6.9	6.8
pH, water, unfiltered, onsite, standard units	--	6.5	6.6	6.6	6.5
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	<5	1,240	1,290	1,350	1,250
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	2,180	1,220	1,340	1,240
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	-240	-211	-135	-155
Eh (standard hydrogen electrode), millivolts ¹	--	-9	20	96	76
pE	--	-0.16	0.35	1.69	1.34
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	0.49	0.18	0.18	0.18
Temperature, in degrees Celsius	--	13.2	12.7	13.4	13.1
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	3.7	10	12	7.1
Hardness, water, milligrams per liter as calcium carbonate	--	607	652	731	641
Calcium, water, filtered, milligrams per liter	<0.022	174	184	210	184
Magnesium, water, filtered, milligrams per liter	<0.011	41.7	46.5	50.4	44.4
Sodium, water, filtered, milligrams per liter	<0.06	22.8	26.4	26.5	25.7
Potassium, water, filtered, milligrams per liter	<0.03	10.0	13.6	18.8	9.77
Sulfate, water, filtered, milligrams per liter	<0.02	11.0	44.3	84.6	3.95
Chloride, water, filtered, milligrams per liter	<0.02	34.7	34.3	33.4	35.1
Fluoride, water, filtered, milligrams per liter	<0.01	0.54	0.43	0.48	0.51
Iodide, water, filtered, milligrams per liter	<0.001	--	0.056	0.049	0.040
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	E0.3	220	240	220	220
Sulfide, spectrophotometric, milligrams per liter	--	0.147	0.224	0.162	0.109
Iron, water, filtered, micrograms per liter	<4.0	45,900	40,500	34,500	47,400
Ferrous iron, spectrophotometric, milligrams per liter	--	>3.30	>3.30	>3.30	>3.30
Manganese, water, filtered, micrograms per liter	<0.2	747	761	814	732
Silica, water, filtered, milligrams per liter as silica	<0.018	35.3	38.3	38.5	38.0
Organic carbon, water, filtered, milligrams per liter	1.01	43.7	38.6	34.8	39.8
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	<0.05	8.11	8.09	6.96	8.62
Ammonia, water, filtered, milligrams per liter as nitrogen	0.026	6.50	6.75	5.35	7.21
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	<0.04	<0.040	<0.040	<0.040	<0.200
Nitrate, water, filtered, milligrams per liter as nitrogen	<0.001	0.011	0.018	0.008	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	<0.004	E0.176	0.197	0.091	0.143

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name				
	EW-11B	EW-11B	EW-11B	EW-11B	EW-11B
	Date sampled				
	October 7, 2014	September 9, 2014	October 7, 2014	October 21, 2014	November 4, 2014
	Time sampled				
	1248	930	1245	925	930
	Sample type				
	Replicate	Environ-mental	Environ-mental	Environ-mental	Environ-mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	869	821	849	917	792
pH, water, unfiltered, laboratory, standard units	6.8	7.0	6.8	6.8	6.8
pH, water, unfiltered, onsite, standard units	--	6.5	6.6	6.6	6.6
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	1,260	1,140	1,260	1,340	1,240
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	1,040	1,300	1,330	1,200
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	-150	-122	-82	-113
Eh (standard hydrogen electrode), millivolts ¹	--	81	109	149	118
pE	--	1.42	1.92	2.62	2.08
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	0.20	0.20	0.18	0.18
Temperature, in degrees Celsius	--	15.2	14.8	13.3	13.5
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	4.3	8.3	4.0	3.6
Hardness, water, milligrams per liter as calcium carbonate	--	581	622	682	612
Calcium, water, filtered, milligrams per liter	170	158	170	188	166
Magnesium, water, filtered, milligrams per liter	47.7	45.5	47.9	51.3	48.4
Sodium, water, filtered, milligrams per liter	34.6	29.0	32.7	30.7	31.8
Potassium, water, filtered, milligrams per liter	11.5	7.15	11.7	13.3	8.31
Sulfate, water, filtered, milligrams per liter	47.9	2.48	46.3	105	6.79
Chloride, water, filtered, milligrams per liter	37.5	39.9	37.5	36.9	39.1
Fluoride, water, filtered, milligrams per liter	0.618	0.60	0.58	0.72	0.73
Iodide, water, filtered, milligrams per liter	0.041	--	0.020	0.041	0.086
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	230	220	230	200	210
Sulfide, spectrophotometric, milligrams per liter	--	0.069	0.098	0.144	0.104
Iron, water, filtered, micrograms per liter	37,900	39,500	37,500	35,800	37,500
Ferrous iron, spectrophotometric, milligrams per liter	--	>3.30	>3.30	>3.30	>3.30
Manganese, water, filtered, micrograms per liter	713	717	704	775	752
Silica, water, filtered, milligrams per liter as silica	34.3	32.7	33.8	33.6	33.5
Organic carbon, water, filtered, milligrams per liter	44.1	47.0	44.7	42.5	46.5
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	8.49	7.92	8.73	7.96	7.84
Ammonia, water, filtered, milligrams per liter as nitrogen	6.3	6.28	6.31	6.15	6.55
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	<0.04	<0.040	<0.040	<0.200	<0.200
Nitrite, water, filtered, milligrams per liter as nitrogen	0.013	0.011	0.018	<0.002	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	0.135	E0.067	0.268	0.073	0.279

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name				
	EW-14A	EW-14A	EW-14A	EW-14A	EW-14A
	Date sampled				
	October 21, 2014	September 11, 2014	October 8, 2014	October 21, 2014	November 4, 2014
	Time sampled				
	1238	1110	1340	1235	1300
	Sample type				
	Replicate	Environ-mental	Environ-mental	Environ-mental	Environ-mental
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	783	733	779	779	793
pH, water, unfiltered, laboratory, standard units	7.1	7.1	7.2	7.4	7.1
pH, water, unfiltered, onsite, standard units	--	6.9	7.0	7.0	6.9
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	1,290	1,320	1,300	1,270	1,270
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	1,290	1,270	1,260	1,170
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	-95	-147	-112	-121
Eh (standard hydrogen electrode), millivolts ¹	--	136	84	119	110
pE	--	2.40	1.48	2.10	1.93
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	0.33	0.20	0.18	0.18
Temperature, in degrees Celsius	--	14.7	15.9	13.6	13.8
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	3.8	14	5.8	8.0
Hardness, water, milligrams per liter as calcium carbonate	--	636	612	615	601
Calcium, water, filtered, milligrams per liter	154	157	150	151	151
Magnesium, water, filtered, milligrams per liter	57.1	59.4	57.5	57.5	54.6
Sodium, water, filtered, milligrams per liter	52.1	54.7	55.6	54.1	51.2
Potassium, water, filtered, milligrams per liter	11.2	10.7	12.3	11.2	11.0
Sulfate, water, filtered, milligrams per liter	12.6	16.2	15.6	11.7	12.3
Chloride, water, filtered, milligrams per liter	40.1	40.9	38.0	39.3	39.7
Fluoride, water, filtered, milligrams per liter	0.97	0.90	1.12	1.13	1.14
Iodide, water, filtered, milligrams per liter	0.028	0.043	0.075	0.036	0.069
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	180	190	190	180	180
Sulfide, spectrophotometric, milligrams per liter	--	0.057	0.132	0.148	0.174
Iron, water, filtered, micrograms per liter	8,200	8,660	10,500	8,180	7,620
Ferrous iron, spectrophotometric, milligrams per liter	--	>3.30	>3.30	>3.30	>3.30
Manganese, water, filtered, micrograms per liter	323	305	337	319	304
Silica, water, filtered, milligrams per liter as silica	40.9	37.9	40.4	41.1	39.1
Organic carbon, water, filtered, milligrams per liter	33.3	33.5	37.1	34.3	35.4
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	8.52	7.41	9.70	8.65	9.17
Ammonia, water, filtered, milligrams per liter as nitrogen	6.91	6.02	6.14	6.89	6.85
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	<0.2	<0.040	<0.040	<0.200	<0.080
Nitrite, water, filtered, milligrams per liter as nitrogen	<0.010	0.001	0.003	<0.002	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	0.214	0.229	0.303	0.233	0.218

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 7. Water-quality data for groundwater samples collected at the confined disposal facility.—Continued

[The water-quality data used in this study are available through a data release at <https://doi.org/10.5066/F7PK0FBJ> (Christian, 2018) and were placed in the U.S. Geological Survey's National Water Information System (U.S. Geological Survey, 2016b). <, less than minimum reporting limit; E, estimated; --, no data; Eh, redox potential; pE, negative base 10 logarithm of the electron activity; NTRU, nephelometric turbidity ratio units; >, greater than maximum reporting limit]

Water-quality constituent	Well name				
	MW-14A	MW-14A	MW-14A	MW-14A	MW-14A
	Date sampled				
	October 22, 2014	September 10, 2014	October 8, 2014	October 22, 2014	November 5, 2014
	Time sampled				
	1700	1235	925	955	905
	Sample type				
	Equipment blank	Environmental sample	Environmental sample	Environmental sample	Environmental sample
Dissolved solids dried at 180 degrees Celsius, water, filtered, milligrams per liter	<20	1,310	1,060	1,450	986
pH, water, unfiltered, laboratory, standard units	E6.3	7.3	7.3	7.2	7.7
pH, water, unfiltered, onsite, standard units	--	6.8	7.0	6.9	6.9
Specific conductance, water, unfiltered, laboratory, microsiemens per centimeter at 25 degrees Celsius	<5	1,670	1,520	1,820	1,450
Specific conductance, water, unfiltered, onsite, microsiemens per centimeter at 25 degrees Celsius	--	1,740	1,520	1,810	1,470
Redox potential (silver/silver chloride [Ag/AgCl] reference electrode), millivolts	--	-126	-160	-140	-220
Eh (standard hydrogen electrode), millivolts ¹	--	105	71	91	11
pE	--	1.84	1.24	1.60	0.19
Dissolved oxygen, water, unfiltered, onsite, milligrams per liter	--	1.64	0.18	0.20	0.18
Temperature, in degrees Celsius	--	15.3	13.2	13.1	13.1
Turbidity, water, unfiltered, broad band light source (400–680 nanometers), detectors at multiple angles including 90 plus -30 degrees, ratiometric correction, NTRU	--	6.0	4.9	4.0	5.5
Hardness, water, milligrams per liter as calcium carbonate	--	975	805	1,040	739
Calcium, water, filtered, milligrams per liter	0.044	284	220	296	197
Magnesium, water, filtered, milligrams per liter	0.012	64.6	62.4	72.8	60.1
Sodium, water, filtered, milligrams per liter	<0.06	28.5	48.0	28.2	41.8
Potassium, water, filtered, milligrams per liter	<0.03	27.8	24	24	18.4
Sulfate, water, filtered, milligrams per liter	0.037	510	233	649	198
Chloride, water, filtered, milligrams per liter	<0.02	17.3	23.4	21	27.8
Fluoride, water, filtered, milligrams per liter	<0.01	0.96	1.09	0.99	1.15
Iodide, water, filtered, milligrams per liter	<0.001	0.013	0.019	0.007	0.019
Carbon, inorganic, water, filtered, as carbon, milligrams per liter	E0.3	130	170	110	160
Sulfide, spectrophotometric, milligrams per liter	--	0.308	0.294	0.348	0.384
Iron, water, filtered, micrograms per liter	5.53	3,100	2,110	3,270	2,410
Ferrous iron, spectrophotometric, milligrams per liter	--	1.48	1.50	2.45	1.50
Manganese, water, filtered, micrograms per liter	<0.2	568	512	803	525
Silica, water, filtered, milligrams per liter as silica	<0.018	28.0	39.3	26.1	38.5
Organic carbon, water, filtered, milligrams per liter	2.53	17.2	24.5	16.8	25.2
Total nitrogen (nitrate plus nitrite plus ammonia plus organic nitrogen), water, filtered, analytically determined, milligrams per liter	<0.25	4.43	4.93	2.36	4.57
Ammonia, water, filtered, milligrams per liter as nitrogen	0.0126	3.02	3.99	1.45	3.37
Nitrate plus nitrite, water, filtered, milligrams per liter as nitrogen	<0.04	<0.040	<0.040	<0.040	<0.040
Nitrite, water, filtered, milligrams per liter as nitrogen	<0.001	0.004	0.003	0.005	<0.010
Orthophosphate, water, filtered, milligrams per liter as phosphorus	<0.004	0.109	0.137	0.07	<0.040

¹Onsite redox values measured with a silver chloride reference electrode using 3.5 moles of potassium chloride were converted to Eh (standard hydrogen electrode) values by addition of 231 millivolts as described in the manufacturer's user manual.

Table 8. Bacterial quality-assurance in groundwater samples from wells at the confined disposal facility.

[CFU/mL, colony forming units per milliliter; HAB, Heterotrophic Aerobic Bacteria; --, no data were collected because the test showed no bacterial reaction with media; SLYM, slime-forming bacteria; IRB, iron-related bacteria; SRB, sulfate-reducing bacteria; CDF, confined disposal facility]

Well name (sample type)	Bacteria type	Date collected	Observation date	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
Lab (sterile buffer water)	HAB	11/4/2014	None	--	--	No reaction	--	--
	SLYM	11/4/2014	None	--	--	No reaction	--	--
	IRB	11/4/2014	None	--	--	No reaction	--	--
	SRB	11/4/2014	None	--	--	No reaction	--	--
Lab (sterile deionized water)	HAB	11/4/2014	None	--	--	No reaction	--	--
	SLYM	11/4/2014	None	--	--	No reaction	--	--
	IRB	11/4/2014	None	--	--	No reaction	--	--
	SRB	11/4/2014	None	--	--	No reaction	--	--
Lab (CDF tap water)	HAB	11/4/2014	None	--	--	No reaction	--	--
	SLYM	11/4/2014	None	--	--	No reaction	--	--
	IRB	11/4/2014	None	--	--	No reaction	--	--
	SRB	11/4/2014	None	--	--	No reaction	--	--
MW-4A (pump blank using sterile buffer water)	HAB	11/6/2014	11/8/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	SLYM	11/6/2014	11/12/2014	6	Moderate	Cloudy growth	Slime forming	500
	IRB	11/6/2014	11/10/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	SRB	11/6/2014	11/11/2014	5	Moderate	Foam at top	Anaerobic	2,200
MW-4A (pump blank using sterile deionized water)	HAB	11/6/2014	11/8/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	SLYM	11/6/2014	11/12/2014	6	Moderate	Cloudy growth	Slime forming	500
	IRB	11/6/2014	11/10/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	SRB	11/6/2014	11/11/2014	5	Moderate	Foam at top	Anaerobic	2,200
MW-4A (pump blank using CDF tap water)	HAB	11/6/2014	None	--	--	No reaction	--	--
	SLYM	11/6/2014	None	--	--	No reaction	--	--
	IRB	11/6/2014	None	--	--	No reaction	--	--
	SRB	11/6/2014	None	--	--	No reaction	--	--
MW-4A (Indiana deion- ized water pump blank)	HAB	11/6/2014	11/8/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	SLYM	11/6/2014	11/11/2014	5	Moderate	Cloudy plates	Slime forming	2,500
			11/12/2014	6	Moderate	Cloudy growth	Slime forming	500
	IRB	11/6/2014	11/10/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	SRB	11/6/2014	11/10/2014	4	Aggressive	Foam at top	Anaerobic	9,000
	SRB	11/6/2014	11/14/2014	8	Moderate	Cloudy	Anaerobic	75

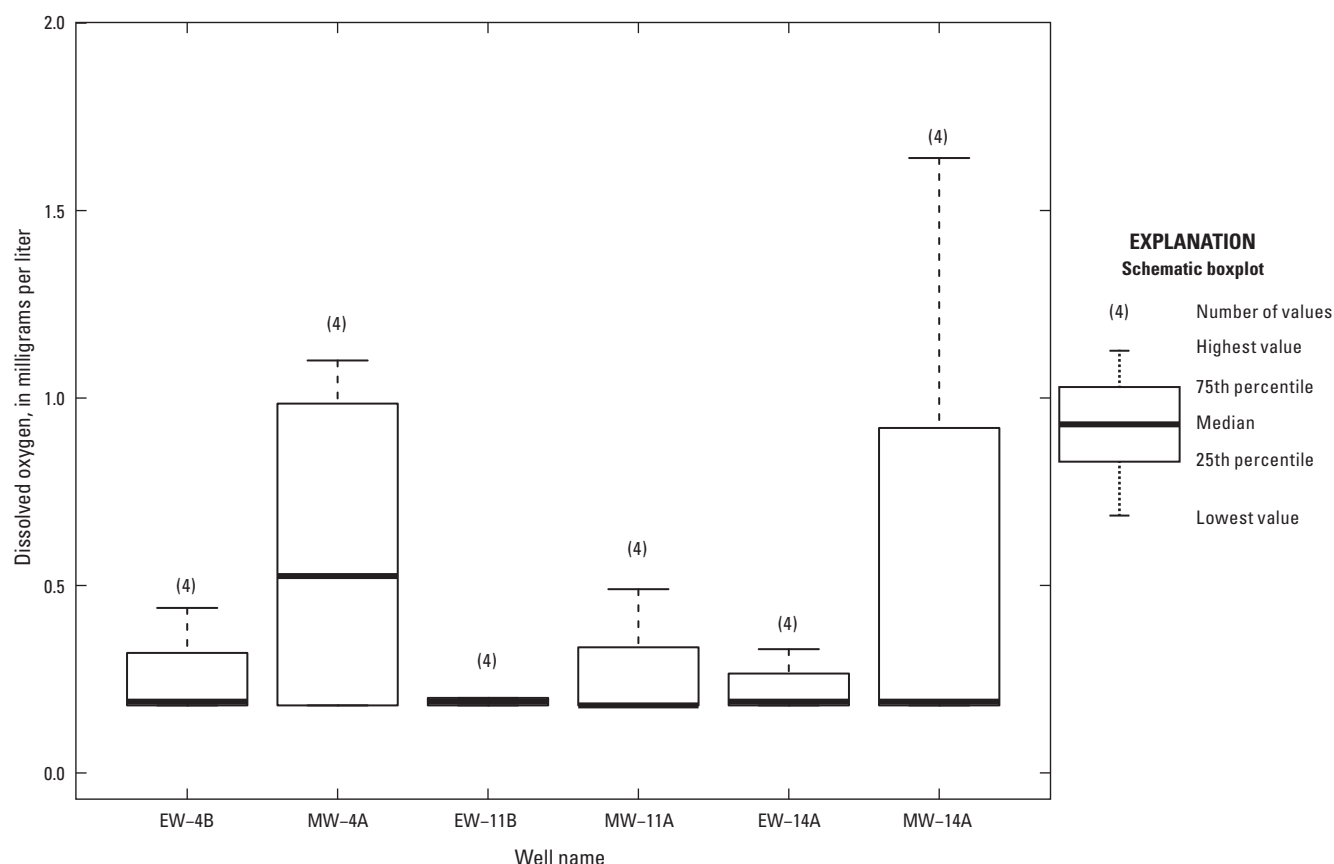


Figure 14. Distribution of dissolved oxygen concentrations in groundwater samples collected onsite from selected wells at the confined disposal facility.

The pH values ranged from 6.4 to 7.0 standard units (median 6.7 standard units) in CDF wells, compared to 6.2 to 7.7 (median 7.2 standard units) in offsite wells. The median and range of pH values were nearly the same in monitoring and extraction wells at the CDF. The pH value was generally higher in EW-14A and MW-14A than in wells at the other sites. The median pH values in EW-14A and MW-14A were 6.95 and 6.9 standard units, respectively, compared to 6.8 and 6.5 standard units in EW-4B and MW-4A, respectively, and to 6.6 and 6.55 standard units in EW-11B and MW-11A, respectively (table 7).

Specific conductance, turbidity, dissolved solids, and hardness values were notably higher in EW-4B and MW-4A than in other wells, whereas redox values were generally lower in EW-4B and MW-4A. Specific conductance values ranged from 1,040 to 4,160 microsiemens per centimeter at 25 °C in CDF wells, compared with 550 to 2,070 microsiemens per centimeter at 25 °C in two offsite wells. The median specific conductance values were 2,335 and 2,970 microsiemens per centimeter at 25 °C in EW-4B and MW-4A, respectively, compared to a range in medians from 1,250 to 1,630 microsiemens per centimeter at 25 °C in other CDF wells (table 7).

Turbidity values in CDF wells ranged from 2.4 to 60 nephelometric turbidity ratio units (NTRU). Median values ranged from 4.2 to 32 NTRU in CDF wells. Median turbidity values were 32 and 17 NTRU in EW-4B and MW-4A, respectively, compared to a range from 4.2 to 8.6 NTRU in all other CDF wells. Dissolved-solids values ranged from 733 to 3,720 mg/L in CDF wells. Median values were 2,060 and 3,135 mg/L in EW-4B and MW-4A, respectively, compared to a range from 779 to 1,185 mg/L in all other CDF wells. Historical turbidity or dissolved-solids data were not available for the offsite wells (table 7).

Hardness values ranged from 581 to 2,630 mg/L in CDF wells, compared to 240 to 580 mg/L in offsite wells (one sample at each well). Median hardness values were 1,505 and 2,135 mg/L in EW-4B and MW-4A, respectively, compared to a range from 614 to 890 mg/L in other CDF wells (table 7).

Redox values ranged from -359 to -82 millivolts in CDF wells (fig. 15) compared to historical values of -85 and -120 millivolts for one sample at each of the two offsite wells. The median redox value was -336 millivolts in EW-4B, compared to a range in medians from -117 to -194 millivolts in all other CDF wells. In summary, (1) the specific conductance, turbidity, dissolved-solids, and hardness values were notably

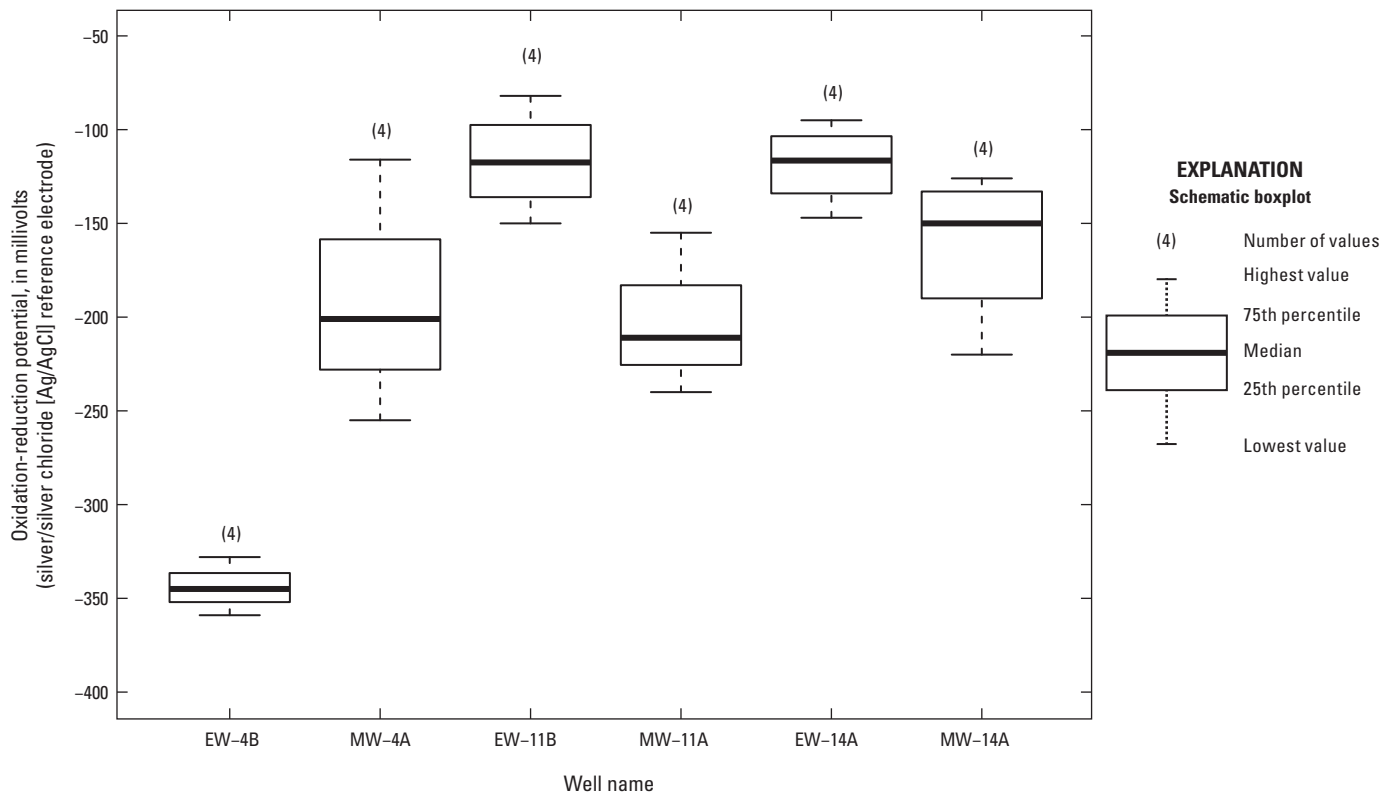


Figure 15. Distribution of the oxidation-reduction potential in groundwater samples from selected wells at the confined disposal facility.

higher in EW-4B and MW-4A than in other wells and (2) the redox values were generally lower in EW-4B and MW-4A than in other wells (table 7).

Field test kits were used to measure ferrous iron concentrations in CDF wells. Concentrations ranged from 1.48 mg/L to the upper reporting limit (3.30 mg/L). Median concentrations ranged from 1.50 to greater than 3.30 mg/L in CDF wells. The lowest median ferrous iron concentration was measured in MW-14A, and the median concentrations exceeded 3.10 mg/L in other CDF wells. Sulfide concentrations, measured with field test kits, ranged from 0.057 to greater than 0.660 mg/L. Median sulfide concentrations were highest in EW-4B (0.58 mg/L) and MW-4A (0.47 mg/L) and lowest in EW-11B (0.10 mg/L) and MW-11A (0.15 mg/L) (fig. 16; table 7). Historical ferrous iron or sulfide data were not available for the offsite wells.

Major cations analyzed included calcium, magnesium, sodium, and potassium. The calcium concentrations ranged from 150 to 541 mg/L in CDF wells, compared to 77 to 160 mg/L in offsite wells. The highest and most variable calcium concentrations were in MW-4A. Median calcium concentrations were 274 and 467 mg/L in EW-4B and MW-4A, respectively, compared to a range from 151 to 252 mg/L in all other CDF wells. In all cases, concentrations were higher in monitoring wells than in corresponding extraction wells.

Magnesium concentrations ranged from 41.7 to 311 mg/L in CDF wells, compared to 12 to 43 mg/L in offsite wells. Magnesium concentrations ranged from 41.7 to 72.8 mg/L in the #11 and #14 well clusters, compared to a range from 177 to 311 mg/L in the #4 well cluster. Sodium concentrations ranged from 22.8 to 58.2 mg/L in CDF wells, compared to 25 to 54 mg/L in offsite wells. Potassium concentrations ranged from 7.15 to 30.8 mg/L in CDF wells, compared to 1.2 to 15 mg/L in offsite wells. Median potassium concentrations were 27.5 and 24.0 mg/L in MW-4A and MW-14A, respectively, compared to a range of median concentrations from 10.0 to 12.0 mg/L in all other CDF wells. In summary, (1) calcium, magnesium, and potassium concentrations were higher in CDF wells than in offsite wells; and (2) calcium and magnesium concentrations were higher in EW-4B and MW-4A than in other wells (table 7).

Major anions analyzed for this study included sulfate, chloride, and fluoride. Alkalinity was not analyzed for this study; therefore, carbonate and bicarbonate concentrations could not be estimated. Sulfate concentrations ranged from 2.48 to 2,050 mg/L in CDF wells, compared to 5.5 (estimated) to 210 mg/L in two offsite wells. The median sulfate concentrations were 864 and 1,520 mg/L in EW-4B and MW-4A, respectively, whereas median concentrations ranged from 13.9 to 371 mg/L in all other CDF wells (fig. 17). Chloride

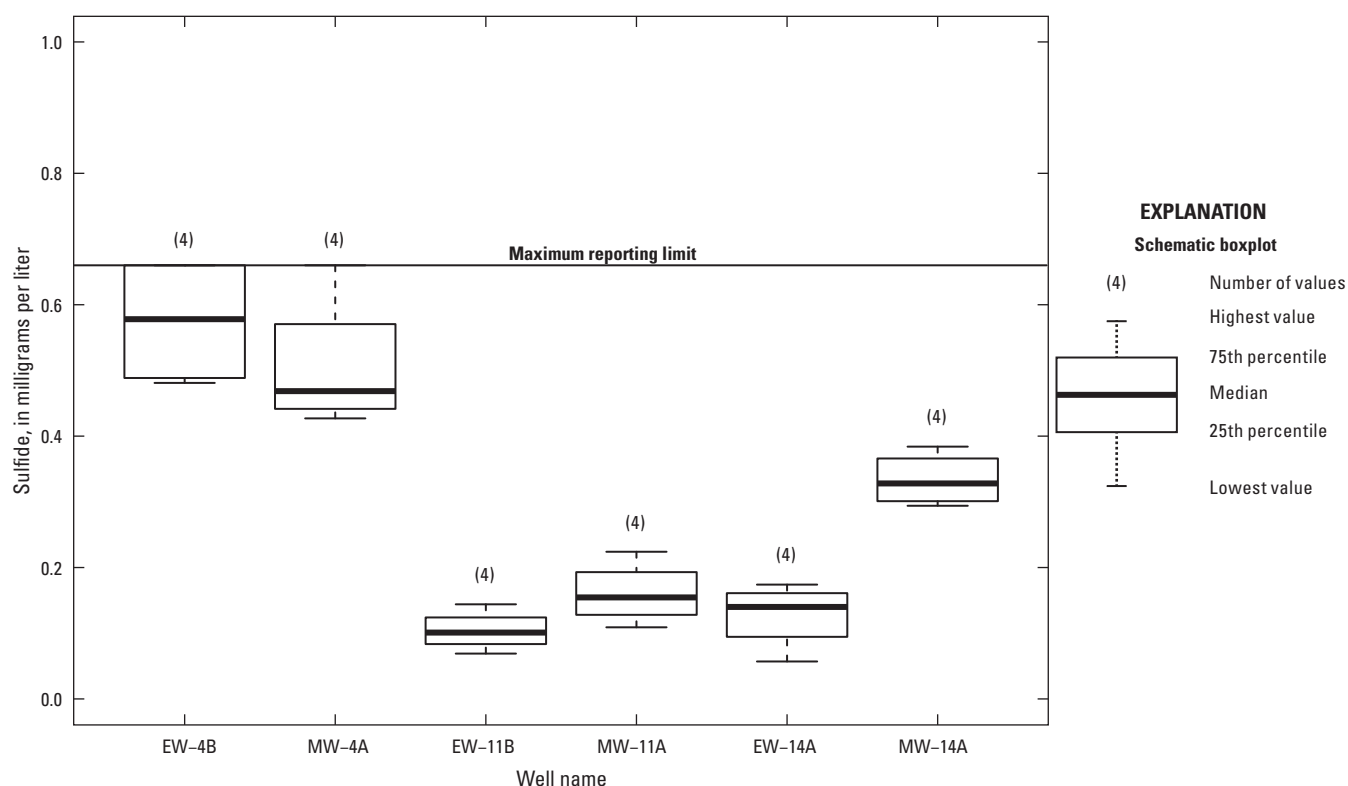


Figure 16. Distribution of sulfide concentrations in groundwater samples from selected wells at the confined disposal facility.

concentrations ranged from 11.0 to 40.9 mg/L in CDF wells, compared to 11.0 to 78.0 mg/L in offsite wells. Median chloride concentrations were 14.8 and 12.5 mg/L in EW-4B and MW-4A, respectively, whereas median concentrations ranged from 22.2 to 39.5 mg/L in all other CDF wells. Fluoride concentrations ranged from 0.43 to 1.15 mg/L in CDF wells, compared to 1.0 and 1.6 mg/L in two offsite wells (one sample at each well). In summary, (1) sulfate concentrations were higher in CDF wells than in offsite wells, (2) chloride and fluoride concentrations were comparable in CDF and offsite wells, and (3) sulfate concentrations were notably higher in EW-4B and MW-4A than in all other wells (table 7).

Trace elements analyzed for this study included total dissolved iron, manganese, iodide, and silica. Iron concentrations ranged from 2,110 to 47,400 mg/L in CDF wells, compared to 1,600 to 2,800 mg/L in offsite wells (one sample at each well). Median iron concentrations were 37,500 and 43,200 mg/L in EW-11B and MW-11A, respectively, but ranged from 2,760 to 11,300 mg/L in all other CDF wells (fig. 18). Most iron likely occurs as ferrous iron (fig. 19). Manganese concentrations ranged from 304 to 1,980 mg/L in CDF wells and were 250 and 690 mg/L in two offsite wells (one sample at each well). The median manganese concentrations in CDF wells ranged from 312 to 1,240 mg/L. Iodide concentrations ranged from 0.007 to 0.086 mg/L in CDF wells; iodide was not

analyzed for in offsite wells. Silica concentrations ranged from 26.1 to 59.0 mg/L in CDF wells and ranged from 16.9 (estimated) to 38 mg/L in two offsite wells. In general, (1) total dissolved-iron concentrations were highest in wells with the lowest rate of pump fouling, and (2) manganese, iodide, and silica concentrations provided little diagnostic value (table 7).

The highest and lowest results for water-quality characteristics and the constituent concentrations were quantified for the four pumping regimes that existed during (and immediately before) sample collection (fig. 20). The water-quality data indicate that 45 and 55 percent of the highest values and concentrations at EW-14A and EW-4B, respectively, were detected during pumping regime 2. The nutrients ammonia, total nitrogen, and orthophosphate were highest in EW-4B and EW-14A during regime 2; nitrate and nitrite were mostly non-detects. The data indicate that 40 to 55 percent of the values and concentrations in EW-11B, MW-11A, and MW-14A were highest during pumping regime 3. Most cations and some onsite parameters were highest in these wells during pumping regime 3. The highest results for water-quality characteristics and constituent concentrations were measured in 62 percent of the samples from well MW-4A during pumping regime 4. The highest redox values were measured in all wells during pumping regimes 1 and 3.

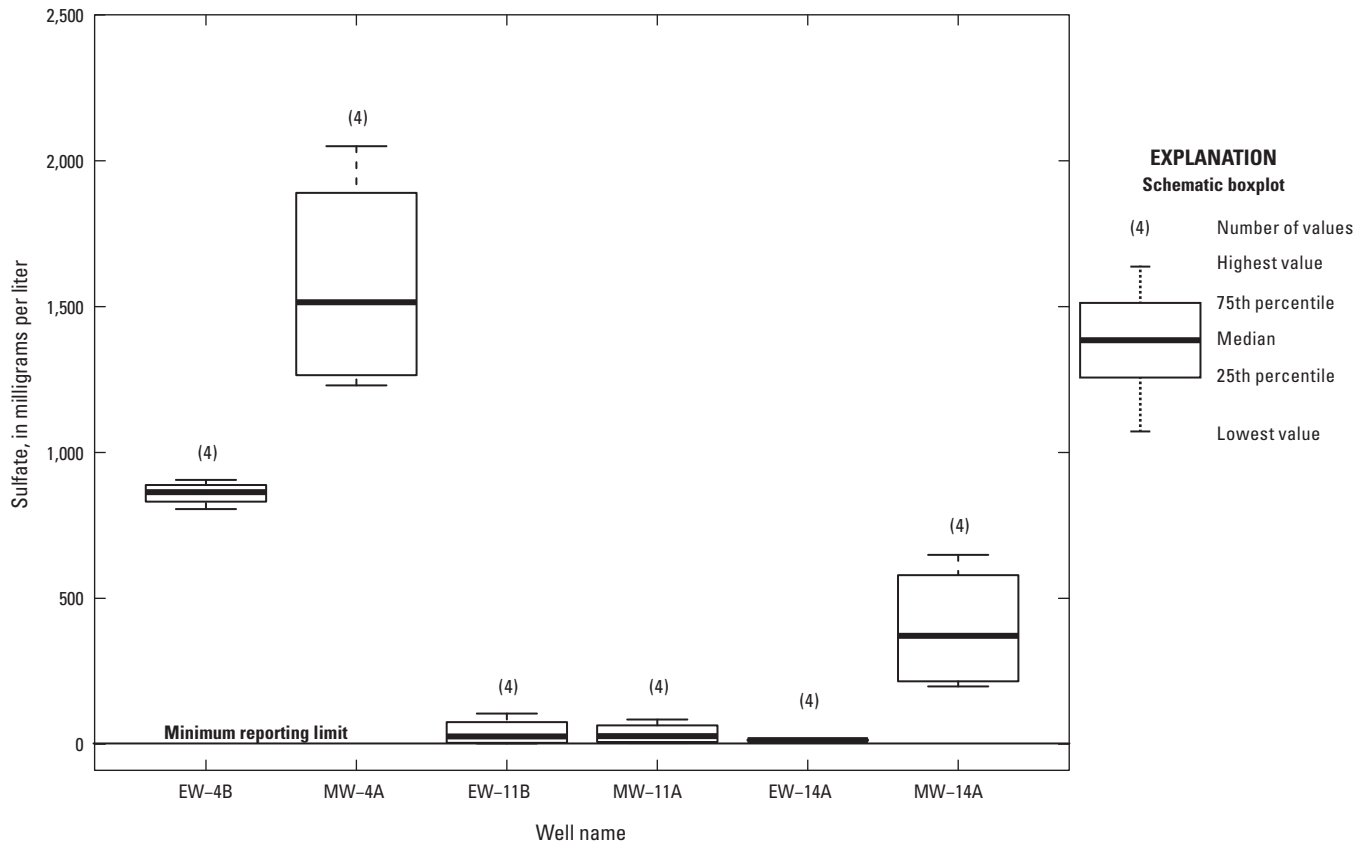
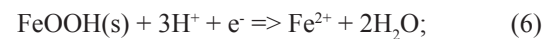
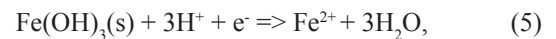


Figure 17. Distribution of sulfate concentrations in groundwater samples from selected wells at the confined disposal facility.

Nutrients analyzed for this study included ammonia, nitrate plus nitrite, nitrite, and orthophosphate. Ammonia concentrations (as equivalents of nitrogen) ranged from 1.45 to 7.21 mg/L in CDF wells, and concentrations were 0.87 and 8.5 mg/L in two offsite wells (one sample in each well). Median ammonia concentrations were 6.24 and 2.68 mg/L in EW-4B and MW-4A, respectively; 6.30 and 6.63 mg/L in EW-11B and MW-11A, respectively; and 6.50 and 3.20 mg/L in EW-14A and MW-14A, respectively. Measurements of nitrate plus nitrite (as equivalents of nitrogen) were less than the MRL in all CDF and was not analyzed at the offsite wells. For some wells, a lower MRL was used to analyze for nitrite than was used to analyze for nitrate plus nitrite (as equivalents of nitrogen). Nitrite concentrations ranged from less than 0.001 to 0.018 mg/L, with the highest concentration measured in wells EW-11B and MW-11A. The difference between total nitrogen concentrations and the sum of the reported nitrogenous analytes can be attributed to the presence of other unanalyzed nitrogen-containing compounds such as organic nitrogen. Orthophosphate concentrations in CDF wells ranged from less than 0.04 to 0.627 mg/L, compared to 0.12 and 0.26 mg/L in two offsite wells (one sample in each well). The median orthophosphate concentrations in extraction wells was generally greater than the median concentrations in monitoring

wells. In summary, (1) ammonia concentrations were higher in extraction wells EW-4B and EW-14A than in their corresponding monitoring wells, (2) nitrite concentrations were higher in EW-11B and MW-11A than other CDF wells, and (3) orthophosphate concentrations were higher in extraction wells than in monitoring wells.

The redox category identified for most water samples was anoxic or mixed (anoxic or oxic-anoxic) (table 9). The dominant redox processes included ferric iron (Fe^{3+}), ferric iron – sulfate ($\text{Fe}^{3+}\text{-SO}_4^{2-}$) and oxygen – ferric iron ($\text{O}_2\text{-Fe}^{3+}$) reduction. These processes correspond to the following respective electron acceptor half reactions:



Fe^{3+} and (or) SO_4^{2-} individual element half reactions; and



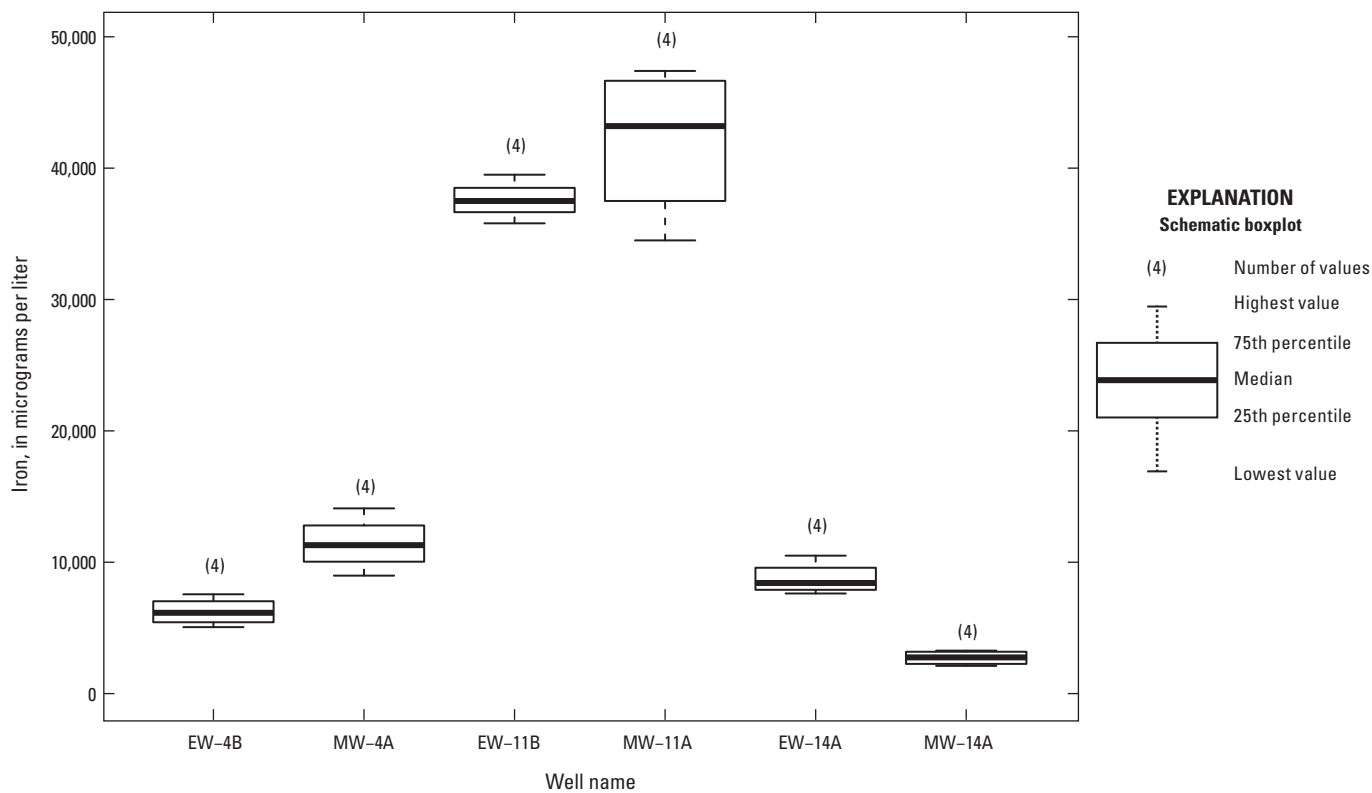


Figure 18. Distribution of iron concentrations in groundwater samples from selected wells at the confined disposal facility.

where

Fe(OH) ₃ (s)	is iron hydroxide (solid),
H ⁺	is hydrogen,
e ⁻	is an electron,
Fe ²⁺	is ferrous iron,
H ₂ O	is water,
FeOOH(s)	is iron oxyhydroxide (solid),
Fe ³⁺	is ferric iron, and
SO ₄ ²⁻	is sulfate.

The redox categories for EW-11B, MW-11A, and EW-14A wells were anoxic Fe³⁺ reduction. Samples from the other wells had variable redox categories and processes.

Dissolved Gases

Dissolved gas concentrations in groundwater samples from extraction and monitoring wells were also used to indicate oxidation-reduction conditions. Extraction wells at the site have been subjected to recurring drawdown of groundwater levels during operation of the gradient control system. Water from extraction wells was considered in the dissolved gas sampling to represent possible mixing of water affected by recent infiltration nearer the water table. Monitoring wells, in comparison, were not regularly pumped during system operation. Groundwater from monitoring wells was considered

in these samples to represent dissolved gas concentrations in the aquifer.

Sampling and analysis methods for dissolved gas concentrations were reproducible between most environmental and replicate samples analyzed for methane, carbon dioxide, nitrogen, and argon; as indicated by RPD statistics for paired samples that were less than 10 percent (table 10). Counts of samples with reproducible concentrations between paired environmental and replicate samples were 26 paired samples analyzed for methane, 22 of 26 paired samples analyzed for carbon dioxide, 23 of 26 paired samples analyzed for argon, and 24 of 26 paired samples analyzed for nitrogen (table 10). Analyses of dissolved oxygen were the least reproducible in these samples, with 16 of 26 paired environmental and replicate samples having RPD statistics less than 10 percent (table 10).

Dissolved gases were identified as having estimated concentrations in environmental water samples when the RPD statistic was greater than 10 percent when compared with the replicate sample (table 10). Samples with estimated concentrations of dissolved gases were used for interpretations in this report because of their overall similarity in magnitude with samples collected from the same well or other wells at the CDF. Dissolved oxygen analyses had the greatest frequency of estimated concentrations, possibly because of the small dissolved oxygen concentrations (0.0 to 0.19 mg/L) in all water samples (table 10). Leakage of air during laboratory

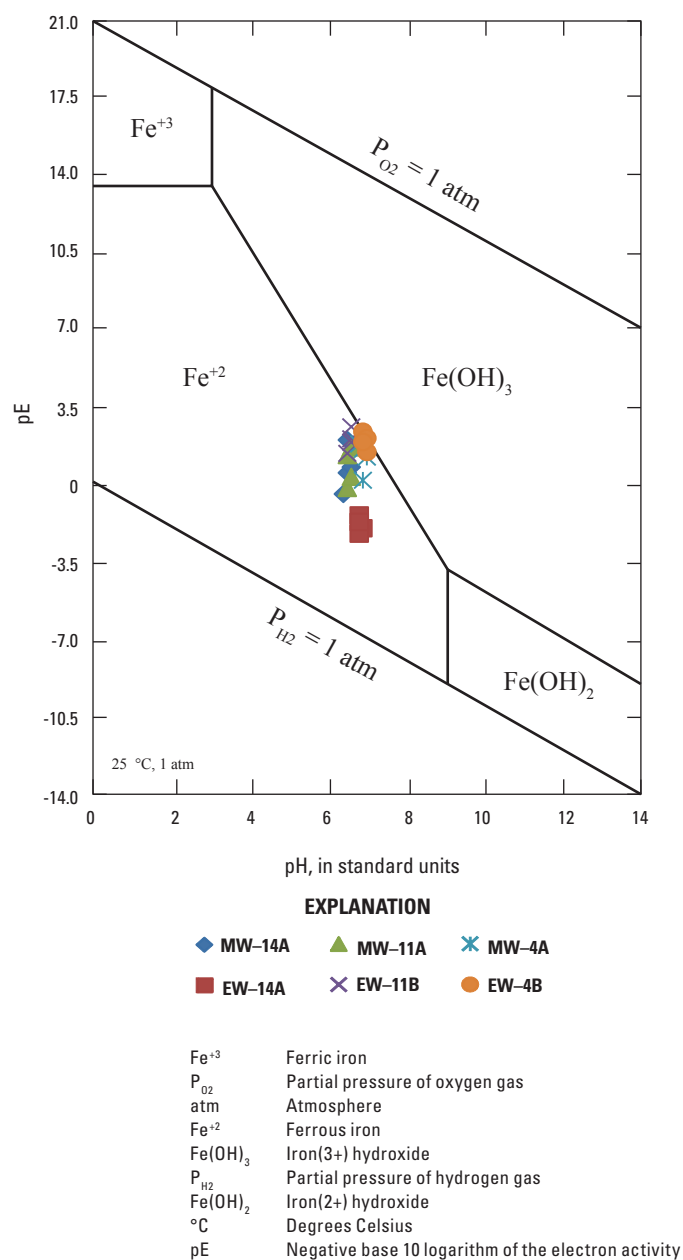


Figure 19. Eh-pH phase diagram showing iron stability fields and data from the confined disposal facility.

analysis into the replicate sample from well MW-4A collected on October 9, 2014, was interpreted as the source of the large RPD statistic difference between paired samples. This interpretation was based on the relative enrichment of oxygen, argon, and nitrogen in the replicate sample. Carbon dioxide, oxygen, argon, and nitrogen concentrations in the paired environmental sample from well MW-4A on October 9, 2014, were identified as estimated concentrations but were used for interpretations in this report because of their overall similarity

in magnitude with samples collected from other wells at the site. Carbon dioxide concentrations in samples from EW-4B on September 11, 2014; EW-11B on October 21, 2014; and MW-14A on October 22, 2014, were also identified as estimated concentrations because of RPD statistic differences greater than 10 percent (table 10).

Dissolved argon concentrations in groundwater were depleted relative to hypothetical concentrations in equilibrium with the atmosphere at temperature and altitude conditions similar to those at the site in all samples except from MW-14A on October 22, 2014 (table 10). Argon concentrations in environmental samples ranged from 0.06 mg/L in a sample from MW-11A to 0.57 mg/L in a sample from MW-14A. In comparison, hypothetical argon concentrations in water in equilibrium with the atmosphere at temperature and altitude conditions similar to those at the site ranged from 0.51 mg/L, for an average monthly July temperature of about 23 °C, to 0.79 mg/L, for an average monthly March temperature of about 3 °C (table 10). These monthly average temperatures were from a weather station at a site about 20.5 miles east of the CDF site (Arguez and others, 2010). The only groundwater samples with argon concentrations in the range that was similar to the hypothetical air-water equilibrium included two of the four samples from monitoring well MW-14A. All other groundwater samples had smaller argon concentrations than this range and were interpreted as having lost argon and other gases because of physical outgassing.

The depletion of argon concentrations in groundwater at the CDF is consistent with a pattern of argon loss from groundwater and unsaturated zone gas described in another study that is related to processes that biotransform and degrade residual hydrocarbons in the aquifer and that generate methane and carbon dioxide. The depletion of argon in groundwater is similar to a pattern described in a study of a crude oil release near Bemidji, Minnesota. (Amos and others, 2005). In that study, oxygen was consumed and methane and carbon dioxide were generated by microbial transformations in anoxic zones above and below the water table. Generation of methane and carbon dioxide can cause other dissolved gases, including argon, to be stripped from groundwater into the unsaturated zone and from the unsaturated zone toward the atmosphere (Amos and others, 2005; Ng and others, 2015). Feasible pathways for argon and other dissolved gas loss from groundwater at the CDF site include fluxes toward the atmosphere through the unsaturated zone, at air-water interfaces in extraction wells, and through gas leakage into subsurface plumbing. Residual hydrocarbons were visually identified in unconsolidated deposits logged in subsurface borings previously installed at the CDF site. In addition, groundwater sampling for this study identified concentrations of organic carbon in groundwater that were considerably greater than the median concentration of 7.1 mg/L in groundwater from the Calumet aquifer (Duweliuss and others, 1996), a possible indication of residues in groundwater from hydrocarbon degradation. The large methane and carbon dioxide concentrations in dissolved gas results from extraction and monitoring wells at the CDF

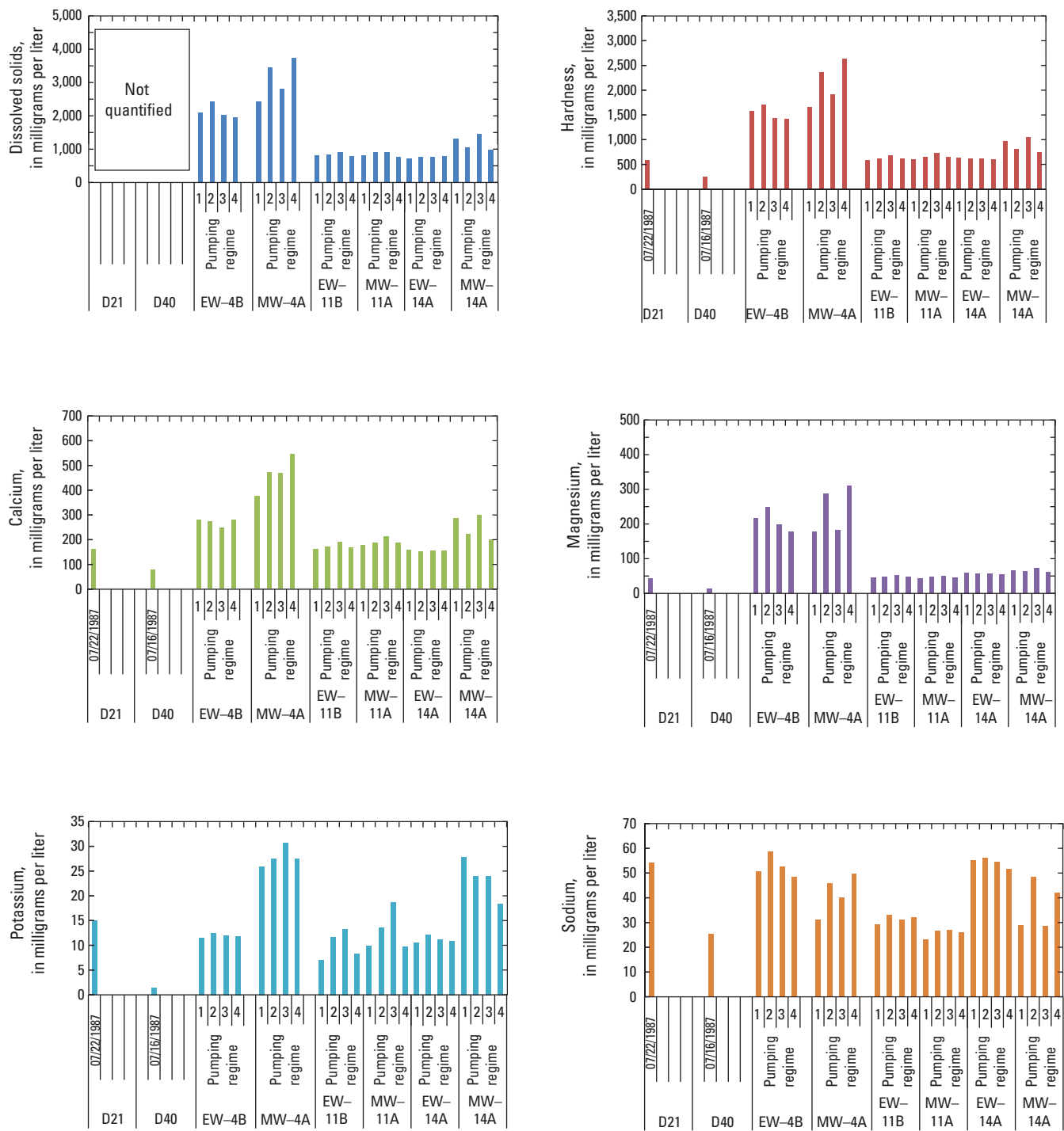


Figure 20. Concentrations of major ions through time during four pumping regimes—regime 1, September 9–11, 2014 (normal operating conditions); regime 2, October 7–9, 2014 (after pump was not operating for at least 8 hours); regime 3, October 20–23, 2014 (after pumping had resumed for 7 days); and regime 4, November 3–6, 2014 (after pumping had resumed for 14 days).

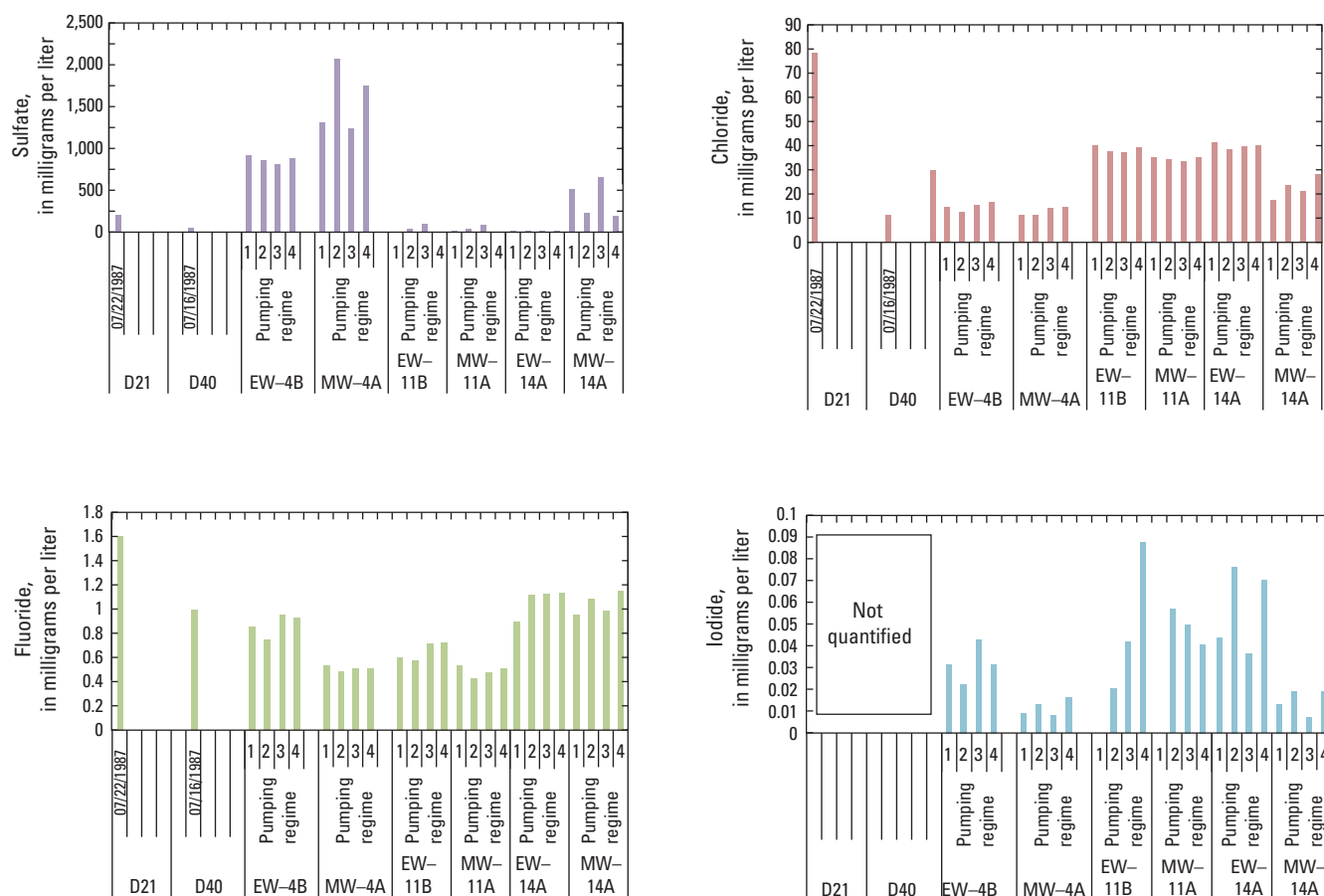


Figure 20. Concentrations of major ions through time during four pumping regimes—regime 1, September 9–11, 2014 (normal operating conditions); regime 2, October 7–9, 2014 (after pump was not operating for at least 8 hours); regime 3, October 20–23, 2014 (after pumping had resumed for 7 days); and regime 4, November 3–6, 2014 (after pumping had resumed for 14 days).—Continued

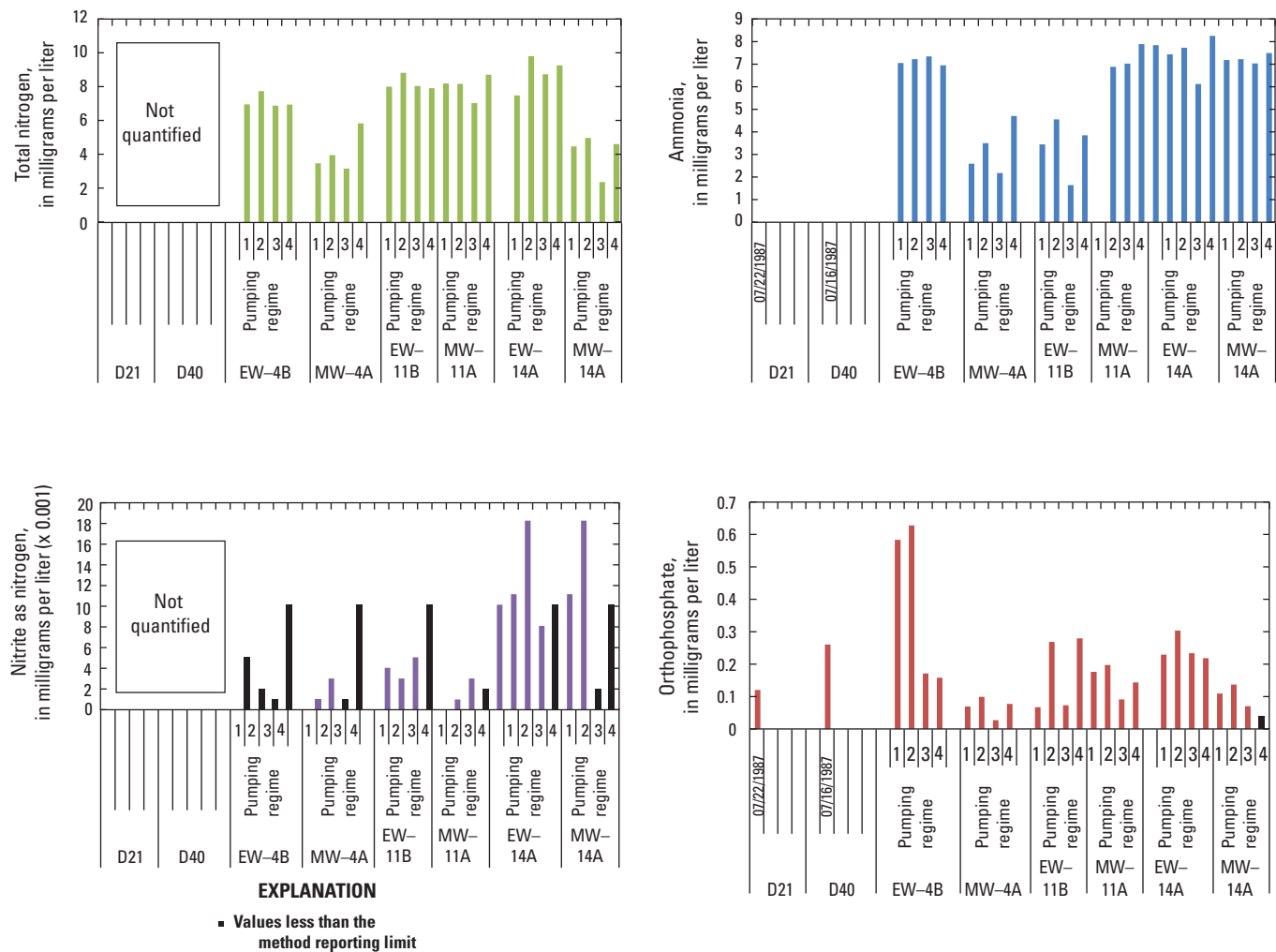


Figure 20. Concentrations of major ions through time during four pumping regimes—regime 1, September 9–11, 2014 (normal operating conditions); regime 2, October 7–9, 2014 (after pump was not operating for at least 8 hours); regime 3, October 20–23, 2014 (after pumping had resumed for 7 days); and regime 4, November 3–6, 2014 (after pumping had resumed for 14 days).—Continued

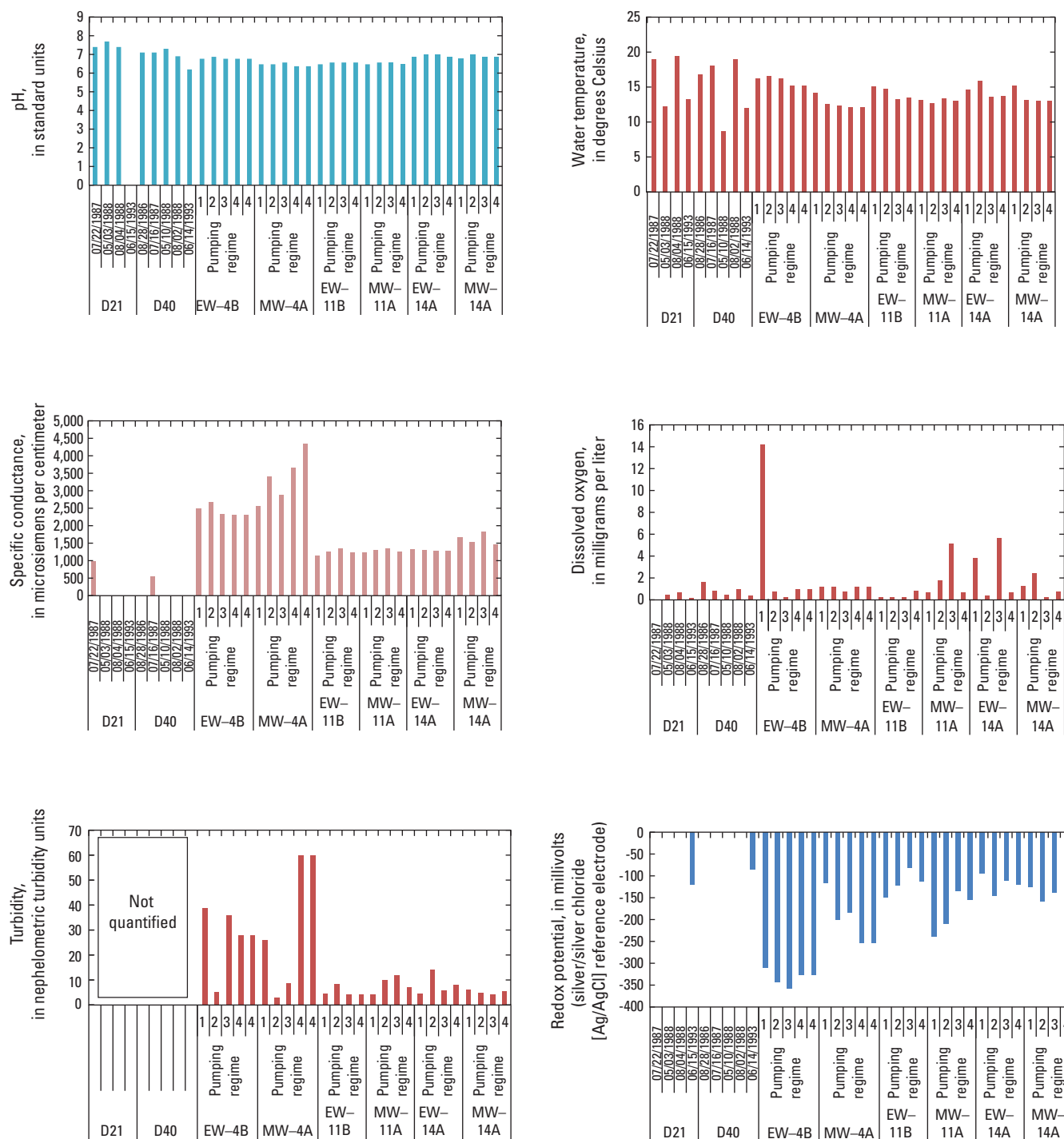


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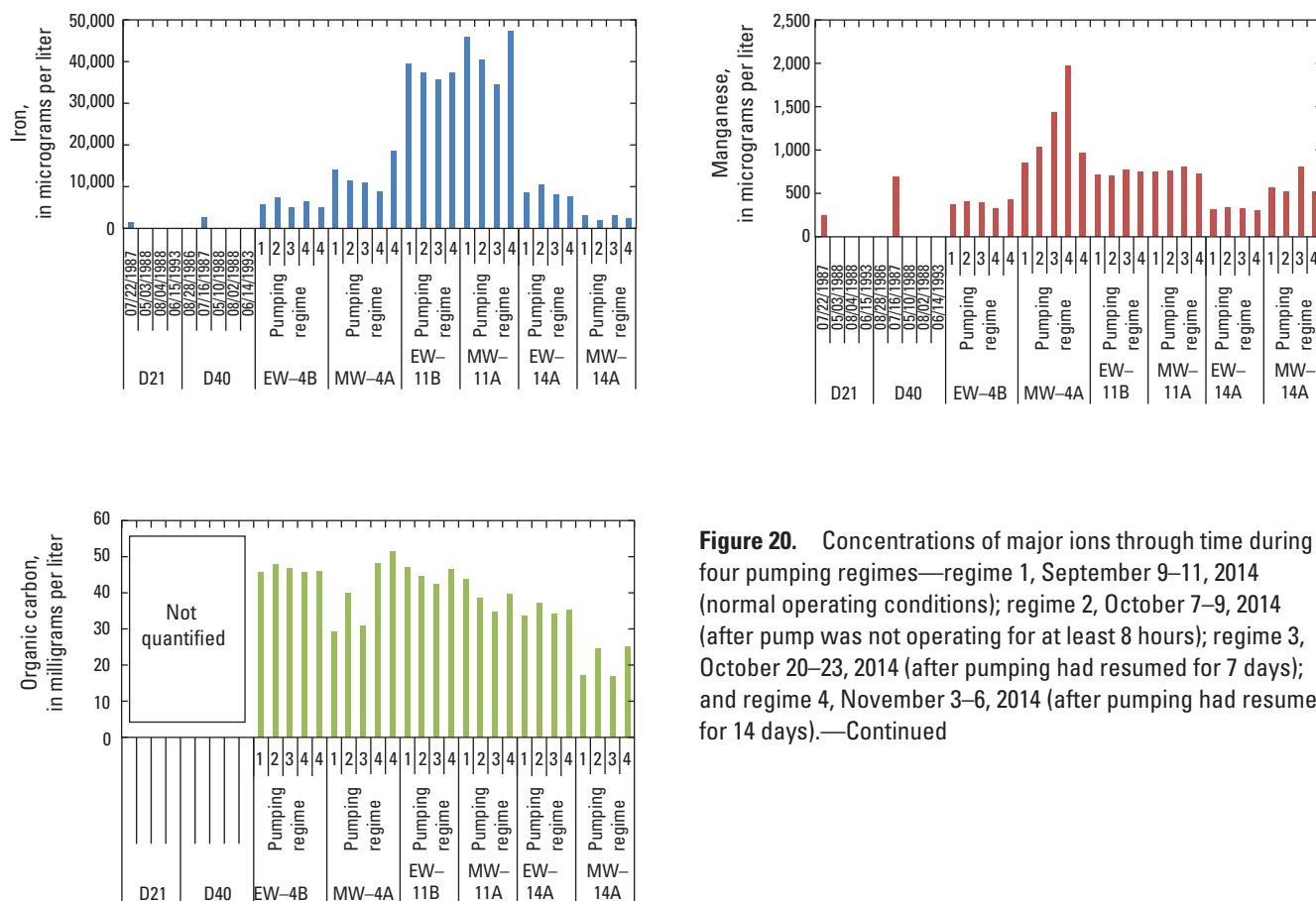


Figure 20. Concentrations of major ions through time during four pumping regimes—regime 1, September 9–11, 2014 (normal operating conditions); regime 2, October 7–9, 2014 (after pump was not operating for at least 8 hours); regime 3, October 20–23, 2014 (after pumping had resumed for 7 days); and regime 4, November 3–6, 2014 (after pumping had resumed for 14 days).—Continued

(table 10) are consistent with their production in the subsurface by anaerobic biotransformation of hydrocarbon compounds (Amos and others, 2005). Carbon dioxide is generated from aerobic hydrocarbon oxidation and as a product of hydrocarbon degradation and methane oxidation by anaerobic, microbially mediated ferric iron reduction (Baedecker and others, 1993).

Groundwater samples analyzed for dissolved gases from the extraction and monitoring wells were substantially anoxic. Dissolved oxygen concentrations in water from the extraction wells ranged from less than 0.001 in EW-11B to 0.096 mg/L in EW-14A. Field measured dissolved oxygen concentrations (table 7) were nearly always greater than laboratory analyzed dissolved oxygen values (table 10), except for two samples from MW-14A in October and November 2014. This difference most likely indicates that some dissolved oxygen was consumed in laboratory analyzed samples after collection.

Methane concentrations in groundwater samples from extraction wells sampled by this study at the CDF ranged from 24.1 to 36.2 mg/L and from monitoring wells ranged from 5.4 to 36.6 (table 10). Methane concentrations in groundwater from the CDF samples were similar to or greater than those reported for an anoxic plume of groundwater (about

10–20 mg/L) in 1998, 2002, and 2003 beneath a crude oil spill at Bemidji, Minn. (Cozzarelli and others, 1999; Amos and others, 2005). Carbon dioxide concentrations in groundwater samples from extraction wells sampled by this study at the CDF ranged from 77 mg/L to an estimated concentration of 260 mg/L and from monitoring wells ranged from an estimated concentration of 52 to 330 mg/L (table 10). Groundwater with the largest carbon dioxide concentrations (155–330 mg/L) also had relatively lower field measured pH values (6.4–6.6) than did water with carbon dioxide concentrations of less than about 140 mg/L (pH of 6.8–7.0; tables 7 and 10). In comparison, Baedecker and others (1993) described a dissolved carbon dioxide concentration of about 218 mg/L and a methane concentration of about 21.8 mg/L in anoxic groundwater beneath a crude oil spill in 1987, and Amos and others (2005) reported dissolved carbon dioxide concentrations of about 100 mg/L in the same groundwater plume in about 2002.

The mole ratios of methane to carbon dioxide were relatively larger in extraction wells EW-4B and EW-14A than in corresponding monitoring wells MW-4A and MW-14A (September 9, 2014, and October 21, 2014, samples; table 10). Water samples from extraction well EW-11B and monitoring wells MW-4A, MW-11A, and MW-14A (October 8, 2014,

Table 9. Redox category and process as computed for groundwater samples.[USACE, U.S. Army Corps of Engineers; CDF, confined disposal facility; E, east; Fe(III), ferric iron; SO₄, sulfate; O₂, oxygen]

Well name	Sample collection date	General redox category	Redox process
USACE CDF extraction well EW-4B, near E Chicago, Indiana	September 11, 2014	Mixed (anoxic)	Fe(III)–SO ₄
USACE CDF extraction well EW-4B, near E Chicago, Indiana	October 9, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-4B, near E Chicago, Indiana	October 22, 2014	Mixed (anoxic)	Fe(III)–SO ₄
USACE CDF extraction well EW-4B, near E Chicago, Indiana	November 5, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-4B, near E Chicago, Indiana	November 5, 2014	Mixed (anoxic)	Fe(III)–SO ₄
USACE CDF monitoring well MW-4A, near E Chicago, Indiana	September 10, 2014	Mixed (oxic-anoxic)	O ₂ –Fe(III)
USACE CDF monitoring well MW-4A, near E Chicago, Indiana	October 9, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-4A, near E Chicago, Indiana	October 23, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-4A, near E Chicago, Indiana	November 6, 2014	Mixed (oxic-anoxic)	O ₂ –Fe(III)
USACE CDF monitoring well MW-4A, near E Chicago, Indiana	November 6, 2014	Mixed (oxic-anoxic)	O ₂ –Fe(III)
USACE CDF extraction well EW-11B, near E Chicago, Indiana	September 9, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-11B, near E Chicago, Indiana	October 7, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-11B, near E Chicago, Indiana	October 21, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-11B, near E Chicago, Indiana	November 4, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-11A, near E Chicago, Indiana	September 9, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-11A, near E Chicago, Indiana	October 7, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-11A, near E Chicago, Indiana	October 20, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-11A, near E Chicago, Indiana	November 3, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-14A, near E Chicago, Indiana	September 11, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-14A, near E Chicago, Indiana	October 8, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-14A, near E Chicago, Indiana	October 21, 2014	Anoxic	Fe(III)
USACE CDF extraction well EW-14A, near E Chicago, Indiana	November 4, 2014	Anoxic	Fe(III)
USACE CDF monitoring well MW-14A, near E Chicago, Indiana	September 10, 2014	Mixed (oxic-anoxic)	O ₂ –Fe(III)
USACE CDF monitoring well MW-14A, near E Chicago, Indiana	October 8, 2014	Mixed (anoxic)	Fe(III)–SO ₄
USACE CDF monitoring well MW-14A, near E Chicago, Indiana	October 22, 2014	Mixed (anoxic)	Fe(III)–SO ₄
USACE CDF monitoring well MW-14A, near E Chicago, Indiana	November 5, 2014	Mixed (anoxic)	Fe(III)–SO ₄

Table 10. Laboratory measured concentrations of dissolved gases in environmental and replicate samples of groundwater from the confined disposal facility, quality-assurance statistics, and hypothetical concentrations of dissolved gas in equilibrium with the atmosphere.

[Blue colors indicate extraction well samples and orange colors indicate monitoring well samples. Darker-blue and darker-orange colors are for lines with data from environmental samples used to interpret groundwater conditions. Lighter-blue and lighter-orange colors are for replicate samples used for quality assurance. USGS, U.S. Geological Survey; mm/dd/yy, month/day/year; h:mm, hours and minutes; °C, degrees Celsius; mg/L, milligrams per liter; Q, estimated concentration; --, not computed; RPD, relative percent difference; na, not applicable]

Well name	USGS station identifier	Date sampled (mm/dd/yy)	Time sampled (hhmm)	Field temperature at collection (°C)	Sample or computation type	Methane (mg/L)	Carbon dioxide (mg/L)	Oxygen (mg/L)	Nitrogen (mg/L)	Argon (mg/L)	Methane/carbon dioxide mole ratio	Comments
EW-4B	413907087291801	09/11/2014	1410	16.32	Environmental	27.8	Q 139	0.030	3.4	0.18	--	Argon depletion from outgassing
					Replicate	27.4	85	0.031	3.7	0.18	0.88	Argon depletion from outgassing
					RPD	1.4	48	3.3	8.5	0	--	na
EW-4B	413907087291801	10/09/2014	1410	16.59	Environmental	27.0	101	Q 0.030	3.5	0.18	0.73	Argon depletion from outgassing
					Replicate	27.1	104	0.027	3.5	0.18	0.71	Argon depletion from outgassing
					RPD	0.4	2.9	11	0	0	--	na
EW-4B	413907087291801	10/22/2014	1353	16.28	Environmental	28.8	93	0.029	3.3	0.17	0.85	Argon depletion from outgassing
					Replicate	28.6	94	0.031	3.6	0.17	0.83	Argon depletion from outgassing
					RPD	0.7	1.1	6.7	8.7	0	--	na
EW-4B	413907087291801	11/05/2014	1230	14.26	Environmental	27.5	90	0.034	3.8	0.19	0.84	Argon depletion from outgassing
					Replicate	27.4	88	0.034	4.0	0.19	0.85	Argon depletion from outgassing
					RPD	0.4	2.2	0.0	5.1	0	--	na
EW-4B	413907087291801	11/05/2014	1345	15.27	Environmental	28.0	96	Q 0.029	3.2	Q 0.17	0.80	Argon depletion from outgassing
					Replicate	28.6	99	0.026	3.3	0.11	0.79	Argon depletion from outgassing
					RPD	2.1	3.1	11	3.1	45	--	na
MW-4A	413908087291901	09/10/2014	1600	14.24	Environmental	9.5	155	Q 0.13	9.5	0.37	0.17	Argon depletion from outgassing
					Replicate	9.8	158	0.092	9.4	0.37	0.17	Argon depletion from outgassing
					RPD	3.1	1.9	34	1.1	0	--	na

Table 10. Laboratory measured concentrations of dissolved gases in environmental and replicate samples of groundwater from the confined disposal facility, quality-assurance statistics, and hypothetical concentrations of dissolved gas in equilibrium with the atmosphere.—Continued

[Blue colors indicate extraction well samples and orange colors indicate monitoring well samples. Darker-blue and darker-orange colors are for lines with data from environmental samples used to interpret groundwater conditions. Lighter-blue and lighter-orange colors are for replicate samples used for quality assurance. USGS, U.S. Geological Survey; mm/dd/yy, month/day/year; hhmm, hours and minutes; °C, degrees Celsius; mg/L, milligrams per liter; Q, estimated concentration; --, not computed; RPD, relative percent difference; na, not applicable]

Well name	USGS station identifier	Date sampled (mm/dd/yy)	Time sampled (hhmm)	Field temperature at collection (°C)	Sample or computation type	Methane (mg/L)	Carbon dioxide (mg/L)	Oxygen (mg/L)	Nitrogen (mg/L)	Argon (mg/L)	Methane/carbon dioxide mole ratio	Comments
MW-4A	413908087291901	10/09/2014	0915	12.57	Environmental	14.8	Q 203	Q 0.064	Q 6.1	Q 0.27	--	Argon depletion from outgassing
					Replicate	13.5	240	8.22	47	1.1	0.15	Leak on preparation of sample for analysis
					RPD	9.2	17	197	154	121	--	na
MW-4A	413908087291901	10/23/2014	0935	12.43	Environmental	12.3	219	Q 0.088	8.4	0.35	0.15	Argon depletion from outgassing
					Replicate	12.5	221	0.076	8.3	0.35	0.16	Argon depletion from outgassing
					RPD	1.6	0.9	15	1.2	0	--	na
MW-4A	413908087291901	11/06/2014	0848	11.85	Environmental	13.9	224	Q 0.070	7.0	0.32	0.17	Argon depletion from outgassing
					Replicate	14.7	233	0.063	6.6	0.29	0.17	Argon depletion from outgassing
					RPD	5.6	3.9	11	5.9	9.8	--	na
MW-4A	413908087291901	11/06/2014	0940	12.24	Environmental	16.6	330	Q 0.048	4.5	0.22	0.14	Argon depletion from outgassing
					Replicate	16.8	327	0.043	4.8	0.23	0.14	Argon depletion from outgassing
					RPD	1.2	0.9	11	6.5	4.4	--	na
EW-11B	413921087290103	09/08/2014	1400	15.22	Environmental	36.2	214	<0.001	1.2	0.09	0.46	Argon depletion from outgassing
					Replicate	35.0	201	<0.001	1.3	0.09	0.48	Argon depletion from outgassing
					RPD	3.4	6.3	--	8.0	0	--	na
EW-11B	413921087290103	10/07/2014	1245	14.83	Environmental	31.9	192	<0.001	1.5	0.10	0.46	Argon depletion from outgassing
					Replicate	33.8	204	<0.001	1.6	0.11	0.45	Argon depletion from outgassing
					RPD	5.8	6.1	--	6.5	9.5	--	na

Table 10. Laboratory measured concentrations of dissolved gases in environmental and replicate samples of groundwater from the confined disposal facility, quality-assurance statistics, and hypothetical concentrations of dissolved gas in equilibrium with the atmosphere.—Continued

[Blue colors indicate extraction well samples and orange colors indicate monitoring well samples. Darker-blue and darker-orange colors are for lines with data from environmental samples used to interpret groundwater conditions. Lighter-blue and lighter-orange colors are for replicate samples used for quality assurance. USGS, U.S. Geological Survey; mm/dd/yy, month/day/year; hhmm, hours and minutes; °C, degrees Celsius; mg/L, milligrams per liter; Q, estimated concentration; --, not computed; RPD, relative percent difference; na, not applicable]

Well name	USGS station identifier	Date sampled (mm/dd/yy)	Time sampled (hhmm)	Field temperature at collection (°C)	Sample or computation type	Methane (mg/L)	Carbon dioxide (mg/L)	Oxygen (mg/L)	Nitrogen (mg/L)	Argon (mg/L)	Methane/carbon dioxide mole ratio	Comments
EW-11B	413921087290103	10/21/2014	0925	13.32	Environmental	31.6	Q 260	0.012	1.4	0.12	0.33	Argon depletion from outgassing
					Replicate	31.7	197	0.012	1.4	0.11	0.44	Argon depletion from outgassing
					RPD	0.3	28	0	0	8.7	--	na
EW-11B	413921087290103	11/04/2014	0930	13.46	Environmental	32.8	207	Q 0.011	1.3	0.10	0.43	Argon depletion from outgassing
					Replicate	32.4	212	0.015	1.3	0.10	0.42	Argon depletion from outgassing
					RPD	1.2	2.4	31	0	0	--	na
MW-11A	413921087290101	09/09/2014	1225	13.22	Environmental	35.9	230	<0.001	Q 1.0	Q 0.07	0.43	Argon depletion from outgassing
					Replicate	35.9	238	<0.001	0.9	0.06	0.41	Argon depletion from outgassing
					RPD	0.0	3.4	--	11	15	--	na
MW-11A	413921087290101	10/07/2014	0920	12.68	Environmental	36.6	230	<0.001	1.1	0.07	0.44	Argon depletion from outgassing
					Replicate	37.5	232	<0.001	1.0	0.07	0.44	Argon depletion from outgassing
					RPD	2.4	0.9	--	9.5	0	--	na
MW-11A	413921087290101	10/20/2014	1310	13.44	Environmental	35.6	225	<0.001	1.7	0.10	0.43	Argon depletion from outgassing
					Replicate	36.1	231	<0.001	1.7	0.10	0.43	Argon depletion from outgassing
					RPD	1.4	2.6	--	0	0	--	na
MW-11A	413921087290101	11/03/2014	1230	13.08	Environmental	35.2	241	<0.001	0.9	0.06	0.40	Argon depletion from outgassing
					Replicate	35.5	242	<0.001	0.9	0.06	0.40	Argon depletion from outgassing
					RPD	0.8	0.4	--	0	0	--	na

Table 10. Laboratory measured concentrations of dissolved gases in environmental and replicate samples of groundwater from the confined disposal facility, quality-assurance statistics, and hypothetical concentrations of dissolved gas in equilibrium with the atmosphere.—Continued

[Blue colors indicate extraction well samples and orange colors indicate monitoring well samples. Darker-blue and darker-orange colors are for lines with data from environmental samples used to interpret groundwater conditions. Lighter-blue and lighter-orange colors are for replicate samples used for quality assurance. USGS, U.S. Geological Survey; mm/dd/yy, month/day/year; hhmm, hours and minutes; °C, degrees Celsius; mg/L, milligrams per liter; Q, estimated concentration; --, not computed; RPD, relative percent difference; na, not applicable]

Well name	USGS station identifier	Date sampled (mm/dd/yy)	Time sampled (hhmm)	Field temperature at collection (°C)	Sample or computation type	Methane (mg/L)	Carbon dioxide (mg/L)	Oxygen (mg/L)	Nitrogen (mg/L)	Argon (mg/L)	Methane/carbon dioxide mole ratio	Comments
EW-14A	413911087285201	09/11/2014	1110	14.66	Environmental	24.1	81	Q 0.087	9.0	0.46	0.82	Argon depletion from outgassing
					Replicate	23.4	79	0.11	9.0	0.45	0.81	Argon depletion from outgassing
					RPD	2.9	2.5	23	0	2.2	--	na
EW-14A	413911087285201	10/08/2014	1340	15.92	Environmental	25.7	77	Q 0.091	8.2	0.44	0.92	Argon depletion from outgassing
					Replicate	25.7	79	0.11	8.5	0.45	0.89	Argon depletion from outgassing
					RPD	0.0	2.6	19	3.6	2.2	--	na
EW-14A	413911087285201	10/21/2014	1235	13.62	Environmental	25.2	83	0.096	8.7	0.45	0.83	Argon depletion from outgassing
					Replicate	25.4	82	0.094	8.8	0.45	0.85	Argon depletion from outgassing
					RPD	0.8	1.2	2.1	1.1	0	--	na
EW-14A	413911087285201	11/04/2014	1300	13.80	Environmental	25.7	82	0.086	9.1	0.46	0.86	Argon depletion from outgassing
					Replicate	25.8	84	0.086	8.8	0.45	0.84	Argon depletion from outgassing
					RPD	0.4	2.4	0	3.4	2.2	--	na
MW-14A	413909087285301	09/10/2014	1235	15.27	Environmental	5.4	61	0.18	13.7	0.51	0.24	Argon depletion from outgassing
					Replicate	5.4	60	0.17	13.9	0.52	0.25	Argon depletion from outgassing
					RPD	0.0	1.7	5.7	1.4	1.9	--	na
MW-14A	413909087285301	10/08/2014	0925	13.17	Environmental	19.3	65	0.069	8.8	0.38	0.81	Argon depletion from outgassing
					Replicate	18.3	66	0.075	8.9	0.38	0.76	Argon depletion from outgassing
					RPD	5.3	1.5	8.3	1.1	0	--	na

Table 10. Laboratory measured concentrations of dissolved gases in environmental and replicate samples of groundwater from the confined disposal facility, quality-assurance statistics, and hypothetical concentrations of dissolved gas in equilibrium with the atmosphere.—Continued

[Blue colors indicate extraction well samples and orange colors indicate monitoring well samples. Darker-blue and darker-orange colors are for lines with data from environmental samples used to interpret groundwater conditions. Lighter-blue and lighter-orange colors are for replicate samples used for quality assurance. USGS, U.S. Geological Survey; mm/dd/yy, month/day/year; hhmm, hours and minutes; °C, degrees Celsius; mg/L, milligrams per liter; Q, estimated concentration; —, not computed; RPD, relative percent difference; na, not applicable]

Well name	USGS station identifier	Date sampled (mm/dd/yy)	Time sampled (hhmm)	Field temperature at collection (°C)	Sample or computation type	Methane (mg/L)	Carbon dioxide (mg/L)	Oxygen (mg/L)	Nitrogen (mg/L)	Argon (mg/L)	Methane/carbon dioxide mole ratio	Comments
MW-14A	413909087285301	10/22/2014	0955	13.10	Environmental	6.2	Q 52	0.19	14.6	0.57	0.33	None
					Replicate	6.7	84	0.18	14.2	0.56	0.22	None
					RPD	7.8	47	5.4	2.8	1.8	--	na
MW-14A	413909087285301	11/05/2014	0905	13.08	Environmental	18.1	65	0.078	8.4	0.38	0.76	Argon depletion from outgassing
					Replicate	19.9	69	0.080	8.7	0.39	0.79	Argon depletion from outgassing
					RPD	9.5	6.0	2.5	3.5	2.6	--	na
Hypothetical dissolved gas concentrations in equilibrium with the atmosphere at temperature, altitude, and dissolved solids conditions similar to those at the site.												
Average monthly March temperature of about 3 °C (1981–2010 normals), water table altitude of 578 feet above the National Geodetic Vertical Datum of 1929 and dissolved solids concentration of 2,000 mg/L						0.000	1.1	13.0	20.6	0.79	0.000	Computed concentrations
Average monthly July temperature of about 23 °C (1981–2010 normals) and water table altitude of 578 feet above the National Geodetic Vertical Datum of 1929 and dissolved solids concentration of 2,000 mg/L						0.000	0.6	8.3	13.6	0.51	0.000	Computed concentrations

and October 21, 2104, samples) had relatively smaller ratios of methane to carbon dioxide and in all but two cases, had lower pH values (tables 7 and 10). The larger ratios of methane to carbon dioxide in samples from extraction wells EW-4B and EW-14A may indicate the effect of relatively larger drawdowns on dissolved gas composition than in samples from nearby monitoring wells. Extraction wells produce a relatively larger fraction of groundwater from closer to the water table than the monitoring wells. Hydrocarbon residues were described in core samples of aquifer material at or near the water table in borings near EW-4B and in EW-14A (U.S. Army Corps of Engineers, 2008a). The water table was described in Amos and others (2005) as the zone where hydrocarbon oxidation and methanogens would be most active. Methane to carbon dioxide ratios also could be increased by precipitation of carbonate minerals in the aquifer.

The lack of dissolved oxygen in groundwater at the site is consistent with consumptive loss of dissolved oxygen by oxidation-reduction processes. Groundwater samples analyzed for dissolved gases from the extraction and monitoring wells were substantially anoxic. Dissolved oxygen concentrations in water from extraction wells ranged from less than 0.001 in EW-11B to 0.096 mg/L in EW-14A.

Dissolved gas results from groundwater samples at the CDF indicate oxidation-reduction processes in the aquifer that can feasibly contribute dissolved iron and other products from hydrocarbon degradation to groundwater produced by extraction wells and to precipitates and solids that accumulate on and impair pump operation. The large concentrations of carbon dioxide and methane, the depleted argon concentrations relative to atmospheric values and the relatively large concentrations of dissolved iron in groundwater samples from the field site are consistent with an iron-reduction mediated hydrocarbon oxidation model that was described for a different crude oil plume by Baedecker and others (1993). Dissolution of ferric iron minerals from the aquifer matrix was considered to be the most likely source of iron reacted in the hydrocarbon degradation model proposed by Ng and others (2015) and Baedecker and others (1993). Simulations in that model also postulated that the aquifer was an open system from which carbon dioxide and methane outgassed from the water table and through the unsaturated zone to the atmosphere. The geochemical model of Ng and others (2015) also postulated the release of soluble ferrous iron and carbon dioxide into groundwater and further proposed that available iron in solution could also decrease through precipitation of ferrous carbonate minerals, such as siderite. Other studies have indicated that the solubility of ferrous iron released through reduction of ferric iron precipitates can be enhanced by forming complexes with organic substances (Jobin and Ghosh, 1972; Rose and Waite, 2003; Munter and others, 2005) such as those indicated by total organic carbon present in groundwater analyzed by this study (table 7). The abundant methane, carbon dioxide, and iron concentrations in groundwater samples and iron and carbonate minerals in solids are also consistent

with a model of microbial mediated oxidation of hydrocarbon residues through reduction of iron in aquifer minerals.

Microbiological Activity

Microbiological activity reaction tests indicated that bacteria were present in all samples (figs. 21A–21K). Additionally, most bacteria are capable of producing slime-like growths (Droycon Bioconcepts, Inc., 2006). As a result, identification of bacteria present in the individual CDF wells was not indicative of a particular type responsible for biofouling. Concentrations of bacteria subtypes varied between wells and the four pumping regimes investigated by this study. Historical microbiological activity data were not available for offsite wells.

Heterotrophic Aerobic Bacteria

Populations of heterotrophic aerobic bacteria were measurable in all samples and indicated no preference for certain well sites (table 11, fig. 21A). Populations of heterotrophic aerobic bacteria in groundwater collected during the first two pumping regimes were about an order of magnitude higher than most samples collected thereafter. The observed reaction patterns indicated that aerobic bacteria were dominant with some facultative anaerobes present (Droycon Bioconcepts, Inc., 2004). Given the anoxic or mixed anoxic conditions at the site, the presence of heterotrophic aerobic bacteria may be due to atmospheric or equipment exposure. The equipment blanks using sterile buffer water also tested positive for heterotrophic aerobic bacteria.

Slime-Forming Bacteria

The populations of three subtypes of slime-forming bacteria were measured, including slime-forming bacteria, pseudomonad and enteric bacteria, and dense slime bacteria (table 12). Concentrations of slime-forming bacteria in groundwater ranged from 500 to 1,750,000 CFU/mL and were detected in all samples (table 12, fig. 21B). Slime-forming bacteria tend to be aerobic but can be present at redox interfaces (Droycon Bioconcepts, Inc., 2004).

Pseudomonad and enteric bacteria populations were measured with slime-forming bacteria and were detected in groundwater from four of the six wells (MW-4A, EW-11B, MW-11A, and EW-14A). Populations ranged from 500 to 440,000 CFU/mL (table 12, fig. 21C). Dense slime bacteria were detected in only three wells (MW-4A, EW-14A, and MW-11A). The populations of dense slime bacteria were as great as 440,000 CFU/mL (table 12, fig. 21D).

Iron-Related Bacteria

The populations of four subtypes of iron-related bacteria were measured, including iron-related bacteria, enteric

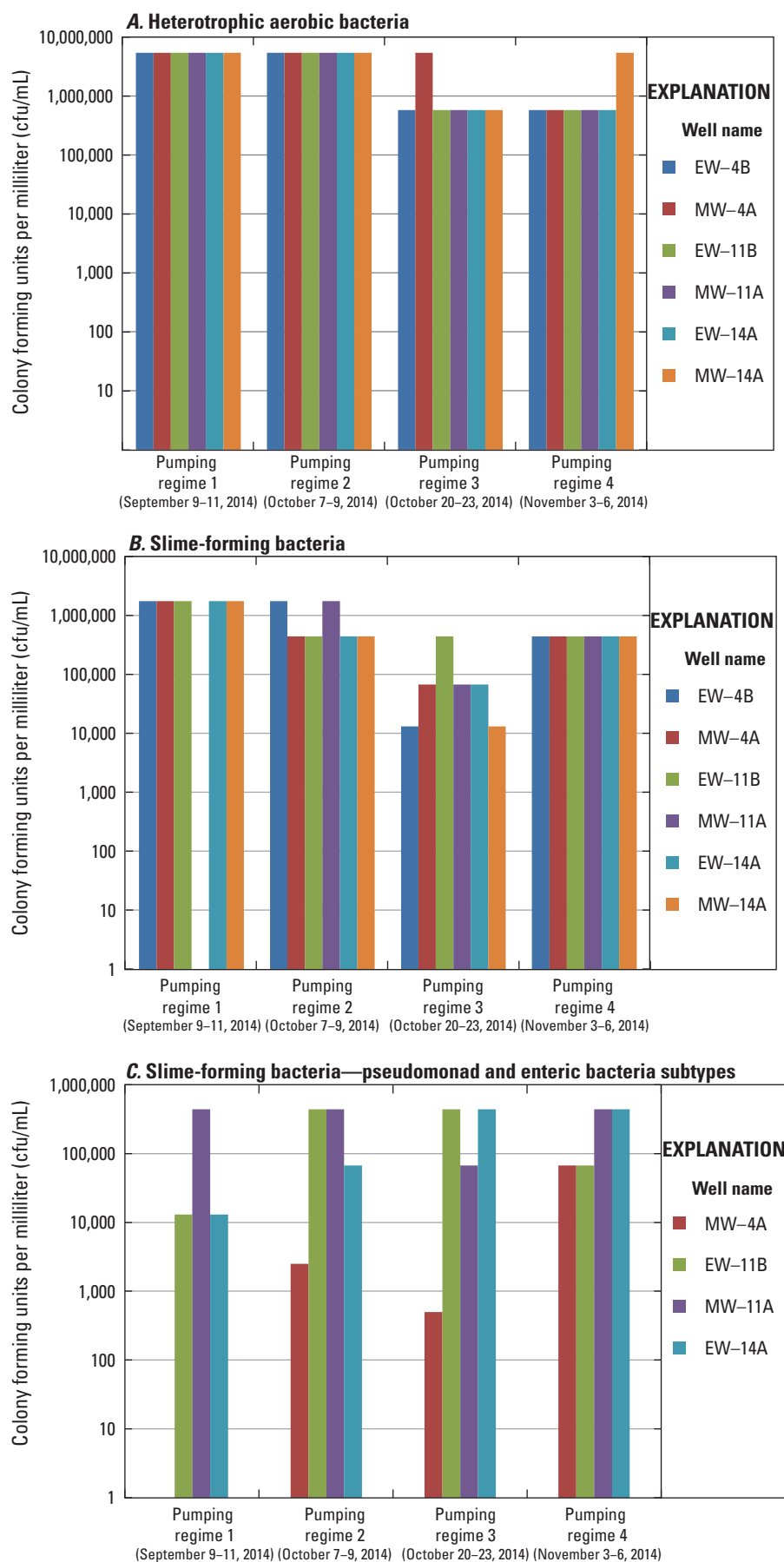


Figure 21. Populations of heterotrophic, slime-forming, iron-related, and sulfate-reducing bacteria subtypes through time during four pumping regimes, including normal operating conditions (September 9–11, 2014), after pump was not operating for at least 8 hours (October 7–9, 2014), after pumping had resumed for 7 days (October 20–23, 2014), and after pumping had resumed for 14 days (November 3–6, 2014).

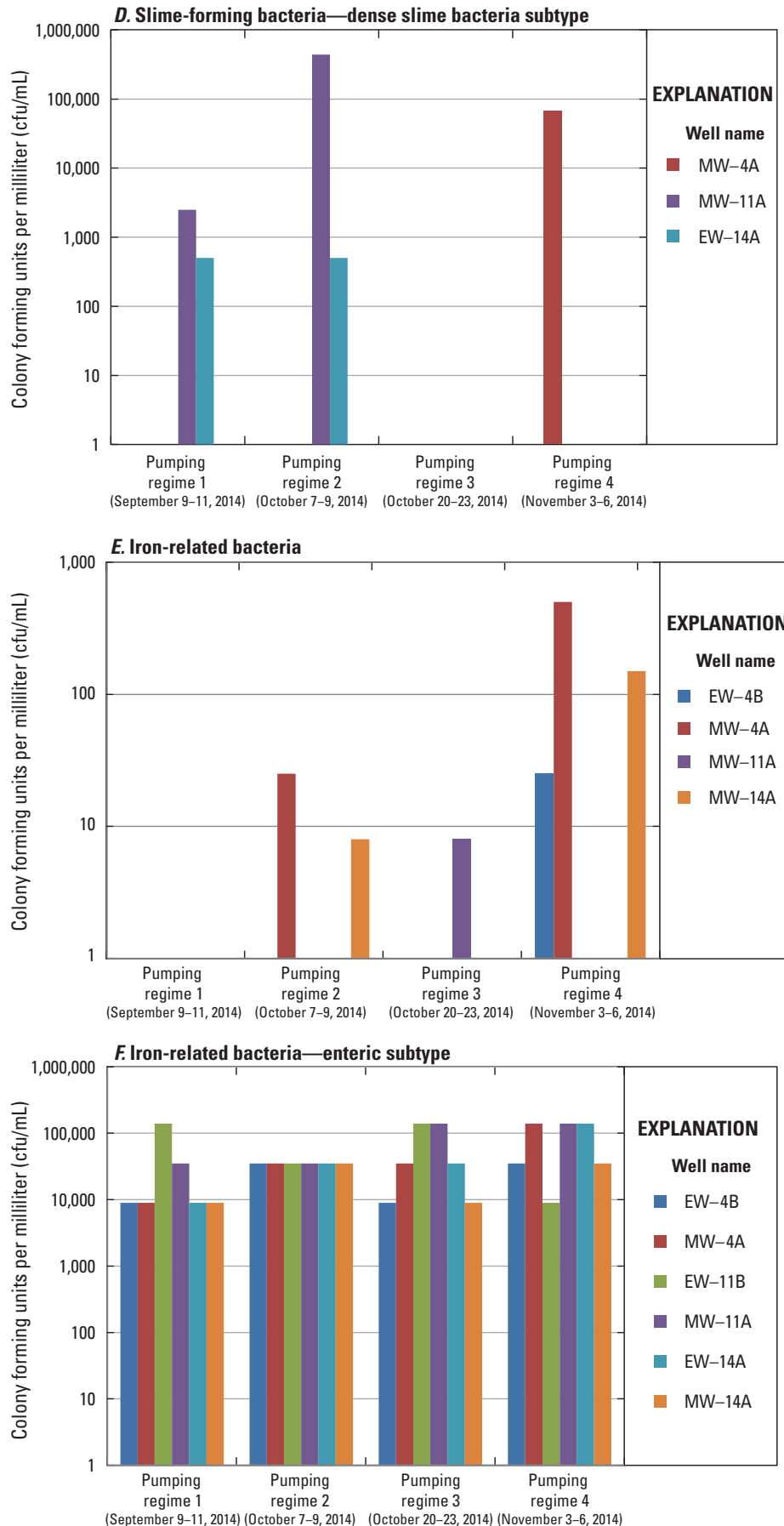


Figure 21. Populations of heterotrophic, slime-forming, iron-related, and sulfate-reducing bacteria subtypes through time during four pumping regimes, including normal operating conditions (September 9–11, 2014), after pump was not operating for at least 8 hours (October 7–9, 2014), after pumping had resumed for 7 days (October 20–23, 2014), and after pumping had resumed for 14 days (November 3–6, 2014).—Continued

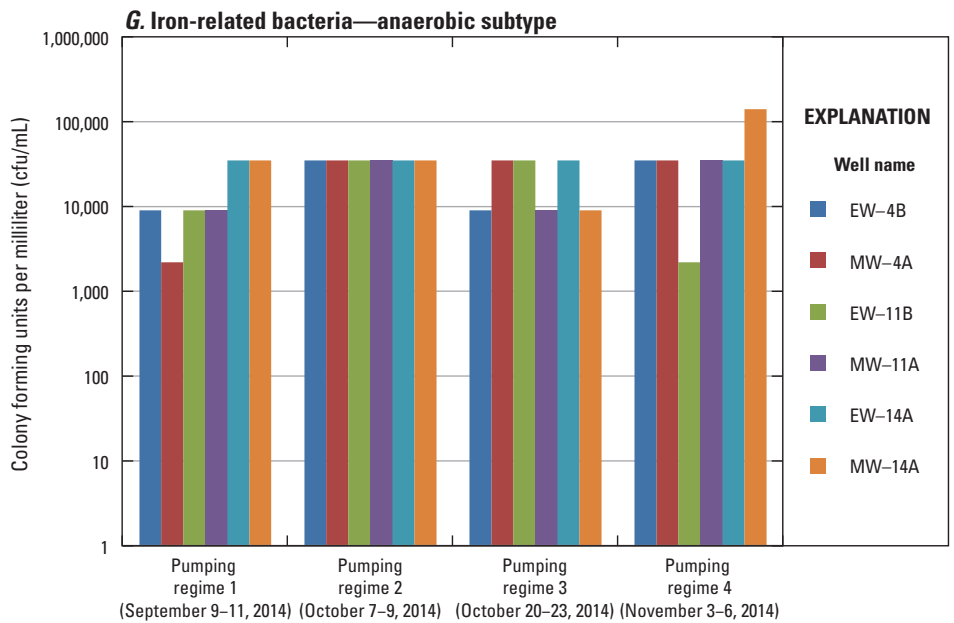
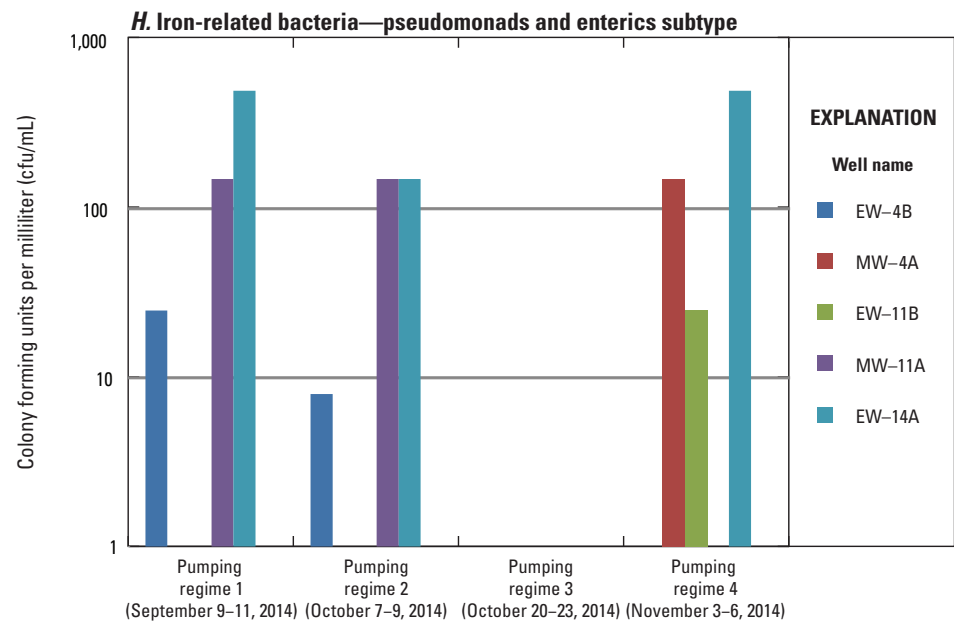


Figure 21. Populations of heterotrophic, slime-forming, iron-related, and sulfate-reducing bacteria subtypes through time during four pumping regimes, including normal operating conditions (September 9–11, 2014), after pump was not operating for at least 8 hours (October 7–9, 2014), after pumping had resumed for 7 days (October 20–23, 2014), and after pumping had resumed for 14 days (November 3–6, 2014).—Continued



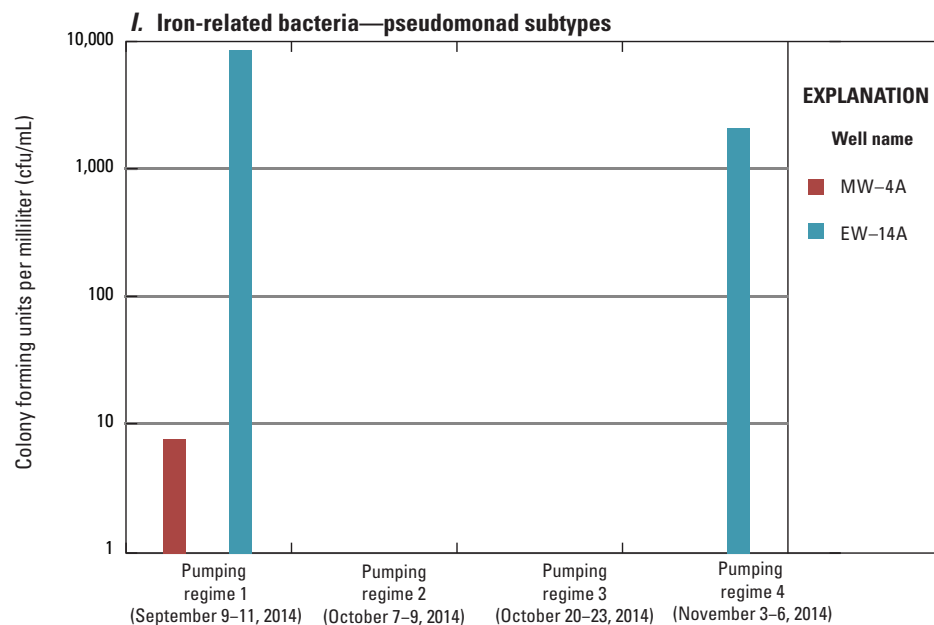
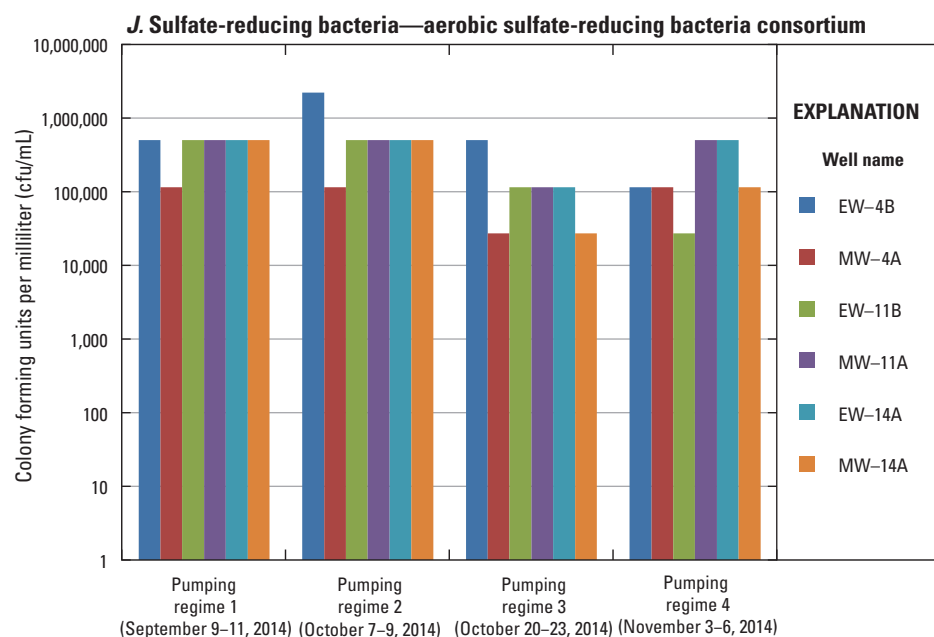


Figure 21. Populations of heterotrophic, slime-forming, iron-related, and sulfate-reducing bacteria subtypes through time during four pumping regimes, including normal operating conditions (September 9–11, 2014), after pump was not operating for at least 8 hours (October 7–9, 2014), after pumping had resumed for 7 days (October 20–23, 2014), and after pumping had resumed for 14 days (November 3–6, 2014).—Continued



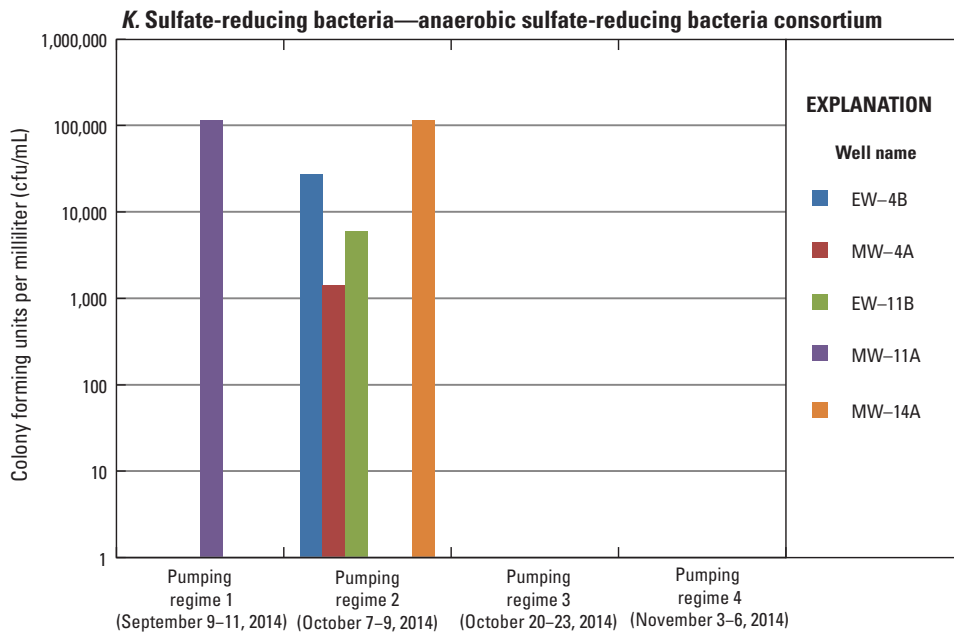


Figure 21. Populations of heterotrophic, slime-forming, iron-related, and sulfate-reducing bacteria subtypes through time during four pumping regimes, including normal operating conditions (September 9–11, 2014), after pump was not operating for at least 8 hours (October 7–9, 2014), after pumping had resumed for 7 days (October 20–23, 2014), and after pumping had resumed for 14 days (November 3–6, 2014).—Continued

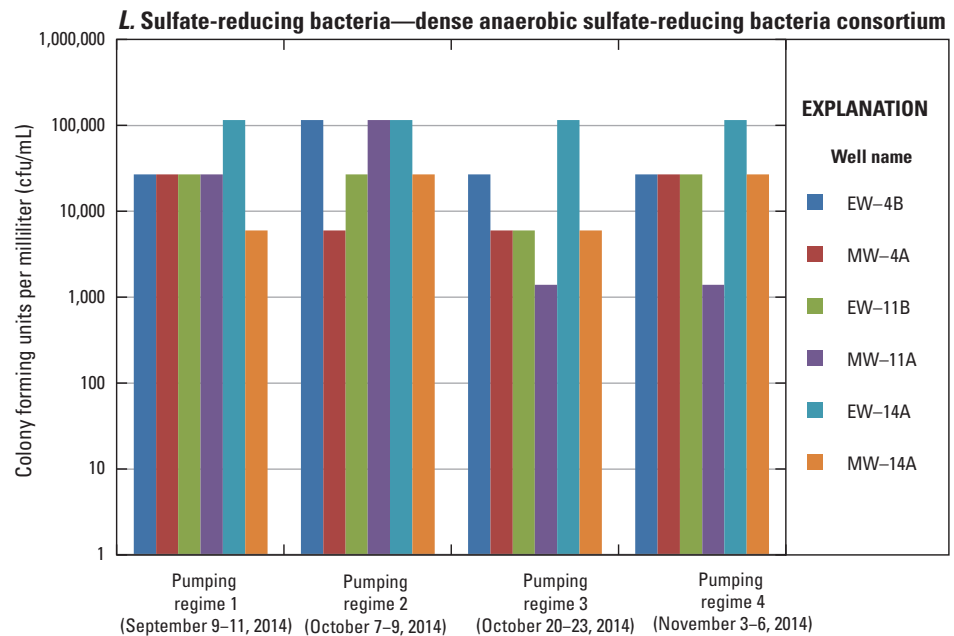


Table 11. Heterotrophic aerobic bacteria activity and population in groundwater samples from wells at the confined disposal facility.

[CFU/mL, colony forming units per milliliter]

Well name	Date sampled	Date observed	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
EW-4B	9/11/2014	9/12/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/9/2014	10/10/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/22/2014	10/24/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	11/5/2014	11/7/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
MW-4A	9/10/2014	9/11/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/9/2014	10/10/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/23/2014	10/24/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	11/6/2014	11/8/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
EW-11B	9/8/2014	9/10/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/7/2014	10/8/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/21/2014	10/23/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	11/4/2014	11/6/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
MW-11A	9/9/2014	9/10/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/7/2014	10/8/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/20/2014	10/22/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	11/3/2014	11/5/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
EW-14A	9/11/2014	9/12/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/8/2014	10/9/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/21/2014	10/23/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	11/4/2014	11/6/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
MW-14A	9/10/2014	9/11/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/8/2014	10/9/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000
	10/22/2014	10/24/2014	2	Aggressive	Bleaching from bottom	Aerobic	575,000
	11/5/2014	11/6/2014	1	Aggressive	Bleaching from bottom	Aerobic	5,400,000

bacteria, anaerobic bacteria, and pseudomonad and enteric bacteria (table 13, figs. 21E–21H). These iron-related bacteria included iron-reducing and iron-oxidizing bacteria. Iron-related bacteria populations ranged from 8 to 500 CFU/mL and were measured in EW-4B, MW-4A, MW-11A, and MW-14A (table 13, fig. 21E).

The populations of enteric bacteria ranged from 9,000 to 140,000 CFU/mL (table 13, fig. 21F). Enteric bacteria were present in groundwater from all wells and did not indicate preference for well or pumping regime. The populations of anaerobic bacteria ranged from 2,200 to 140,000 CFU/mL (table 13, fig. 21G). The population of pseudomonads and enterics bacteria measured by the iron-related bacteria test

ranged from less than the minimum measurable quantity to 500 CFU/mL. These bacteria were detected in groundwater from all wells except for MW-14A and did not indicate relation to any of the tested pumping regimes (table 13, fig. 21H).

As with the sulfate-reducing bacteria, iron-related bacteria accumulate on surfaces and the system must be disrupted by an action, such as a change in pumping rate, to dislodge them. The iron-related bacteria prefer oxygenated conditions, but research indicates that the bacteria can use the iron in oxidative and reductive states (Droycon Bioconcepts, Inc., 2004). The method used in this study detects both forms of iron-related bacteria. The analytical method used indicated that the iron-related bacteria were the anaerobic variety.

Table 12. Slime-forming bacteria activity and population in groundwater from wells at the confined disposal facility.

[CFU/mL, colony forming units per milliliter]

Well name	Date sampled	Date observed	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
EW-4B	9/11/2014	9/12/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
	10/9/2014	10/10/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
	10/22/2014	10/26/2014	4	Moderate	Cloudy growth	Slime forming	13,000
	11/5/2014	11/7/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
MW-4A	9/10/2014	9/11/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
	10/9/2014	10/11/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		10/14/2014	5	Moderate	Blackened liquid	Pseudomonads and enterics	2,500
	10/23/2014	10/26/2014	3	Aggressive	Cloudy growth	Slime forming	67,000
		10/29/2014	6	Moderate	Blackened liquid	Pseudomonads and enterics	500
	11/6/2014	11/8/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		11/9/2014	3	Aggressive	Blackened liquid	Pseudomonads and enterics	67,000
		11/9/2014	3	Aggressive	Dense slime	Dense slime	67,000
EW-11B	9/8/2014	9/9/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
		9/12/2014	4	Moderate	Blackened liquid	Pseudomonads and enterics	13,000
	10/7/2014	10/9/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		10/9/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
	10/21/2014	10/23/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		10/23/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
	11/4/2014	11/6/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		11/7/2014	3	Aggressive	Blackened liquid	Pseudomonads and enterics	67,000
MW-11A	9/9/2014	9/11/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
		9/15/2014	5	Moderate	Slime ring	Dense slime	2,500
	10/7/2014	10/8/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
		10/9/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
		10/9/2014	2	Aggressive	Dense slime	Dense slime	440,000
	10/20/2012	10/23/2014	3	Aggressive	Cloudy growth	Slime forming	67,000
		10/23/2014	3	Aggressive	Blackened liquid	Pseudomonads and enterics	67,000
	11/3/2014	11/5/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
		11/5/2014	2	Aggressive	Cloudy growth	Slime forming	440,000

Table 12. Slime-forming bacteria activity and population in groundwater from wells at the confined disposal facility.—Continued

[CFU/mL, colony forming units per milliliter]

Well name	Date sampled	Date observed	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
EW-14A	9/11/2014	9/12/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
		9/15/2014	4	Moderate	Blackened liquid	Pseudomonads and enterics	13,000
		9/17/2014	6	Moderate	Slime ring	Dense slime	500
	10/8/2014	10/10/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
		10/11/2014	3	Aggressive	Blackened liquid	Pseudomonads and enterics	67,000
		10/14/2014	6	Moderate	Slime ring	Dense slime	500
	10/21/2014	10/23/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
		10/24/2014	3	Aggressive	Cloudy growth	Slime forming	67,000
	11/4/2014	11/6/2014	2	Aggressive	Blackened liquid	Pseudomonads and enterics	440,000
		11/6/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
MW-14A	9/10/2014	9/11/2014	1	Aggressive	Cloudy growth	Slime forming	1,750,000
	10/8/2014	10/10/2014	2	Aggressive	Cloudy growth	Slime forming	440,000
	10/22/2014	10/26/2014	4	Moderate	Cloudy growth	Slime forming	13,000
	11/5/2014	11/7/2014	2	Aggressive	Cloudy growth	Slime forming	440,000

Sulfate-Reducing Bacteria

The populations of three subtypes of sulfate-reducing bacteria were measured, including aerobic sulfate-reducing bacteria consortium, anaerobic sulfate-reducing bacteria consortium, and dense anaerobic sulfate-reducing bacteria consortium (table 14, figs. 21I–21K). The aerobic sulfate-reducing bacteria consortiums were detected in every sample. Populations of aerobic sulfate-reducing bacteria consortium ranged from 27,000 to 2,200,000 CFU/mL (table 14, fig. 21I). Populations were generally greater from mid-September through mid-October and may indicate that pumping regime 2 favors higher concentrations of sulfate-reducing bacteria.

Anaerobic bacteria were detected once in five of the six wells sampled. The detections were in mid-September through mid-October. Populations ranged from 1,400 to 115,000 CFU/mL (table 14, fig. 21J). The number of positive detections for anaerobic bacteria was relatively limited but may indicate a preference for certain seasonal hydrogeologic settings for pumping regimes 1 and 2. The dense anaerobic sulfate-reducing bacteria consortium was detectable in all groundwater samples. Populations of the dense anaerobic sulfate-reducing bacteria consortium ranged from 1,400 to 115,000 CFU/mL (table 14, fig. 21K). Well EW-14A had the largest populations of dense anaerobic sulfate-reducing bacteria consortium in all samples during every pumping regime (table 14, fig. 21K). A seasonal preference was not indicated by these data. Sulfate-reducing bacteria are anaerobic and tend to grow deep within

biofilms and microbial communities in the well (Droycon Bioconcepts, Inc., 2004). The biofilms are often attached to well components, as opposed to floating in the water; therefore, as a result, biofilms must be disturbed and dispersed into the water column before they can be accurately measured in a groundwater sample. Visual observation groundwater samples in the BARTs containers indicated that the anaerobic bacteria were dominated by *Desulfovibrio*. This reaction pattern was indicated in all samples. Additionally, these results correspond to the ferric iron – sulfate (Fe^{3+} - SO_4^{2-}) reducing environment and lower iron-sulfate (Fe/S) ratios computed during redox analysis in water from MW-14A and EW-14A.

The largest and smallest populations of the 11 measured bacterial communities were determined for the 4 pumping regimes that existed during (and immediately before) sample collection (fig. 21A–K). The largest and smallest populations were not always unique maxima or minima because they occasionally occurred during more than one pumping regime. For example, the populations of heterotrophic aerobic bacteria in water from EW-4B on September 11, 2014 and October 9, 2014 were assigned a population of 5,400,000 CFU/ml based on visual observation of the BART container, and that was the maximum population observed among the four samples collected from EW-4B. In some cases, therefore, the maximum or minimum population may have occurred during multiple pumping regimes.

The results indicated that the maximum populations of the 11 bacteria communities occurred during pumping regime

Table 13. Iron-related bacteria activity and population in groundwater from wells at the confined disposal facility.

[CFU/mL, colony forming units per milliliter]

Well name	Date collected	Observation date	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
EW-4B	9/11/2014	9/15/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
		9/15/2014	4	Aggressive	Foam at top	Anaerobic	9,000
		9/19/2014	8	Moderate	Solution black	Pseudomonads and enterics	25
	10/9/2014	10/12/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/12/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		10/18/2014	9	Not aggressive	Black throughout	Pseudomonads and enterics	8
	10/22/2014	10/26/2014	4	Aggressive	Foam at top	Anaerobic	9,000
		10/26/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	11/5/2014	11/8/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		11/8/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		11/13/2014	8	Moderate	Brown gel at bottom	Iron-related bacteria	25
MW-4A	9/10/2014	9/14/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
		9/15/2014	5	Moderate	Foam at top	Anaerobic	2,200
		9/19/2014	9	Not aggressive	Green throughout	Pseudomonads and enterics	8
	10/9/2014	10/10/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/10/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		10/17/2014	8	Moderate	Brown gel at bottom	Iron-related bacteria	25
	10/23/2014	10/26/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/26/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
	11/6/2014	11/8/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		11/9/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		11/12/2014	6	Moderate	Brown gel at bottom	Iron-related bacteria	500
		11/13/2014	7	Moderate	Black throughout	Pseudomonads and enterics	150
EW-11B	9/8/2014	9/10/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		9/12/2014	4	Aggressive	Foam at top	Anaerobic	9,000
	10/7/2014	10/10/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/10/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
	10/21/2014	10/23/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		10/24/2014	3	Aggressive	Foam at top	Anaerobic	35,000
	11/4/2014	11/8/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
		11/9/2014	5	Moderate	Foam at top	Anaerobic	2,200
		11/12/2014	8	Moderate	Black throughout	Pseudomonads and enterics	25

Table 13. Iron-related bacteria activity and population in groundwater from wells at the confined disposal facility.—Continued

[CFU/mL, colony forming units per milliliter]

Well name	Date collected	Observation date	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
MW-11A	9/9/2014	9/12/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		9/13/2014	4	Aggressive	Foam at top	Anaerobic	9,000
		9/16/2014	7	Moderate	Solution black at top	Pseudomonads and enterics	150
	10/7/2014	10/10/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		10/10/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/14/2014	7	Moderate	Black throughout	Pseudomonads and enterics	150
	10/20/2014	10/22/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		10/24/2014	4	Aggressive	Foam at top	Anaerobic	9,000
		10/29/2014	9	Not aggressive	Brown gel at bottom	Iron-related bacteria	8
	11/3/2014	11/5/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		11/6/2014	3	Aggressive	Foam at top	Anaerobic	35,000
EW-14A	9/11/2014	9/14/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		9/15/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
		9/15/2014	4	Aggressive	Green at bottom	Pseudomonads	9,000
		9/17/2014	6	Moderate	Solution black	Pseudomonads and enterics	500
	10/8/2014	10/11/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/11/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		10/15/2014	7	Moderate	Black throughout	Pseudomonads and enterics	150
	10/21/2014	10/24/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/24/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
	11/4/2014	11/6/2014	2	Aggressive	Orange at top	Enteric (red cloudy)	140,000
		11/7/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		11/9/2014	5	Moderate	Green throughout	Pseudomonads and enterics	2,200
		11/10/2014	6	Moderate	Black throughout	Pseudomonads and enterics	500
MW-14A	9/10/2014	9/13/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		9/14/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	10/8/2014	10/11/2014	3	Aggressive	Foam at top	Anaerobic	35,000
		10/11/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		10/17/2014	9	Not aggressive	Brown gel at bottom	Iron-related bacteria	8
	10/22/2014	10/26/2014	4	Aggressive	Foam at top	Anaerobic	9,000
		10/26/2014	4	Aggressive	Orange at top	Enteric (red cloudy)	9,000
	11/5/2014	11/6/2014	2	Aggressive	Foam at top	Anaerobic	140,000
		11/7/2014	3	Aggressive	Orange at top	Enteric (red cloudy)	35,000
		11/12/2014	7	Moderate	Brown gel at bottom	Iron-related bacteria	150

Table 14. Sulfate-reducing bacteria activity and population in groundwater from wells at the confined disposal facility.

[CFU/mL, colony forming units per milliliter; SRB, sulfate-reducing bacteria]

Well name	Date collected	Observation date	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
EW-4B	9/11/2014	9/13/2014	2	Aggressive	Slight black on ball only	Aerobic SRB consortium	500,000
		9/15/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
	10/9/2014	10/10/2014	1	Aggressive	Slight black on ball only	Aerobic SRB consortium	2,200,000
		10/12/2014	3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
		10/13/2014	4	Aggressive	Cloudy	Anaerobic	27,000
	10/22/2014	10/24/2014	2	Aggressive	Slight black on ball only	Aerobic SRB consortium	500,000
		10/26/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
	11/5/2014	11/8/2014	3	Aggressive	Slight black on ball only	Aerobic SRB consortium	115,000
		11/9/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
MW-4A	9/10/2014	9/13/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		9/14/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
	10/9/2014	10/12/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		10/14/2014	5	Aggressive	Black in base	Dense anaerobic SRB consortium	6,000
		10/15/2014	6	Moderate	Cloudy	Anaerobic	1,400
	10/23/2014	10/27/2014	4	Aggressive	Black on ball	Aerobic SRB consortium	27,000
		10/28/2014	5	Aggressive	Black in base	Dense anaerobic SRB consortium	6,000
	11/6/2014	11/9/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		11/10/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
EW-11B	9/8/2014	9/10/2014	2	Aggressive	Slight black on ball only	Aerobic SRB consortium	500,000
		9/12/2014	4	Aggressive	Black in base and cloudy	Dense anaerobic SRB consortium	27,000
	10/7/2014	10/9/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		10/11/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
		10/12/2014	5	Aggressive	Cloudy	Anaerobic	6,000
	10/21/2014	10/24/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		10/26/2014	5	Aggressive	Black in base	Dense anaerobic SRB consortium	6,000
	11/4/2014	11/8/2014	4	Aggressive	Black on ball	Aerobic SRB consortium	27,000
		11/10/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000

Table 14. Sulfate-reducing bacteria activity and population in groundwater from wells at the confined disposal facility.—Continued

[CFU/mL, colony forming units per milliliter; SRB, sulfate-reducing bacteria]

Well name	Date collected	Observation date	Days after test start	Bacteria aggressiveness	Observation	Bacteria determination	Approximate bacteria population (CFU/mL)
MW-11A	9/9/2014	9/11/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		9/12/2014	3	Aggressive	Cloudy	Anaerobic	115,000
		9/13/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
	10/7/2014	10/9/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		10/10/2014	3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
	10/20/2014	10/23/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		10/26/2014	6	Moderate	Black in base	Dense anaerobic SRB consortium	1,400
	11/3/2014	11/5/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		11/9/2014	6	Moderate	Black in base	Dense anaerobic SRB consortium	1,400
	EW-14A	9/11/2014	9/13/2014	2	Aggressive	Black on ball	Aerobic SRB consortium
9/14/2014			3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
10/8/2014		10/10/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		10/11/2014	3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
10/21/2014		10/24/2014	3	Aggressive	Black on ball	Aerobic SRB consortium	115,000
		10/24/2014	3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
11/4/2014		11/6/2014	2	Aggressive	Black on ball	Aerobic SRB consortium	500,000
		11/7/2014	3	Aggressive	Black in base	Dense anaerobic SRB consortium	115,000
MW-14A		9/10/2014	9/12/2014	2	Aggressive	Slight black on ball only	Aerobic SRB consortium
	9/15/2014		5	Aggressive	Black in base	Dense anaerobic SRB consortium	6,000
	10/8/2014	10/10/2014	2	Aggressive	Slight black on ball only	Aerobic SRB consortium	500,000
		10/11/2014	3	Aggressive	Cloudy	Anaerobic	115,000
		10/12/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000
	10/22/2014	10/26/2014	4	Aggressive	Slight black on ball only	Aerobic SRB consortium	27,000
		10/27/2014	5	Aggressive	Black in base	Dense anaerobic SRB consortium	6,000
	11/5/2014	11/8/2014	3	Aggressive	Slight black on ball only	Aerobic SRB consortium	115,000
		11/9/2014	4	Aggressive	Black in base	Dense anaerobic SRB consortium	27,000

1 in EW-14A, during pumping regime 2 in wells EW-4B, EW-11B, and MW-11A, and during pumping regime 4 in wells MW-4A. The maximum populations in MW-14A occurred during pumping regimes 2 and 4; five communities were greatest during each of the two pumping regimes. The results indicated that the minimum populations occurred during pumping regimes 1 and 3 in water from MW-4A, during pumping regime 3 at EW-4B, MW-11A, EW-14A, and MW-14A, and during pumping regime 4 in EW-11B.

X-Ray Diffraction Analyses

Qualitative X-ray analysis indicated a preponderance of amorphous phases, calcite, and sulfur, with lesser quantities of dolomite and quartz (table 15; appendix 2). XRD traces for samples from wells EW-4C, MW-4B, and EW-11D indicated substantial quantities of amorphous material. XRD traces for samples from EW-4C, EW-4D, and MW-4B indicated mineralogic sulfur, whereas samples from EW-11D and EW-20D did not.

Quantitative analysis of the X-ray data also identified the presence of ferrihydrite, goethite, and organic carbon phases in

Table 15. Summary of X-ray diffraction analysis of solids collected as pump scrapings from wells at the confined disposal facility.

Well name	Date sampled	Time sampled	Description
EW-4C	October 23, 2014	1130	Crystalline sulfur plus amorphous phase(s)
EW-4D	September 11, 2014	1310	Sulfur; dolomite
EW-11D	September 19, 2014	0830	Amorphous material with a trace of calcite
EW-20D	September 19, 2014	0900	Calcite with possible trace quartz
EW-20D	October 23, 2014	1100	Nearly pure calcite
EW-20D	October 23, 2014	1100	Nearly pure calcite
MW-4B	October 9, 2014	1525	Crystalline sulfur plus amorphous phase(s)
MW-4B	October 9, 2014	1520	Crystalline sulfur plus amorphous phase(s)

some samples. Scraping and flocculent samples from EW-4C, EW-4D, and MW-4B contained notably larger quantities of sulfur (21–28 percent by mass), ferrihydrite (34–47 percent), and organic carbon (25–38 percent) than were observed in samples from the other wells (table 16). The sample from EW-11D almost entirely comprised of ferrihydrite (40 percent) and organic carbon (55 percent) with no sulfur. Scraping samples from EW-20D almost entirely comprised of calcite (86–97 percent) with lesser quantities of organic carbon and ferrihydrite.

Scanning Electron Microscopy

Most minerals identified with SEM detected euhedral crystal habit, indicating that precipitation had fallen near or at the site of sample collection. Particularly conspicuous were calcite and sulfur, which were present in rhombic and prismatic habits, respectively (fig. 22; appendix 3). Data results for solids from EW-20D indicated euhedral calcite crystals. Results indicating sulfur crystals included samples from EW-4D and MW-4B (table 17). In some images, such as one from MW-4B, the sulfur crystals were surrounded by material believed to be biofilm. Other results indicating biofilm included samples from EW-4D and EW-20D (table 17). Biofilms appeared as hazy, mossy, or cloudy zones.

Vacuoles were identified in scraping samples from EW-4D and MW-4D. Vacuoles are membrane-filled sacs in plants and fungi. The primarily intact calcified vacuoles likely indicate groundwater transport of some mineralogic material from the nearby geologic deposits into the borehole.

The SEM/EDS and SEM/BSE analyses were done on solid-phase samples from EW-4D, EW-11D, and MW-4B. All samples contained carbon, iron, and sulfur. A sample from MW-4B also contained calcium. The sample from EW-11D additionally contained phosphorous and silicon.

Inductively Coupled Plasma Mass Spectrometry Analyses

In most samples, the weight percent of iron exceeded all other analyzed cations; calcium and magnesium were the second and third most abundant elements, respectively (table 18). Exceptions to this observation were samples from EW-20D and MW-4A where calcium was more abundant than iron (by weight), and from MW-11A where proportions of aluminum, calcium, iron, and magnesium were nearly equal.

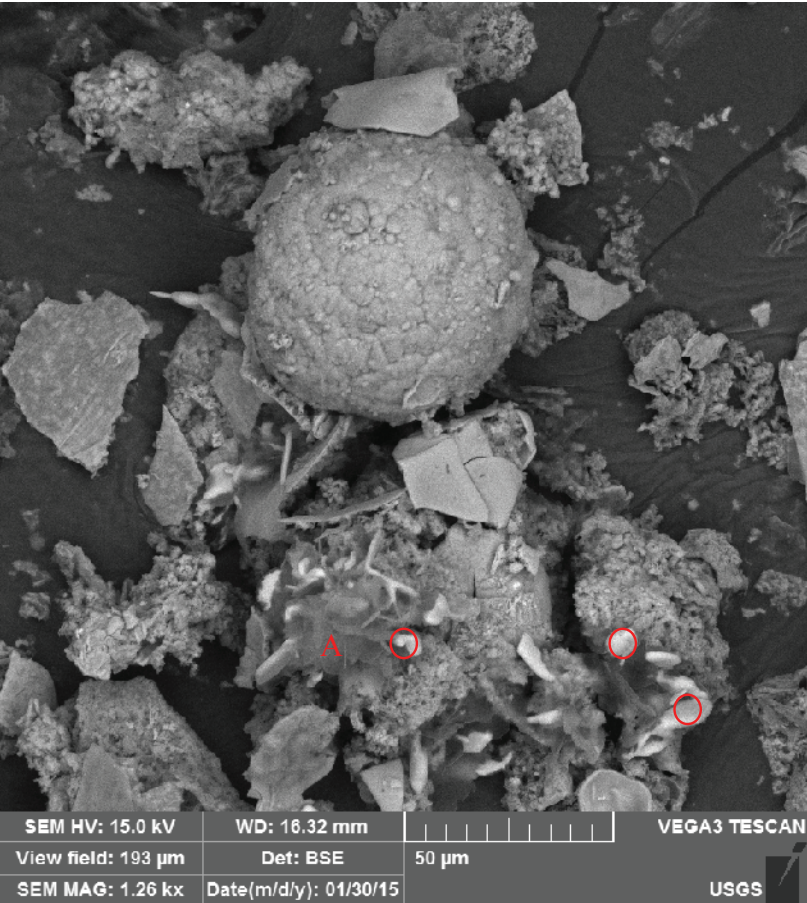
Carbon and Sulfur Isotope Analyses

Eleven measurements of carbon and sulfur isotopes were made on pump scrapings and flocculent in groundwater from wells EW-4C, EW-4D, EW-6C, EW-11D, EW-20D, and MW-4B (table 19). The weight percent of carbon in samples ranged from 7.5 to 29.0. Carbon isotope values ranged from -36.1 to -12.3‰ d¹³C. These values are mostly in the range expected for subsurface dissolved inorganic carbon (-5 to -25‰) that would be produced by weathering of carbonate and silicate minerals in the geologic deposits (Kendall and others, 1995). Carbon isotope values lighter than -30‰ may be attributable to root respiration and oxidation of natural organic matter, as well as residual petroleum, natural gas, or bacterial methane.

The weight percent of sulfur in samples ranged from 0.1 to 16.3. Sulfur isotope values ranged from -31.1 to +6.9‰ d³⁴S. The values measured in scrapings from EW-20D (+4.7 to +6.9‰) were notably heavier than values measured in

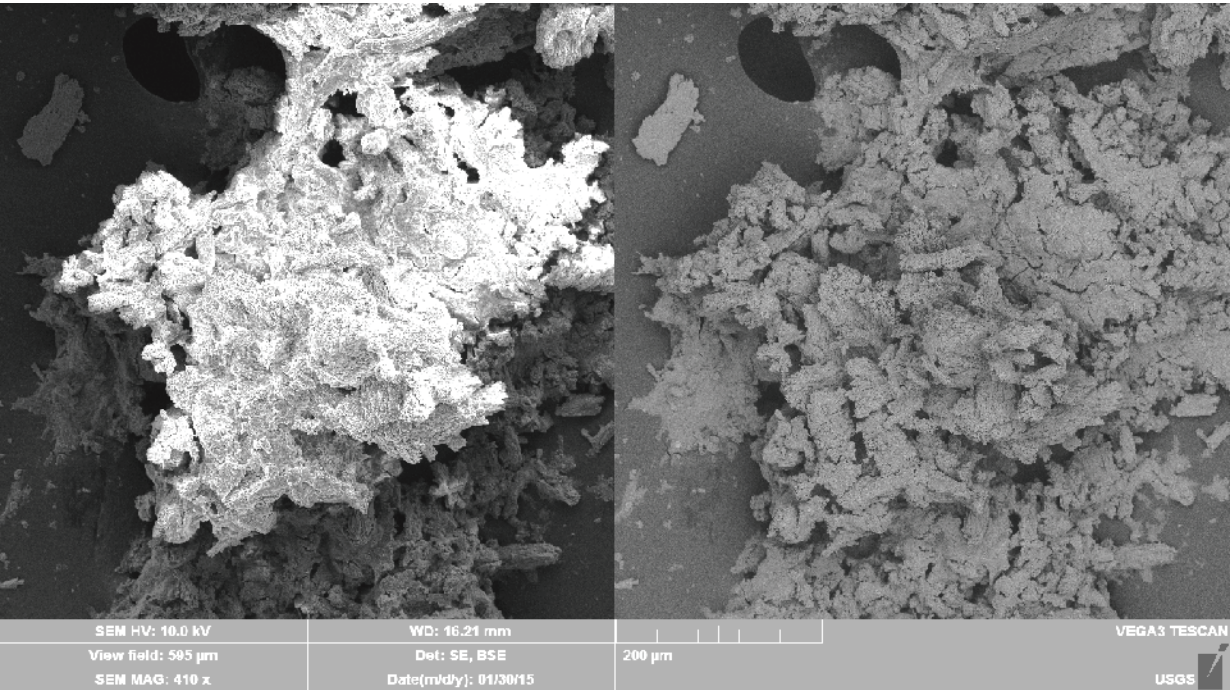
[Values are reported in units of normalized weight percent, computed as (mineral percent of sample multiplied by specific gravity of mineral) divided by total mass of the sample]

Mineral	Well name/sample collection date and time							
	EW-4C	EW-4D	EW-11D	EW-20D	EW-20D	EW-20D	MW-4B	MW-4B
	October 23, 2014	September 11, 2014	September 19, 2014	September 19, 2014	October 23, 2014	October 23, 2014	October 9, 2014	October 9, 2014
	1130	1310	0830	0900	1100	1100	1525	1520
Quartz	1	3	1	0	0	1	1	0
Calcite	5	0	2	91	86	97	1	2
Dolomite	0	2	1	0	0	0	0	0
Sulfur	23	21	0	0	0	0	27	28
Organic carbon phases	25	38	55	8	8	3	36	33
Ferrihydrite	47	34	40	0	5	0	36	37
Goethite (synthetic)	0	1	0	0	0	0	0	0
Total	100	100	100	100	100	100	100	100



The areas circled in red are S crystals. Presumably the spherical object is a whole vacuole. The area labeled “A” is likely carbon biofilm.

Figure 22. Scanning electron microscopy (SEM) images of solid-phase samples from extraction wells EW-4D and EW-20D at the confined disposal facility showing euhedral sulfur and calcite, amorphous material, and biofilms.



This sample is a homogeneous matrix energy dispersive spectroscopy analysis that indicates calcium and carbon; likely calcium carbonate. Taking images was problematic because the sample was not well grounded. The crystals were held together by a biofilm; the cracking was because of drying as seen in this image.

Table 17. Summary of scanning electron microscopy/energy dispersive spectroscopy and scanning electron microscopy/backscatter electrons observations made on solids collected as pump scrapings from wells at the confined disposal facility.

[SEM, scanning electron microscopy; EDS, energy dispersive spectroscopy; BSE, backscatter electrons; C, carbon; Ca, calcium; Fe, iron; Mg, magnesium; --, no observation; S, sulfur; O, oxygen; Al, aluminum; Si, silicon; P, phosphorus; >, greater than; CaCO₃, calcium carbonate]

Well name	Date sampled	SEM/EDS observations	SEM/BSE observations	Additional comments
EW-4C image 1	October 23, 2014	Matrix contains C, Ca, Fe, and Mg in spots	--	--
EW-4D image 1	September 11, 2014	Fe, C, S	More Fe than S	Biofilm
EW-4D image 2	September 11, 2014	--	--	Relative abundances for various mins. Biofilm shows no C
EW-4D image 3	September 11, 2014	C, O, S present in most; Al, Ca, Fe, Si in some	--	Nine spectral analyses
EW-4D image 4	September 11, 2014	--	C, Fe, S	Mineralized biostructures and vacuole; S crystals, C biofilm
EW-4D image 5	September 11, 2014	--	C, Fe, S; except sulfur crystals on broken vacuole plate	--
EW-4D image 6	September 11, 2014	--	S crystals, spherical vacuole, C biofilm	--
EW-6C image 1	November 6, 2014	C, Ca, Fe, P, S, and Si in matrix; Fe>Ca>P>Si>C in platy structures	--	--
EW-11D image 1	September 19, 2014	C, Ca, Fe, P, Si, and S in spots	Uniform in composition	Biofilm
EW-20D image 1	October 23, 2014	C, Ca, likely CaCO ₃ matrix	--	Crystals bound together by biofilm
EW-20D image 2	October 23, 2014	--	Euhedral CaCO ₃ precipitate	--
MW-4B image 1	October 9, 2014	--	Matrix is C, Ca, Fe, S; crystals are S with C	--
MW-4B image 2	October 9, 2014	--	Hollow vacuoles	--
MW-4B image 3	October 9, 2014	--	S crystals with interesting morphology	--
MW-4B image 4	October 9, 2014	--	Large S crystals	--
MW-4B image 5	October 9, 2014	--	Cluster euhedral sulfur crystals	--
MW-4B image 6	October 9, 2014	C, Ca, Fe, S matrix with minor Mg and Si	String has high C, Fe, S with trace Ca and Mg	Biofilm
MW-4B image 7	October 9, 2014	--	--	--
MW-4B image 8	October 9, 2014	--	Sulfur crystals surrounded by biofilm; vacuole and matrix C, Fe and S with minor Ca and Mg	--

Table 18. Inductively coupled plasma mass spectroscopy analyses of samples collected as pump scrapings and on filter with 0.45-micron pore size during groundwater sample collection at the confined disposal facility.

[mg/g, micrograms of analyte per gram of digested solid material]

Well name	Digestion completion	Alumi-num (mg/g)	Boron (mg/g)	Calcium (mg/g)	Lithium (mg/g)	Magne-sium (mg/g)	So-dium (mg/g)	Phos-phorous (mg/g)	Potas-sium (mg/g)	Silicon (mg/g)	Titanium (mg/g)	Vana-dium (mg/g)	Chro-mium (mg/g)	Manga-nese (mg/g)	Iron (mg/g)
EW-4B sample 1	Almost	7,800	19	23,000	9.7	11,000	480	740	1,800	1,900	180	31	29	240	140,000
EW-4B sample 2	Almost	9,900	24	25,000	12	11,000	870	3,700	2,400	3,100	220	63	51	270	87,000
EW-4C	Incomplete	280	2.3	17,000	0.31	2,100	140	93	190	190	10	1.8	4.6	22	300,000
EW-4D	Incomplete	530	2.0	9,000	0.72	3,400	110	270	210	140	21	5.9	14	25	210,000
EW-6C	Almost	360	38	25,000	2.2	2,600	440	7,800	530	1,400	41	21	620	270	230,000
EW-11D	Incomplete	320	9.1	24,000	0.53	1,300	130	16,000	270	1,100	66	15	4.9	130	140,000
EW-20D sample 1	Complete	340	3.6	380,000	2.1	3,200	220	1,000	190	310	5.2	1.3	4.7	430	10,000
EW-20D sample 2	Complete	680	11	350,000	1.6	4,300	270	1,800	210	2,000	9.7	2.7	2.4	620	20,000
EW-20D sample 3	Complete	690	7.4	340,000	1.5	4,400	260	1,800	200	1,600	10	2.8	3.1	640	21,000
MW-4A sample 1	Incomplete	13,000	21	59,000	18	30,000	230	890	3,500	1,600	200	32	35	390	31,000
MW-4A sample 2	Incomplete	13,000	28	56,000	17	29,000	350	1,100	3,400	2,000	210	32	34	520	32,000
MW-4B sample 1	Incomplete	35	0.94	12,000	0.16	3,100	200	73	150	100	2.6	1.7	3.6	13.0	260,000
MW-4B sample 2	Incomplete	16	1.8	9,000	0.20	3,000	200	95	110	83	2.3	1.8	0.53	9.1	180,000
MW-11A sample 1	Incomplete	21,000	14	27,000	25	19,000	210	530	4,300	3,200	68	30	27	300	33,000
MW-11A sample 2	Incomplete	21,000	13	31,000	24	18,000	220	700	4,400	2,700	82	31	25	390	50,000
MW-14A sample 1	Incomplete	13,000	48	31,000	18	11,000	1,400	4,900	5,100	2,400	160	44	48	5400	75,000
MW-14A sample 2	Incomplete	13,000	39	28,000	20	9,500	1,800	3,400	5,300	2,200	170	37	53	280	63,000

Table 18. Inductively coupled plasma mass spectroscopy analyses of samples collected as pump scrapings and on filter with 0.45-micron pore size during groundwater sample collection at the confined disposal facility.—Continued

[mg/g, micrograms of analyte per gram of digested solid material]

Well name	Digestion completion	Cobalt (mg/g)	Nickel (mg/g)	Copper (mg/g)	Zinc (mg/g)	Arsenic (mg/g)	Ribidium (mg/g)	Strontium (mg/g)	Molybdenum (mg/g)	Cadmium (mg/g)	Cesium (mg/g)	Barium (mg/g)	Lead (mg/g)	Uranium (mg/g)
EW-4B sample 1	Almost	8.6	5,500	2,200	31,000	170	18.0	33	3.0	3.8	1.0	76	330	0.40
EW-4B sample 2	Almost	12	6,000	2,900	43,000	180	22.0	43	4.4	4.8	1.1	149	430	0.47
EW-4C	Incomplete	1.1	8.4	3,800	130	62	5.3	20	1.1	0.10	2.3	6.0	320	0.11
EW-4D	Incomplete	3.9	17	67	110	13	1.0	9.1	1.1	0.09	0.06	11	4.0	0.06
EW-6C	Almost	9.9	700	38	104	380	0.70	160	91	0.26	0.03	840	8.8	0.16
EW-11D	Incomplete	1.6	4.7	13	43	20	0.82	140	1.3	0.03	0.06	350	1.8	0.12
EW-20D sample 1	Complete	0.74	22	3.1	1.9	0.41	0.21	1,100	1.1	0.01	0.01	310	0.60	0.01
EW-20D sample 2	Complete	0.65	9.1	1.8	7.0	1.4	0.41	840	0.54	0.01	0.01	390	0.31	0.00
EW-20D sample 3	Complete	0.64	9.5	20	9.5	1.3	0.40	830	0.60	0.01	0.02	370	2.0	0.00
MW-4A sample 1	Incomplete	10	36	100	820	28	23.0	44	11	1.9	1.3	110	180	2.6
MW-4A sample 2	Incomplete	7.6	28	97	730	43	22.0	50	5.3	1.7	1.3	140	180	1.6
MW-4B sample 1	Incomplete	1.0	11	42	29	10	0.64	27	0.77	0.04	0.04	15	4.8	0.02
MW-4B sample 2	Incomplete	0.52	2.4	8.4	7.4	2.6	0.52	19	0.44	0.02	0.05	12	1.5	0.01
MW-11A sample 1	Incomplete	13	30	42	470	31	26.0	37	9.7	0.70	1.6	72	56	4.3
MW-11A sample 2	Incomplete	12	29	42	440	35	25.0	50	7.8	0.74	1.7	140	53	4.1
MW-14A sample 1	Incomplete	23	44	182	760	130	23.0	96	24	1.6	1.5	250	53	2.1
MW-14A sample 2	Incomplete	22	62	260	1,300	90	25.0	61	57	2.3	1.6	110	66	4.1

Table 19. Carbon and sulfur isotope composition for solid samples collected as pump scrapings from wells at the confined disposal facility.

[mg, milligrams; ‰, parts per thousand; %, percent]

Well name	Date	U.S. Geological Survey sample name	Approximate sample weight (mg)	Weight percent carbon in the sample	$\delta^{13}\text{C}^1$ (‰)	Weight percent sulfur in the sample	$\delta^{34}\text{S}^{2,3}$ (‰)
EW-4C	October 23, 2014	Sample C	2	7.5	-26.1	8.7	-30.4
EW-4C (replicate)	October 23, 2014	Sample C replicate	2	7.9	-25.3	16.3	-31.1
EW-4D	September 11, 2014	Sample D	2	19.2	-29.0	15.3	-10.4
EW-6C	November 6, 2014	Sample B	2	15.6	-36.1	2.5	-15.7
EW-11D	September 19, 2014	Sample A	2	8.0	-32.4	2.1	-8.4
EW-20D	September 19, 2014	Sample G	40	11.8	-12.3	0.1	6.2
EW-20D	October 23, 2014	Sample H	40	12.3	-19.4	0.1	6.9
EW-20D	October 23, 2014	Sample I	40	12.4	-19.9	0.2	4.7
MW-4B-1	October 9, 2014	Sample F	2	15.9	-29.1	9.6	-25.5
MW-4B-2	October 9, 2014	Sample E	2	28.6	-30.3	9.4	-23.2
MW-4B-2 (replicate)	October 9, 2014	Sample E replicate	2	29.0	-30.2	5.7	-24.1

¹ $\delta^{13}\text{C} = \{ [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}}] - 1 \} * 1,000\text{‰}$; where $(^{13}\text{C}/^{12}\text{C})$ is the ratio of carbon isotope ^{13}C to carbon isotope ^{12}C in the sample or the standard, and ‰ is the unit parts per thousand.

² $\delta^{34}\text{S} = \{ [(^{34}\text{S}/^{32}\text{S})_{\text{sample}} / (^{34}\text{S}/^{32}\text{S})_{\text{standard}}] - 1 \} * 1,000\text{‰}$; where $(^{34}\text{S}/^{32}\text{S})$ is the ratio of sulfur isotope ^{34}S to sulfur isotope ^{32}S in the sample or the standard, and ‰ is the unit parts per thousand.

³Despite taking steps to enhance combustion, sample matrix effects resulted in high sulfur carryover, whereas carbon chromatography was unaffected. The Vario Isotope Cube (Elementar) elemental analyzer setup traps sulfur for a specified length of time, then releases it by heating the sulfur trap. This setup allows us to measure isotopic values on sharp peaks even in the case of slow-eluting samples such as these. A blank was run after each sample to mitigate the effects of sulfur carryover on subsequent samples.

In cases where evaluation was possible, sulfur carryover $\delta^{34}\text{S}$ values agreed with sample $\delta^{34}\text{S}$ values to within 3‰, suggesting fractionation was limited. However, sulfur carryover implies that ‰S values represent a lower bound, and that interpretation of $\delta^{34}\text{S}$ values should be limited to large variations.

samples from other wells. The isotopically lighter values were measured in EW-4C (-31.1 and -30.4‰) and MW-4B (-25.5 to -23.2‰) and midrange (-8.4 to -15.7‰) values were measured in scrapings from EW-4D, EW-6C, and EW-11D.

The relatively heavier values of sulfur isotopes for EW-20D are the most similar to values that would be expected in waters equilibrated with natural waters. Alternatively, the sulfur isotope values may be indicating that precipitation is a strong influence and that microbiological processes are not as active in this area of the CDF. Lighter sulfur isotope values are likely a result of microbiologically mediated fractionation and are consistent with the rapid well fouling and frequent pump replacement in the EW4 wells. A plot of $\delta^{34}\text{S}$ with weight percent of sulfur in the sample shows a potential relation that indicates lighter isotopes with increasing weight percent sulfur (fig. 23). This observation is consistent with elevated aqueous sulfur concentrations and sulfide mineral formation by bacterial reduction of aqueous sulfate or, alternatively, the degradation of sulfur present in crude oil.

The sulfur isotope values are notably different among EW-4C, EW-4D, and MW-4B. The EW-4D sample was collected about 1 month earlier than the other samples and may

represent values during a different hydrologic period or pumping regime. Alternatively, EW-4D is located further to the north and may be affected by other hydrogeologic or biogeochemical constraints. A sandier subsurface, for example, which transmits more groundwater, might support more aerobic conditions that would be a less favorable setting for sulfur-reducing bacteria. The pump in EW-4C was replaced seven times during water year 2014, compared to two times in EW-4D.

A plot of sulfur and carbon isotopic composition, excluding the EW-20D wells, may show an inverse correlation between the two isotopic ratios (fig. 24). A possible explanation for the observation would be that increased bacterial activity in the more organic-rich settings is removing dissolved inorganic carbon by degassing; the result is isotopically heavier carbon being enriched in settings where higher microbiological activity is creating isotopically lighter sulfur.

Equilibrium Mineral-Saturation Indices

The computed saturation indices for groundwater samples from EW-4B and MW-4A indicated that most miner-

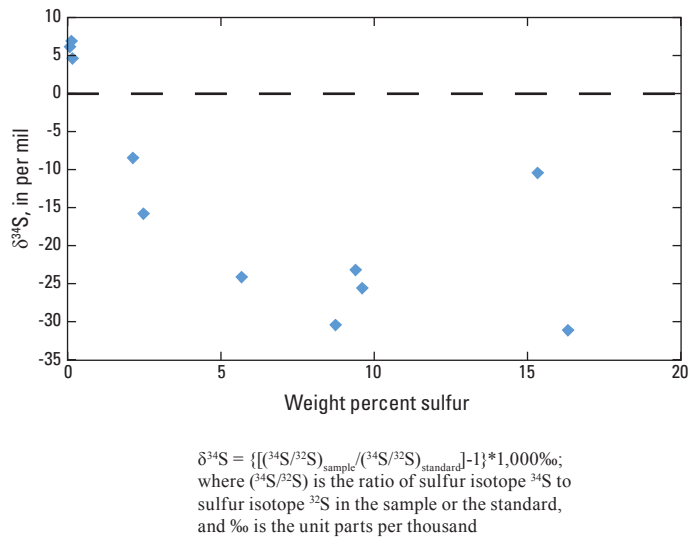


Figure 23. Plot of sulfur isotopic composition with weight percent sulfur in samples collected at the confined disposal facility.

als identified with SEM and X-ray analysis on solids from EW-4D and MW-4B, including calcite, dolomite, and quartz, were supersaturated (table 20; Christian, 2018). These results indicated that those minerals could theoretically precipitate abiotically from groundwater in the borehole. Goethite and hematite, iron-bearing minerals, were also supersaturated in most of the groundwater samples from EW-4B and MW-4A. Sulfur was identified in solid samples from EW-4D and MW-4B but was undersaturated in all groundwater samples from EW-4B and MW-4A; this result may indicate that bioslimes are creating microenvironments in the well where the water chemistry facilitates precipitation of elemental sulfur.

The computed saturation indices for groundwater samples from EW-11B and MW-11A indicated that most groundwater samples were slightly undersaturated or supersaturated with respect to calcite and dolomite; calcite was identified in the solids from EW-11D. The saturation indices for calcite ranged from -0.11 to 0.10 with a mean value of 0.01. Goethite, hematite, and quartz were supersaturated in all samples from EW-11B and MW-11A. Amorphous solids, often iron-rich compounds, were identified in the solids from EW-11D but goethite was not. Sulfur was undersaturated in all groundwater samples from EW-11B and MW-11A.

The computed saturation indices for groundwater samples from EW-14A and MW-14A indicated that most groundwater samples were supersaturated with respect to calcite, dolomite, goethite, hematite, and quartz. Solids were not collected from this well cluster for SEM or X-ray analysis, but these data indicate that mineral precipitation is favored in these wells. Sulfur was undersaturated in all groundwater samples from EW-14A and MW-14A.

Mineral-saturation indices computed for groundwater samples from the six CDF wells varied somewhat consistently

through time (fig. 25). To determine if the variations were related to weather or other hydrologic variables or if the variations could be attributed to the differences among the four pumping regimes is not possible; however, the variations were observed in monitoring wells and the extraction wells. The computed saturation indices were generally highest in groundwater collected during the second sampling event (October 9–11, 2014). That event, with no pumping for several hours before sample collection, might represent a period of increased groundwater residence and equilibration with minerals in the surrounding aquifer materials. The second sampling event also may indicate a period of increased isolation from oxygen, hence, lower redox and greater solubility of some chemical constituents. This result may indicate that continuous pumping at lower discharge rates may be preferable to cycling between no pumping and pumping at higher discharge rates.

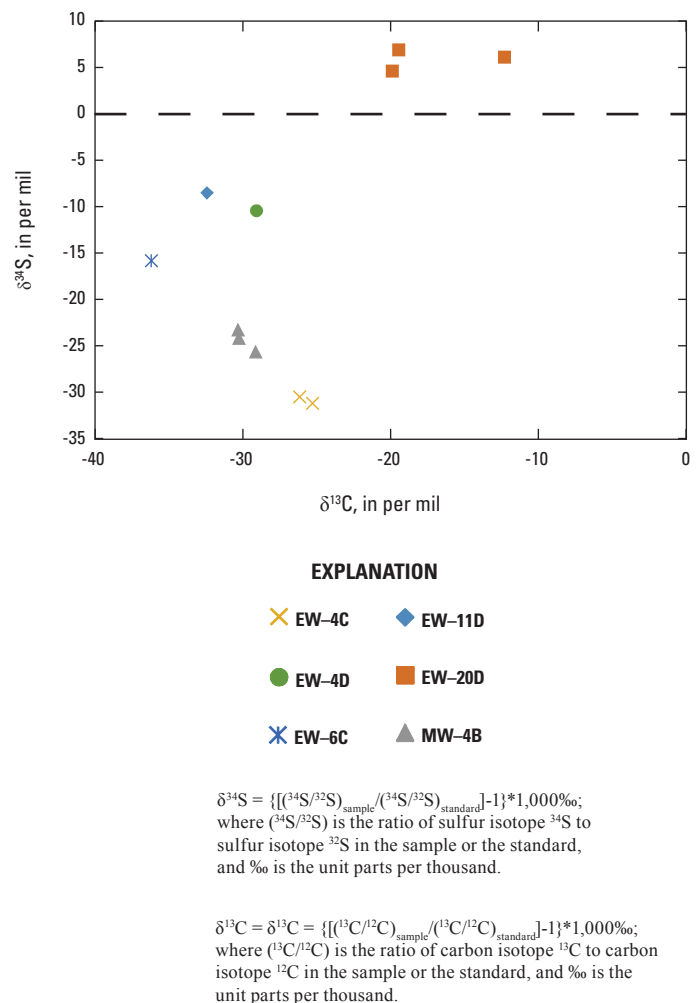


Figure 24. Plot of sulfur and carbon isotopic composition in samples collected at the combined disposal facility.

Table 20. Mineral saturation indices computed using PHREEQC and groundwater quality data collected at the confined disposal facility from September 9 to November 6, 2014.

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. pE, negative base 10 logarithm of the electron activity; g, gas; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered; na, not applicable]

		September 9–11, 2014					
		EW-4B	MW-4A	EW-11B	MW-11A	EW-14A	MW-14A
Redox couple		S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)
Computed pE		-3.19	-2.49	-2.74	-2.65	-3.10	-2.90
Computed Eh (volts)		-0.183	-0.143	-0.156	-0.151	-0.177	-0.166
Mineral name	Mineral formula	Saturation index					
Anhydrite	CaSO ₄	-0.93	-0.69	-3.44	-2.78	-2.65	-1.02
Aragonite	CaCO ₃	0.13	-0.33	-0.26	-0.24	0.15	0.08
Calcite	CaCO ₃	0.28	-0.18	-0.11	-0.08	0.30	0.23
Chalcedony	SiO ₂	0.56	0.60	0.41	0.47	0.48	0.34
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-6.16	-8.53	-9.94	-10.27	-7.17	-8.11
Carbon dioxide ¹	CO ₂ (g)	-0.98	-0.92	-0.68	-0.68	-1.06	-1.10
Dolomite	CaMg(CO ₃) ₂	0.68	-0.49	-0.54	-0.61	0.39	0.04
Iron(III) hydroxide	Fe(OH) ₃ (a)	-7.45	-5.32	-5.02	-4.93	-4.88	-5.42
Mackinawite	FeS (ppt)	0.96	0.71	0.41	0.75	0.31	0.44
Fluorite	CaF ₂	-0.89	-1.13	-1.12	-1.14	-0.79	-0.58
Goethite	FeOOH	-1.88	0.18	0.51	0.52	0.63	0.12
Gypsum	CaSO ₄ ·2H ₂ O	-0.53	-0.26	-3.03	-2.34	-2.24	-0.62
Hydrogen	H ₂ (g)	-7.25	-8.03	-7.55	-7.72	-7.63	-7.82
Water	H ₂ O (g)	-1.73	-1.79	-1.76	-1.82	-1.78	-1.76
Hydrogen sulfide	H ₂ S (g)	-2.00	-4.04	-4.86	-4.57	-5.07	-4.30
Halite	NaCl	-7.78	-8.12	-7.53	-7.70	-7.25	-7.93
Hausmannite	Mn ₃ O ₄	-32.49	-32.83	-33.07	-33.41	-31.97	-31.39
Hematite	Fe ₂ O ₃	-1.79	2.31	2.98	3.00	3.22	2.20
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	-0.18	-4.31	-4.99	-3.77	-1.14	-1.81
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	-28.22	-20.43	-2.15	-23.62	-24.19	-22.14
Mackinawite	FeS	1.70	1.45	1.14	1.49	1.04	1.17
Manganite	MnOOH	-13.89	-13.68	-13.93	-13.84	-13.51	-13.33
Melanterite	FeSO ₄ ·7H ₂ O	-6.74	-4.15	-6.24	-5.51	-6.11	-5.12
Ammonia	NH ₃ (g)	-8.17	-9.02	-8.48	-8.57	-8.13	-8.51
Oxygen	O ₂ (g)	-2.03	-1.76	-2.39	-2.02	-2.17	-1.47
Pyrite	FeS ₂	12.98	11.53	9.90	10.76	9.68	10.75
Pyrochroite	Mn(OH) ₂	-7.36	-7.54	-7.55	-7.54	-7.17	-7.09
Pyrolusite	MnO ₂ ·H ₂ O	-27.75	-27.51	-27.84	-28.00	-27.46	-27.08
Quartz	SiO ₂	1.01	1.06	0.87	0.93	0.94	0.80
Rhodochrosite	MnCO ₃	-0.22	-0.37	-0.13	-0.13	-0.12	-0.08
Sepiolite	Mg ₂ Si ₃ O _{7.5} ·OH·3H ₂ O	-3.06	-4.49	-5.79	-5.83	-33.80	-4.69
Sepiolite	Mg ₂ Si ₃ O _{7.5} ·OH·3H ₂ O (d)	-5.72	-7.10	-8.42	-8.41	-6.42	-7.32
Siderite	FeCO ₃	-1.26	0.56	1.33	1.36	1.06	0.38
Quartz/chalcedony	SiO ₂ (a)	-0.31	-0.28	-0.47	-0.42	-0.40	-0.53
Sulfur	S	-0.83	-2.11	-3.39	-2.96	-3.54	-2.56
Sylvite	KCl	-7.95	-7.72	-7.66	-7.56	-7.47	-7.46
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-1.46	-3.79	-5.57	-5.81	-2.66	-3.87
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	-6.21	-1.84	-0.21	0.74	0.10	-2.21

¹For a gas, SI = log₁₀(fugacity). Fugacity = pressure * phi/1 atm. For ideal gases, phi = 1.

Table 20. Mineral saturation indices computed using PHREEQC and groundwater quality data collected at the confined disposal facility from September 9 to November 6, 2014.—Continued

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. pE, negative base 10 logarithm of the electron activity; g, gas; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered; na, not applicable]

		October 9–11, 2014					
		EW-4B	MW-4A	EW-11B	MW-11A	EW-14A	MW-14A
Redox couple		S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)
Computed pE		-3.05	-2.44	-2.71	-2.71	-3.33	-3.13
Computed Eh (volts)		-0.176	-0.138	-0.155	-0.153	-0.191	-0.178
Mineral name	Mineral formula	Saturation index					
Anhydrite	CaSO ₄	-0.98	-0.52	-2.16	-2.17	-2.67	-1.43
Aragonite	CaCO ₃	0.34	-0.39	-0.14	-0.12	0.24	0.30
Calcite	CaCO ₃	0.49	-0.24	0.01	0.03	0.39	0.45
Methane	CH ₄ (g)	na	na	na	na	na	na
Chalcedony	SiO ₂	0.59	0.67	0.43	0.51	0.49	0.51
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-5.28	-8.18	-9.34	-9.56	-6.39	-6.81
Carbon dioxide ¹	CO ₂ (g)	-0.96	-1.01	-0.78	-0.78	-1.16	-1.19
Dolomite	CaMg(CO ₃) ₂	1.18	-0.52	-0.32	-0.37	0.59	0.54
Iron(III) hydroxide	Fe(OH) ₃ (a)	-4.99	-5.42	-4.74	-4.77	-4.66	-5.29
Mackinawite	FeS (ppt)	1.01	0.53	0.69	1.02	0.90	0.53
Fluorite	CaF ₂	-1.05	-1.21	-1.12	-1.32	-0.63	-0.50
Goethite	FeOOH	0.60	0.01	0.78	0.67	0.90	0.17
Gypsum	CaSO ₄ ·2H ₂ O	-0.59	-0.08	-1.75	-1.73	-2.27	-1.00
Hydrogen	H ₂ (g)	-7.72	-8.15	-7.81	-7.80	-7.45	-7.76
Water	H ₂ O (g)	-1.73	-1.84	-1.78	-1.83	-1.74	-1.82
Hydrogen sulfide	H ₂ S (g)	-4.18	-4.10	-4.75	-4.43	-4.77	-4.42
Halite	NaCl	-7.79	-7.96	-7.51	-7.64	-7.26	-7.80
Hausmannite	Mn ₃ O ₄	-31.40	-32.98	-32.39	-32.87	-31.12	-31.03
Hematite	Fe ₂ O ₃	3.16	1.97	3.51	3.28	3.77	2.28
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	0.31	-3.91	-2.55	-3.01	-0.23	-0.95
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	-21.15	-20.56	-21.90	-22.14	-23.68	-23.22
Mackinawite	FeS	1.74	1.26	1.42	1.75	1.64	1.26
Manganite	MnOOH	-13.47	-13.57	-13.63	-13.60	-13.36	-13.04
Melanterite	FeSO ₄ ·7H ₂ O	-4.76	-4.10	-5.01	-4.97	-6.06	-5.59
Ammonia	NH ₃ (g)	-8.04	-9.01	-8.40	-8.49	-7.95	-8.30
Oxygen	O ₂ (g)	-2.42	-2.45	-2.39	-2.46	-2.38	-2.45
Pyrite	FeS ₂	11.31	11.45	10.55	11.26	10.36	10.72
Pyrochroite	Mn(OH) ₂	-7.17	-7.49	-7.37	-7.35	-6.93	-6.76
Pyrolusite	MnO ₂ ·H ₂ O	-27.05	-27.62	-27.47	-27.81	-27.19	-27.18
Quartz	SiO ₂	1.05	1.14	0.89	0.98	0.95	0.98
Rhodochrosite	MnCO ₃	-0.01	-0.42	-0.05	-0.04	0.03	0.13
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O	-2.42	-4.07	-5.34	-5.27	-3.31	-3.45
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O (d)	-5.09	-6.63	-7.96	-7.83	-5.96	-6.03
Siderite	FeCO ₃	0.99	0.34	1.39	1.40	1.26	0.48
Quartz/chalcedony	SiO ₂ (a)	-0.27	-0.21	-0.45	-0.38	-0.38	-0.37
Sulfur	S	-2.53	-2.07	-3.03	-2.74	-3.40	-2.77
Sylvite	KCl	-7.99	-7.70	-7.47	-7.44	-7.43	-7.61
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-0.50	-3.31	-4.93	-5.02	-1.84	-2.25
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	0.14	-1.99	1.21	0.96	0.90	-2.00

¹For a gas, SI = log₁₀(fugacity). Fugacity = pressure * phi/1 atm. For ideal gases, phi = 1.

Table 20. Mineral saturation indices computed using PHREEQC and groundwater quality data collected at the confined disposal facility from September 9 to November 6, 2014.—Continued

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. pE, negative base 10 logarithm of the electron activity; g, gas; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered; na, not applicable]

		October 22–23, 2014					
		EW-4B	MW-4A	EW-11B	MW-11A	EW-14A	MW-14A
		S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)
		Redox couple					
		Computed pE	-3.03	-2.58	-2.65	-2.69	-3.26
Computed Eh (volts)		-0.174	-0.147	-0.151	-0.153	-0.186	-0.168
Mineral name	Mineral formula	Saturation index					
Anhydrite	CaSO ₄	-1.00	-0.66	-1.80	-1.86	-2.81	-0.94
Aragonite	CaCO ₃	0.20	0.08	-0.14	-0.05	0.21	0.06
Calcite	CaCO ₃	0.35	0.23	0.01	0.10	0.37	0.22
Methane	CH ₄ (g)	na	na	na	na	na	na
Chalcedony	SiO ₂	0.55	0.62	0.44	0.50	0.53	0.34
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-5.65	-8.16	-9.50	-9.40	-6.68	-7.75
Carbon dioxide ¹	CO ₂ (g)	-1.08	-0.79	-0.80	-0.75	-1.17	-1.30
Dolomite	CaMg(CO ₃) ₂	0.83	0.22	-0.36	-0.24	0.50	0.00
Iron(III) hydroxide	Fe(OH) ₃ (a)	na	-5.32	-4.75	-4.82	na	-5.19
Mackinawite	FeS (ppt)	0.75	0.64	0.80	0.95	0.83	0.59
Fluorite	CaF ₂	-0.82	-1.07	-0.89	-1.20	-0.58	-0.52
Goethite	FeOOH	na	0.10	0.71	0.64	na	0.26
Gypsum	CaSO ₄ ·2H ₂ O	-0.60	-0.22	-1.37	-1.38	-2.38	-0.51
Hydrogen	H ₂ (g)	-7.77	-8.07	-7.91	-7.84	-7.50	-7.90
Water	H ₂ O (g)	-1.73	-1.84	-1.82	-1.81	-1.81	-1.82
Hydrogen sulfide	H ₂ S (g)	-4.32	-4.13	-4.60	-4.42	-4.72	-4.38
Halite	NaCl	-7.74	-7.91	-7.55	-7.66	-7.27	-7.85
Hausmannite	Mn ₃ O ₄	-31.30	-32.21	-32.57	-32.61	-31.74	-30.80
Hematite	Fe ₂ O ₃	na	2.15	3.37	3.24	na	2.47
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	-1.43	-4.72	-4.24	-3.74	-0.74	-2.06
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	na	-20.91	-21.30	-21.56	na	-21.82
Mackinawite	FeS	1.48	1.38	1.54	1.68	1.57	1.32
Manganite	MnOOH	-13.40	-13.31	-13.54	-13.57	-13.35	-12.93
Melanterite	FeSO ₄ ·7H ₂ O	-4.87	-4.35	-4.66	-4.80	-6.25	-4.95
Ammonia	NH ₃ (g)	-8.05	-9.10	-8.50	-8.55	-8.03	-8.86
Oxygen	O ₂ (g)	-2.42	-2.46	-2.45	-2.45	-2.45	-2.41
Pyrite	FeS ₂	10.97	11.45	10.97	11.21	10.45	10.97
Pyrochroite	Mn(OH) ₂	-7.13	-7.19	-7.34	-7.34	-6.95	-6.72
Pyrolusite	MnO ₂ ·H ₂ O	-27.01	-27.44	-27.58	-27.64	-27.56	-27.02
Quartz	SiO ₂	1.01	1.09	0.91	0.97	0.99	0.80
Rhodochrosite	MnCO ₃	-0.09	0.11	-0.04	0.00	-0.03	0.06
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O	-2.74	-4.13	-5.36	-5.20	-3.35	-4.36
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O (d)	-5.40	-6.68	-7.94	-7.78	-5.94	-6.93
Siderite	FeCO ₃	0.75	0.70	1.33	1.34	1.11	0.39
Quartz/chalcedony	SiO ₂ (a)	-0.32	-0.26	-0.44	-0.38	-0.35	-0.55
Sulfur	S	-2.62	-2.18	-2.79	-2.69	-3.33	-2.59
Sylvite	KCl	-7.91	-7.54	-7.42	-7.32	-7.46	-7.43
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-0.98	-3.38	-5.08	-4.86	-2.08	-3.54
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	-1.27	-2.93	-0.03	0.05	0.33	-2.25

¹For a gas, SI = log10(fugacity). Fugacity = pressure * phi/1 atm. For ideal gases, phi = 1.

Table 20. Mineral saturation indices computed using PHREEQC and groundwater quality data collected at the confined disposal facility from September 9 to November 6, 2014.—Continued

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. pE, negative base 10 logarithm of the electron activity; g, gas; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered; na, not applicable]

		November 5–6, 2014					
		EW-4B	MW-4A	EW-11B	MW-11A	EW-14A	MW-14A
Redox couple		S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)	S(-2)/S(6)
Computed pE		-2.91	-2.30	-2.79	-2.69	-3.16	-3.03
Computed Eh (volts)		-0.166	-0.131	-0.159	-0.153	-0.179	-0.173
Mineral name	Mineral formula	Saturation index					
Anhydrite	CaSO ₄	-0.99	-0.51	-3.01	-3.21	-2.78	-1.52
Aragonite	CaCO ₃	0.01	0.12	-0.15	-0.19	0.11	0.11
Calcite	CaCO ₃	0.16	0.28	0.00	-0.04	0.26	0.26
Methane	CH ₄ (g)	nd	nd	nd	nd	nd	nd
Chalcedony	SiO ₂	0.59	0.74	0.44	0.50	0.50	0.50
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-6.37	-8.25	-9.49	-10.16	-7.35	-7.44
Carbon dioxide ¹	CO ₂ (g)	-1.04	-0.37	-0.77	-0.65	-1.08	-1.16
Dolomite	CaMg(CO ₃) ₂	0.44	0.58	-0.34	-0.52	0.27	0.17
Iron(III) hydroxide	Fe(OH) ₃ (a)	-5.26	-5.56	-4.85	-4.98	-5.00	-5.39
Mackinawite	FeS (ppt)	0.78	0.28	0.70	0.63	0.73	0.58
Fluorite	CaF ₂	-0.76	-1.24	-0.91	-1.17	-0.57	-0.48
Goethite	FeOOH	0.27	-0.14	0.61	0.47	0.47	0.06
Gypsum	CaSO ₄ ·2H ₂ O	-0.58	-0.06	-2.58	-2.78	-2.35	-1.08
Hydrogen	H ₂ (g)	-7.82	-8.22	-7.65	-7.64	-7.52	-7.76
Water	H ₂ O (g)	-1.76	-1.85	-1.81	-1.82	-1.80	-1.82
Hydrogen sulfide	H ₂ S (g)	-4.11	-4.19	-4.73	-4.69	-4.60	-4.26
Halite	NaCl	-7.73	-7.79	-7.50	-7.64	-7.29	-7.71
Hausmannite	Mn ₃ O ₄	-31.94	-34.20	-32.81	-33.59	-32.28	-31.49
Hematite	Fe ₂ O ₃	2.51	1.66	3.18	2.90	2.90	2.06
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	-1.31	-6.35	-2.63	-3.97	-1.30	-4.10
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	-21.73	-21.02	-24.16	-24.68	-24.83	-23.47
Mackinawite	FeS	1.52	1.01	1.43	1.36	1.46	1.31
Manganite	MnOOH	-13.52	-13.93	-13.68	-13.90	-13.55	-13.18
Melanterite	FeSO ₄ ·7H ₂ O	-4.79	-4.13	-5.82	-5.97	-6.25	-5.55
Ammonia	NH ₃ (g)	-8.17	-9.00	-8.45	-8.54	-8.12	-8.47
Oxygen	O ₂ (g)	-2.43	-1.67	-2.45	-2.45	-2.45	-2.45
Pyrite	FeS ₂	11.28	11.19	10.45	10.43	10.48	10.93
Pyrochroite	Mn(OH) ₂	-7.27	-7.88	-7.35	-7.57	-7.15	-6.91
Pyrolusite	MnO ₂ ·H ₂ O	-27.27	-28.02	-27.83	-28.12	-27.71	-27.35
Quartz	SiO ₂	1.05	1.21	0.91	0.97	0.97	0.97
Rhodochrosite	MnCO ₃	-0.20	-0.18	-0.03	-0.13	-0.14	0.02
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O	-3.11	-3.99	-5.36	-5.69	-3.85	-3.87
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O (d)	-5.74	-6.53	-7.95	-8.27	-6.44	-6.45
Siderite	FeCO ₃	0.60	0.81	1.38	1.39	0.99	0.41
Quartz/chalcedony	SiO ₂ (a)	-0.28	-0.14	-0.44	-0.38	-0.38	-0.38
Sulfur	S	-2.38	-2.09	-3.19	-3.16	-3.19	-2.61
Sylvite	KCl	-7.90	-7.77	-7.59	-7.57	-7.47	-7.40
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-1.62	-3.25	-5.07	-5.63	-2.80	-2.90
Vivianite	Fe ₃ (PO ₄) ₂ ·8H ₂ O	-0.95	-3.70	1.21	0.54	-0.06	-3.65

¹For a gas, SI = log10(fugacity). Fugacity = pressure * phi/1 atm. For ideal gases, phi = 1.

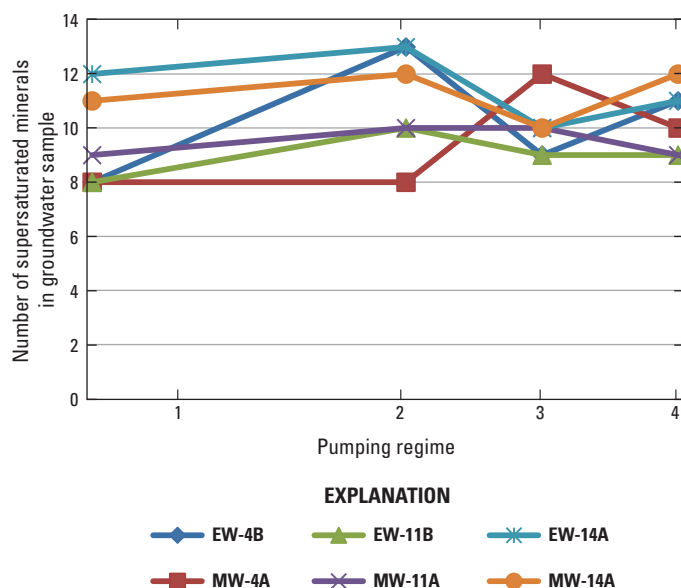


Figure 25. Mineral-saturation indices computed for groundwater samples collected on four occasions at the confined disposal facility.

Mineral-saturation indices were used to explore the effect of overpumping and inducing shallow, oxygenated water into the well screen on mineral precipitation (table 21). Shallow groundwater was not sampled at the CDF; therefore, a water-quality analysis from a monitoring well approximately 0.25 mile south of the CDF, D40, was used as a substitute. The D40 analysis provides a potential example of shallow groundwater in the area of the CDF; however, the area immediately surrounding D40 has not been anthropogenically affected to the extent that the area of CDF has been affected. For example, the assumption is that oil is present at the air-water interface over most of the CDF (Cohen and others, 2002) and oil has not been present at well D40.

Mineral-saturation indices were computed for multiple hypothetical mixtures of groundwater from EW-4B, collected on October 9, 2014, and groundwater from D40, collected on June 14, 1993. A range of mixtures that included zero to 100 percent groundwater from D40 and EW-4B were analyzed. The analyses indicated that adding larger proportions of groundwater from D40 to groundwater from EW-4B resulted in fewer saturation indices that were supersaturated (fig. 26). Larger proportions of groundwater from D40 resulted in lower saturation indices for calcite and dolomite. The minerals hematite, goethite, quartz, and chalcedony remained supersaturated, but the saturation indices decreased with larger proportions of groundwater from D40.

Petroleum Hydrocarbons

Although a prestudy scan of scrapings from well EW-4B indicated that petroleum hydrocarbons were not present, the

preponderance of historical data motivated the collection of a second sample during November 2016. The second sample was scanned for the presence of petroleum hydrocarbons at the USGS laboratory in the South Atlantic Water Science Center Studies Unit. The chromatograph of that sample indicated the presence of longer-chain organics similar to those present in gasoline (fig. 27).

Relation of Geochemical and Microbiologic Characteristics to Well Efficiency

The measurements, analyses, and observations made on groundwater samples collected from wells at the CDF provided multiple lines of evidence that may be used to identify traits of wells that require frequent pump replacement. These traits include highly variable depth to groundwater in the well, higher concentrations of inorganic constituents, lower redox values, in place precipitation of minerals formed in aerobic and anaerobic conditions, and aggressive bacterial activity. The presence of petroleum hydrocarbons may be another trait but the occurrence of those compounds was only qualitatively identified on one occasion in a well with a historically high rate of pump failure. Disrupting one or more of those traits might reduce the frequency of pump replacement.

The depth to water was notably more variable in two wells than the other wells. Water-level data for the EW-4B and EW-14A wells indicated that during some pumping regimes, including those measured during sampling, the water level nearly reached the depth of the screen. This reaction of groundwater levels to pumping likely indicates that the aquifer material near these wells has a reduced hydraulic conductivity compared to other wells. The effect of relatively higher drawdown and decreased well efficiency in these wells may create a periodic cone of depression that brings water from nearer the land surface into contact with water from nearer the base of the aquifer. Water nearer land surface likely is more oxygenated and, therefore, has different chemical and redox properties and potentially contains light nonaqueous phase liquid hydrocarbons. Relatively higher pumping rates in these wells may also induce additional flow from deeper parts of the aquifer that likely contain water with higher concentrations of inorganic constituents and lower redox potential and water that may contain dense nonaqueous phase liquid. Mixing water with different chemical properties from near land surface and near the base of the aquifer may encourage mineral precipitation in the borehole. More frequent pump cycling for shorter duration might reduce drawdown in the well while maintaining the required inward gradient. Additional wells using reduced pumping rates might be required to maintain the inward gradient.

Location of the well screens near the base of the aquifer likely induces flow of water from near the base of the aquifer

Table 21. Mineral-saturation indices computed using PHREEQC and mixtures of groundwater from D40 (June 14, 1993) and EW-4B (October 9, 2014).

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. g, gas; --, no data; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered]

Mineral name	D40/EW-4B ¹ Mineral formula	100/0 Mineral saturation index	75/25 Mineral saturation index	50/50 Mineral saturation index	25/75 Mineral saturation index	0/100 Mineral saturation index
Anhydrite	CaSO ₄	-3.20	-1.61	-1.31	-1.12	-0.98
Aragonite	CaCO ₃	-0.95	-0.59	-0.28	0.02	0.34
Calcite	CaCO ₃	-0.80	-0.44	-0.12	0.17	0.49
Methane	CH ₄ (g)	-38.28	-4.94	-4.59	-4.31	--
Chalcedony	SiO ₂	0.16	0.33	0.44	0.53	0.59
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	-13.27	-10.56	-8.69	-7.04	-5.28
Carbon dioxide ²	CO ₂ (g)	-0.59	-0.65	-0.72	-0.82	-0.96
Dolomite	CaMg(CO ₃) ₂	-2.00	-0.94	-0.18	0.49	1.18
Iron(III) hydroxide	Fe(OH) ₃ (a)	-1.57	-5.56	-5.55	-5.31	-4.99
Mackinawite	FeS (ppt)	--	0.63	1.13	1.45	1.01
Fluorite	CaF ₂	--	-2.21	-1.62	-1.29	-1.05
Goethite	FeOOH	3.84	-0.10	0.06	0.24	0.60
Gypsum	CaSO ₄ ·2H ₂ O	-2.76	-1.18	-0.89	0.71	-0.59
Hydrogen	H ₂ (g)	-16.34	-7.95	-7.8	-7.67	-7.72
Water	H ₂ O (g)	-1.85	-1.82	-1.79	-1.76	-1.73
Hydrogen sulfide	H ₂ S (g)	--	-3.94	-3.62	-3.47	-4.18
Halite	NaCl	-7.58	-7.60	-7.64	-7.7	-7.79
Hausmannite	Mn ₃ O ₄	-26.24	-33.81	-33.14	-32.44	-31.40
Hematite	Fe ₂ O ₃	9.63	1.74	2.08	2.43	3.16
Hydroxyapatite	Ca ₅ (PO ₄) ₃ OH	--	-5.21	-3.06	-1.35	0.31
Jarosite-K	KFe ₃ (SO ₄) ₂ (OH) ₆	-14.08	-22.92	-22.25	-21.87	-21.15
Mackinawite	FeS	--	1.36	1.86	2.18	1.74
Manganite	MnOOH	--	-13.93	-13.84	-13.73	-13.47
Melanterite	FeSO ₄ ·7H ₂ O	-6.04	-4.70	-4.63	-4.69	-4.76
Nitrogen	N ₂ (g)	--	-1.51	-1.16	-0.92	--
Ammonia	NH ₃ (g)	-9.93	-9.39	-9.02	-8.74	-8.04
Oxygen	O ₂ (g)	-2.24	-71.51	-71.39	-71.25	-2.42
Pyrite	FeS ₂	--	11.49	12.13	12.43	11.31
Pyrochroite	Mn(OH) ₂	-7.93	-7.76	-7.58	-7.41	-7.17
Pyrolusite	MnO ₂ ·H ₂ O	-19.96	-27.98	-27.76	-27.52	-27.05
Quartz	SiO ₂	0.63	0.79	0.91	0.99	1.05

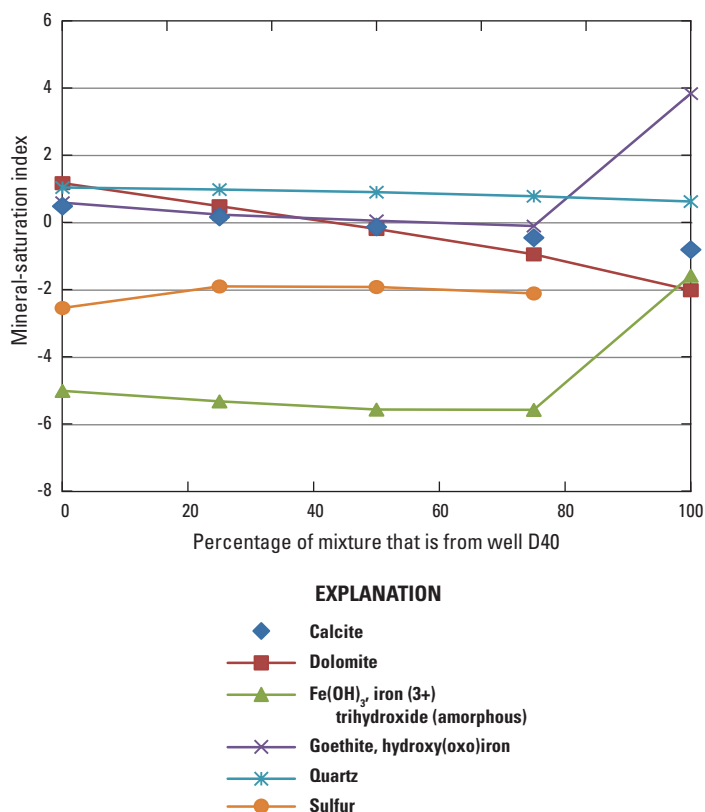
Table 21. Mineral-saturation indices computed using PHREEQC and mixtures of groundwater from D40 (June 14, 1993) and EW-4B (October 9, 2014).—Continued

[Simulations used the sulfide-sulfate redox couple (and measured concentrations of sulfide and sulfate) to compute redox potential (Eh) and speciated the concentration of dissolved inorganic carbon to achieve electroneutrality. Other redox sensitive species, such as iron and manganese, were entered as total dissolved concentrations and speciated using the specified redox couple and other related data. Supersaturated phases are shaded in gray. g, gas; --, no data; a, amorphous; ppt, freshly precipitated and possibly amorphous; d, disordered]

Mineral name	D40/EW-4B ¹	100/0	75/25	50/50	25/75	0/100
	Mineral formula	Mineral saturation index	Mineral saturation index	Mineral saturation index	Mineral saturation index	Mineral saturation index
Rhodochrosite	MnCO ₃	-0.44	-0.32	-0.21	-0.11	-0.01
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH.3H ₂ O	-8.30	-6.25	-4.86	-3.66	-2.42
Sepiolite	Mg ₂ Si ₃ O _{7.5} OH.3H ₂ O (d)	-10.84	-8.83	-7.47	-6.3	-5.09
Siderite	FeCO ₃	0.52	0.65	0.76	0.85	0.99
Quartz/ chalcedony	SiO ₂ (a)	-0.73	-0.55	-0.43	-0.35	-0.27
Sulfur	S	--	-2.10	-1.91	-1.89	-2.53
Sylvite	KCl	-8.52	-8.10	-7.98	-7.95	-7.99
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	-9.43	-6.37	-4.26	-2.42	-0.50
Vivianite	Fe ₃ (PO ₄) ₂ .8H ₂ O	--	-1.17	-0.53	-0.2	0.14

¹Ratio of the percent D40 in mixture to the percent EW-4B in mixture.

²For a gas, SI = log₁₀(fugacity). Fugacity = pressure * phi/1 atm. For ideal gases, phi = 1.

**Figure 26.** Mineral-saturation indices computed for hypothetical mixtures of groundwater from wells D40 and EW-4B at the confined disposal facility.

material as well. Water from the base of the aquifer material receives less mixing with dilute infiltrating precipitation and has longer residence in the subsurface than groundwater from nearer land surface, and as a result is likely characterized by lower redox values and higher concentrations of dissolved organic carbon and inorganic constituents. If present, dense nonaqueous phase liquid hydrocarbons would likely be present near the base of the aquifer. Wells with shallower well screens might reduce potential for introduction of dense nonaqueous phase liquids into the borehole.

The concentrations of some bulk properties and inorganic constituents were notably higher in EW-4B and MW-4A than were observed in the other four wells investigated by this study. Elevated results included specific conductance, total dissolved solids, turbidity, hardness, calcium, ferrous iron, dissolved carbon dioxide, and sulfide. The EW-4B and MW-4A wells also had the lowest redox values. Although water-quality may be changing in EW-4B in response to pumping and drawdown, the water in the monitoring well (MW-4A) also contains relatively elevated values and concentrations. Dissolved gas results indicated oxidation-reduction processes in the aquifer that can feasibly contribute iron, carbon dioxide, and other constituents derived from hydrocarbon degradation to precipitates and solids that accumulate on and impair pump operation. These characteristics indicate that the hydrogeologic setting, before petroleum hydrocarbon contamination, and ambient water quality in the area surrounding these wells are partly responsible for the poorer than average water quality. These variables may not be easily addressed using

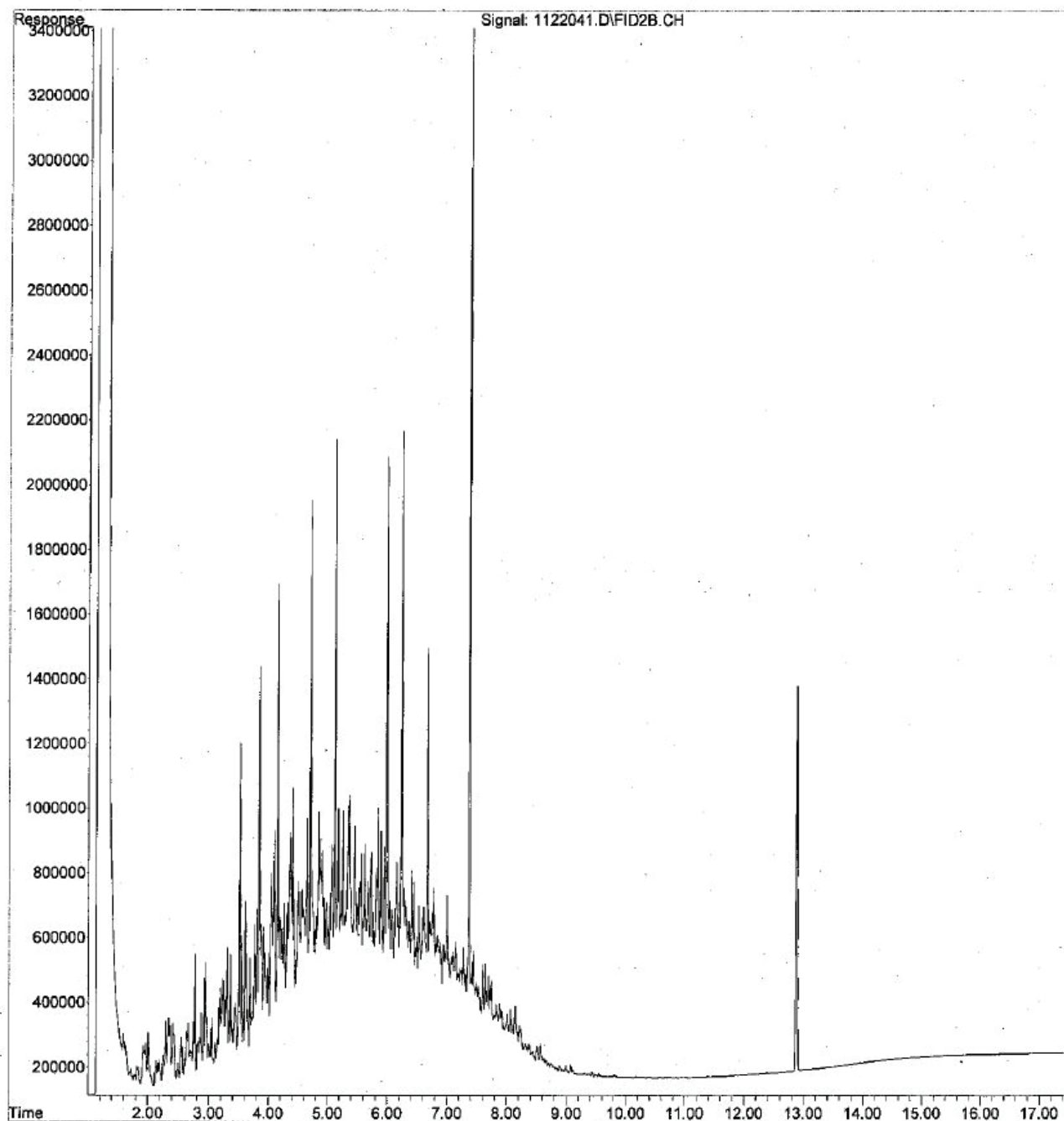
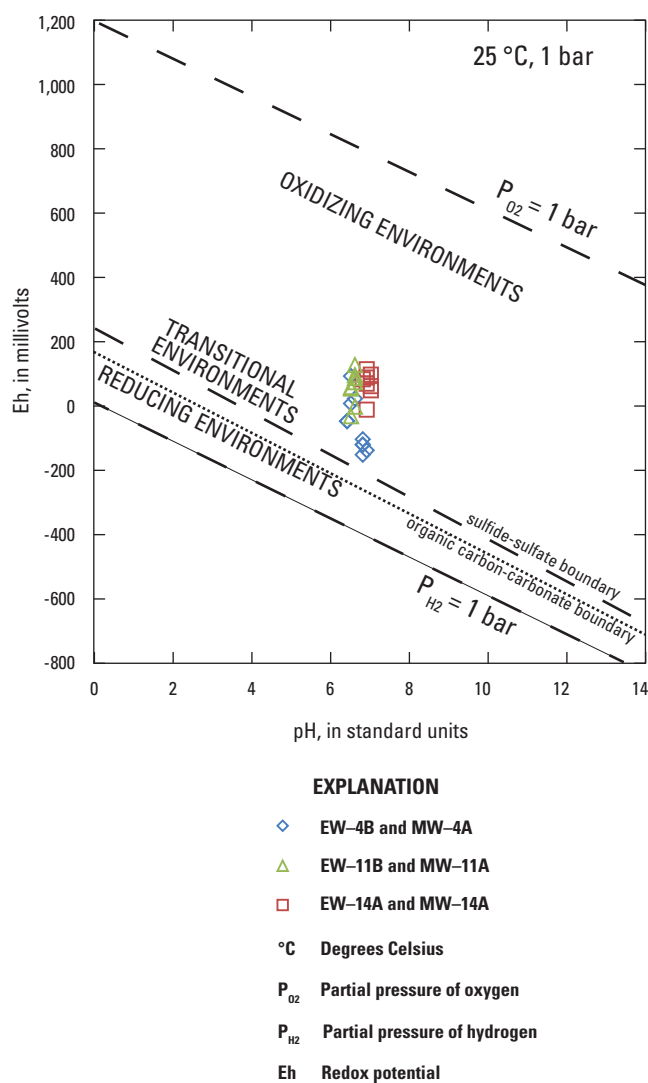


Figure 27. Chromatograph scan of scrapings collected from the pump in well EW-4B on November 3, 2016.

engineering controls; however, physical and biochemical techniques do exist to alter the inorganic chemistry and to enhance the rate of hydrocarbon degradation and removal. These methods might include injection of surfactants to reduce the viscosity and enhance the transport of hydrocarbon residues, injection of microbiological nutrients or oxidants to enhance hydrocarbon degradation, use of pump and treat systems, and manipulating redox conditions to reduce mineral precipitation in the borehole. An assessment of hydrocarbon distribution at

the site might be useful for understanding the extent and concentrations of those compounds and their potential contribution to the well-fouling issue.

The redox conditions in groundwater in the CDF wells are in a theoretical plot of Eh with pH (25 °C and 1 bar pressure) that indicates oxidizing, reducing, and transitional water chemistry environments (fig. 28). Data from this study plotted on a stability diagram from Krauskopf and Bird (1995). The plot indicates that water samples from EW-4B and MW-4A



Source of boundaries shown: Phase diagram after Krauskopf, K.B., and Bird, D.K., 1995, Introduction to Geochemistry, 3rd edition, McGraw Hill, p. 227.

Figure 28. Diagram showing the redox environment for groundwater in six wells at the confined disposal facility.

are in a transitional environment that is nearest to the theoretical boundary between reducing and oxidizing environments as well as the sulfide-sulfate boundary and the organic carbon-carbonate boundary. Groundwater samples for the other four wells are in the domain of transitional environments but nearer to dominantly oxidizing conditions. The inferences from this plot correlate with solid-phase observations of euhedral sulfur crystals in EW-4D and MW-4B. Altering the redox condition in the well might be possible by providing an alternative electron acceptor, such as oxygen, by using a bubbling mechanism. Complicating this potential mitigation strategy, however, might be (1) competition with active microbiological communities and (2) formation of oxidized minerals that

would contribute to additional pump clogging. Microbiological communities have sufficient populations and activity to consume more oxygen than can be provided; at the same time, significant oxygenation may eliminate borehole environments that bacteria now comfortably inhabit by changing the redox halo surrounding the pump or physically dislodging bacteria from the pump. Oxidation of the abundant metals that appear to exist in the ambient water in this area of the CDF, however, may negatively affect the pump infrastructure and well by forming solid, encrusting, oxidation products.

Multiple analyses indicated the relative activity of microbiologic communities. Although all wells had measurable communities of multiple bacteria types, additional tests, which included bacterial activity, XRD, SEM, dissolved gas, and isotopic quantification, indicated elevated activity in wells with biofouling issues relative to wells with infrequent or no pump-replacement history.

Aggressive bacterial activity was identified in wells requiring frequent pump replacement. Effects of biofouling by slime growth on pump infrastructure are exacerbated by the accumulation of mineral matter on bacterial polysaccharides. The XRD analyses identified notable quantities of crystalline sulfur and calcite. Black coloration, similar to that observed at the CDF, of slime-forming bacteria by the entrapment of sulfur and calcite crystals is commonly observed (Droycon Bioconcepts, Inc., 2004). Slime-forming bacteria thrive near redox fronts. Although heterotrophic aerobic bacteria, iron-reducing bacteria, and sulfate bacteria were present in measurable populations in groundwater at the CDF, the bacteria generally prefer redox conditions that are less variable.

Sulfur precipitates under relatively restricted redox conditions; however, microenvironments may exist within the borehole or within accumulations of slime. These observations agree with Brown and others (1999) that anaerobic bacteria survive in aerobic conditions or at a redox interface if the bacteria are encapsulated within layers of slime that are more tolerant of aerobic conditions. Some of the earliest described bacteria were large organisms with inclusions of visible sulfur crystals and a large aqueous vacuole (Salman and others, 2013). SEM observations on CDF samples reported the presence of calcified vacuoles. Physical or chemical disturbance (and prevention) of slime-forming bacteria in the borehole may be required to prevent pump failure.

Brown and others (1999) determined that biofouling also was occurring in the aquifer material surrounding the well screen. Aquifer tests at the CDF by Lampe and Unthank (2016) determined that the hydraulic conductivity of the skin surrounding the well was 7–60 percent (median 19 percent) less than the hydraulic conductivity of the surrounding geologic deposits. This observation seems consistent with the possibility that biofouling occurred in the materials immediately adjacent to the well screen. Resumption of relatively high well discharges following pump replacement at the CDF, however, indicates that the primary cause of well inefficiency and eventual pump replacement is likely due to factors occurring within

the borehole. Occasional redevelopment of the wells might help to alleviate reduced pump discharges.

The impact of changing the pumping regime on water chemistry was difficult to discern. The water-quality data indicated that most of the highest concentrations and parameter values were detected in groundwater from wells requiring the most frequent pump replacement (EW-4B and EW-14A) when the pumps had been off for 8–16 hours before sample collection. Nutrients, which may be required for bacterial growth, were among those elevated constituents. These results contrast with observations made on other CDF wells where the highest concentrations and parameter values were detected after pumping had resumed for 2 weeks or more. The largest populations of slime-forming and sulfate-reducing bacteria were measured during the initial sampling and when the pumps had been off for 8–16 hours. The smallest populations of those bacteria were measured 1 week after pumping had resumed.

The historic observation of light nonaqueous phase liquid, the qualitative detection in one pump scraping from well EW-4B, and results of dissolved gas analysis indicate that the presence of petroleum hydrocarbons may be a factor that adversely affects extraction-well efficiency. Petroleum hydrocarbons, especially dense nonaqueous phase liquid, may clog the aquifer material, well components, and pump infrastructure. Microbiologic processing of hydrocarbons in the aquifer material may influence dissolved concentrations of some inorganic constituents and mineral precipitation. Surfactants can be used to reduce hydrocarbon viscosity and increase compound mobility. Oxidation, pump and treat systems, and enhanced natural attenuation may be used to reduce concentrations of hydrocarbons in the aquifer material.

Summary and Conclusions

The U.S. Geological Survey, in cooperation with the U.S. Army Corps of Engineers, led a study during June 2014 through November 2014 to specifically identify the hydrologic, chemical, and microbiologic processes affecting declining pump efficiency and frequent pump failure at a confined disposal facility (CDF), for dredge material from the Indiana Harbor and Indiana Harbor Canal, in East Chicago, Indiana.

Pumping efficiency in extraction wells is required at the CDF to maintain inward, horizontal gradients at the site. Maintenance of gradients on all sides of the CDF enables isolation and control of residual hydrocarbons and leachate from the dredged sediment as well as control of existing site issues. The gradients are maintained by 96 extraction wells installed during 2008 in the permeable, surficial deposits of the CDF inside a groundwater cutoff wall. The groundwater cutoff wall consists of an impermeable bentonite slurry that extends from land surface to at least 3 feet below the interface between the surficial sand deposits and an underlying fine-grained deposit. Two monitoring wells are in each nest of extraction wells and

are used to indicate a need for pumps in extraction wells to begin and stop pumping.

During 2012, fouling became evident in some extraction wells at the CDF. Fouling was indicated by the accumulation of a black gelatinous matter that formed on the intake of the extraction-well pumps. In some wells, pump efficiency progressively decreased and eventually required pump replacement (fig. 4). Of the affected extraction wells, fouling was more frequently evident in some wells than in other wells (fig. 5).

The investigation described in this report analyzed for possible chemical, microbiological, and geochemical processes in the borehole that could explain pump fouling. Groundwater samples were collected in the same 3 sets of paired wells on 4 occasions, and solid-phase samples were collected from 4 of those wells and 11 additional wells. Paired well sets included an extraction well and a nearby monitoring well. Water samples were collected during four pumping regimes to determine if the pumping schedule affected the water chemistry. The four pumping regimes were as follows: (1) normal pumping intensity and duration, (2) no pumping for 8–16 hours before sample collection, (3) 2 weeks after resuming normal pumping conditions, and (4) 4 weeks after resuming normal pumping conditions. Water samples were analyzed for bulk water properties, inorganic aqueous constituents, and dissolved gases. Discrete solid-phase samples were analyzed for chemical composition, carbon and sulfur isotopes, mineralogy, solid-phase morphology, and bacterial activity.

The results of this study indicate that several factors may be contributing to high rates of pump failure in some extraction wells at the CDF. These factors occur at wells that require frequent pump replacement but do not occur, or occur to a lesser extent, at wells that do not require frequent replacement. The factors affecting pump efficiency or failure may include one or more of the following: (1) extraction rates that likely induce flow from the base of the permeable materials where dense nonaqueous phase liquid hydrocarbons may exist with relatively higher concentrations of dissolved constituents and lower redox values than exist at shallower depths; (2) substantial drawdown during pumping that likely brings oxygen, oxygenated water, and water of notably different chemistry, which may include light nonaqueous phase liquid, into contact with water being induced from the base of the permeable deposits; (3) mineral solids precipitating in or near the borehole; (4) measurable populations of aggressive bacterial communities that include slime-forming organisms capable of encapsulating pump infrastructure and attaching solids; and (5) some parts of the geologic deposits at the CDF have relatively lower permeability. Some of these factors might be addressed through various potential mitigation steps.

The following is a list of mitigation strategies that address the potential factors causing well fouling at the CDF and indicators of mitigation success. The information is summarized in table 22. The application and effectiveness of some of these methods have been reported in the literature but other methods might be tested in pilot or laboratory studies.

Table 22. Summary of potential issues affecting pump efficiency at the confined disposal facility with synopsis of impacts, mitigation strategies, and criteria for evaluating improvements from mitigation as developed from literature sources and observations from this investigation.

Issue	Impact on extraction wells	Mitigation strategy	Evaluation criteria
Legacy hydrocarbons exist across the site. Extraction wells induce flow of hydrocarbons toward the well screen and pump. Hydrocarbons may be lighter or heavier than water and exist near the water table or near the base of the formation.	Hydrocarbon residues accumulate on pumps and infrastructure and possibly in the gravel pack and surrounding formation.	Alter pumping routine to cause less drawdown. Consider pumping longer periods at lower rates. Additional extraction wells might be needed. Consider use of medium-depth wells to avoid dense nonaqueous phase liquids. Natural attenuation, pump and treat systems, or air sparging may be used to reduce amounts of hydrocarbons on site.	Monitor hydrocarbon distribution across the site in three dimensions. Use specific capacity or recovery tests to monitor changes in well efficiency. Monitor the pump replacement rate.
Hydrocarbons accumulate in the well and pump infrastructure.	Hydrocarbon accumulations clog well screens, pumps, and infrastructure causing pump inefficiency and failure.	Add a constant drip of surfactant that has low-foaming properties in low concentrations to increase solubility and mobility of hydrocarbons.	Inspect pumps for accumulation of hydrocarbons in the well and on the pumps. Use specific capacity or recovery tests to evaluate the efficiency of the extraction well. Monitor the pump replacement rate.
Extraction causes water levels in the well and surrounding formation to drop near to the depth of the well screen and brings water with different water chemistry into the pump.	Minerals and amorphous compounds precipitate in the well and adhere to bacteria on pumps and infrastructure.	Install packers into problematic wells to eliminate borehole drawdown. Consider pumping longer periods at lower rates to reduce drawdown in the aquifer near the well.	Monitor bacteria and mineral accumulation on pumps and in the wells. Occasional X-ray and scanning electron microscopy may indicate mitigation impact on mineral precipitation. Use specific capacity or recovery tests to evaluate the efficiency of the extraction well. Monitor the pump replacement rate.
Bacteria accumulate in the gravel pack, on the well screen, on the pump, and on the pump infrastructure. Bacteria accumulate solids that harden accumulations on the pump.	Bacteria and solid accumulations reduce flow causing pump inefficiency and failure.	Add a constant drip of a biocide in a low concentration to inhibit bacterial accumulations. Agitate the borehole by surging, jetting, or air sparging to dislodge and mobilize bacteria. Periodically redevelop the well to clear the well screen.	Inspect pumps for accumulations and types of bacteria while employing mitigation strategies. Use specific capacity or recovery tests to evaluate the efficiency of the extraction well. Monitor the pump replacement rate.
Bacteria are attracted to and adhere to the pump partly because of the pump texture, vibration, and temperature.	Bacteria and solid accumulations reduce flow causing pump inefficiency and failure.	Modify the thermal properties of the pump, modify the exterior of the pump, or apply a replacement physical shield.	Monitor accumulation of bacteria on pumps while employing different pump modifications.

1. *Pump rate, duration, frequency.*—Changing the pumping regimes to reduce the range of groundwater-level fluctuation and thereby (perhaps) minimize the aeration of water and contact with water in quasi-equilibrium with shallow sediments, to maximize the depth of water standing in the well (while maintaining the required gradient), and to minimize the volume of dewatered porous media near the extraction wells may change the chemistry and microbiology of the borehole. Using a borehole packer to isolate the pump from water and oxygen standing in the borehole might be considered in combination with changing the pumping regime. This manipulation of the pumping regimes would of course need to be evaluated while maintaining the required inward gradient. Continuous water-quality monitoring through several pumping cycles could be done to determine the effect of various pumping programs on water quality. Discrete inorganic and organic analyte samples also should be collected.
2. *Isolating the well site from water of certain water quality.*—The groundwater quality in some areas of the CDF may contain elements that create issues for the pump systems by either providing energy sources for the bacteria or by containing constituents that are harmful (for example, hydrocarbons) or facilitate precipitation of minerals. The need to maintain a uniform inward gradient may reduce the flexibility of relocating extraction wells away from areas with problematic water quality. Raising the screen in problematic wells might reduce the influx of dense nonaqueous phase liquid. Natural attenuation, in place treatment, or pump and treat systems might be considered to reduce concentrations of some organic constituents. The success of natural attenuation at oxidizing hydrocarbons might be evaluated with soil-gas or groundwater isotope measurements or borehole concentrations of hydrocarbons analyses, or both.
3. *Depth of well screens.*—Raising well screens to depths that do not induce flow from the base of the permeable deposits (which contain water with high total dissolved solids, low redox, and perhaps dense nonaqueous phase liquids) might decrease constituent concentrations and reduce mineral precipitation in the borehole and might reduce the introduction of dense nonaqueous phase liquids into the borehole. This approach would require modification of pumping regimes because some wells nearly go dry using the current regimes with pumps located at the bottom of the well. Continuous monitoring of onsite parameters, which include redox, dissolved oxygen, and specific conductance and discrete sampling for concentrations of hydrocarbons before and after pump relocation, could be used to indicate if this strategy has benefits.
4. *Biocides.*—The introduction of biocides may be a viable option to eliminate slime-producing bacteria buildup in the borehole. Drawbacks to chemical ameliorates are that they require constant capital investment or maintenance, may damage the pump infrastructure or well components, or may cause water-quality degradation. Water-quality degradation may not be a concern at the CDF, and slow degradation of well components may be more cost efficient to address than frequent pump replacement as a result of biofouling. Consideration might be given to regular addition of bactericides to problematic wells or a constant-drip system that would maintain a more constant concentration than occasional chemical shocking. Regular measurements of bacterial populations might be used to evaluate the effectiveness of biocides and guide the frequency and concentration of well additives.
5. *Chemical Manipulation.*—As an alternative or in addition to using biocides, manipulation of redox conditions in the well might be used to eliminate redox fronts that favor bacterial growth.
 - A. Increasing the persistence of iron-organic complexes by limiting the in-well oxidation of reduced iron could limit formation of precipitates such as those described as accumulating on some extraction-well pumps at the CDF. Analytical results from this study indicate an association of elevated dissolved-iron concentrations, reduced conditions in groundwater, and presence of organic carbon in groundwater that indicate the possible enhancement of ferrous iron solubility through iron-organic complexes. These complexes are short lived in the presence of dissolved oxygen and ferric iron (Munter and others, 2005); the dissociation can decrease iron solubility in produced water. Maintaining chemically reduced conditions should benefit this issue and could be monitored with continuous water-quality data.
 - B. Use of surfactants with low foaming properties to maintain or increase the mobility of hydrocarbons might be done with a constant drip system in problematic wells. The success of this treatment could be qualitatively evaluated by inspection of pump scrapings and camera logging the well screen and infrastructure.
6. *Thermal properties of pump.*—Some bacteria are attracted to heat and grow faster at higher temperatures. Increased pump insulation might decrease the pumps attractiveness as a bacterial anchor point. Pump modifications could be done in collaboration with the pump manufacturer, and laboratory tests could be done to determine the temperature dependence of bacterial attraction.
7. *Turbulence properties of pump.*—Bacteria populations may increase with increasing borehole turbulence to a point. Adding turbulence to the borehole or pump to the point where bacteria become dislodged from the pump is

desirable. Pump modifications could be done in collaboration with the pump manufacturer, and laboratory tests could be done to determine the threshold of turbulence separating biological attraction and discomfort.

8. *Texture of pump exterior.*—The current pump texture is smooth stainless steel. An outer spray coat of polytetrafluoroethylene or other material could be tested for effectiveness at discouraging bacterial adhesion (Banerjee and others, 2011). N-acetyl-L-cysteine (also known as N-acetylcysteine) may be used to reduce and prevent biofilm formation on stainless steel surfaces (Olausson and others, 2003). N-acetyl-L-cysteine decreased bacterial adhesion and detached bacteria adhering to stainless-steel surfaces. N-acetyl-L-cysteine inhibited growth of some bacteria and reduced the production of extracellular polymeric substances. Active research in the resistance of bacterial adhesion is also examining the use of polyethylene glycol and oligoethylene glycol (Banerjee and others, 2011). Visual inspection of bacterial accumulation to evaluate the effectiveness of these technologies could be done in the laboratory or borehole, or both.
9. *Physical pump protection.*—A physical barrier that encapsulates the pump and provides an alternative substrate for bacterial adhesion may not cost much for materials but may require routine replacement; the latter requires expensive manpower.

None of these remedies in singular or combination are guaranteed to reduce or eliminate the pump fouling. A few of the remedies have indicated some efficacy in applications described in the literature. The CDF water quality, hydrogeochemical setting, and pumping regime likely are unique; therefore, pilot scale testing or trial and error evaluations might be required. Examination of the well screen and gravel pack also might be considered to determine if screen slots and formation pore spaces are being occluded by bacterial or mineralogical accumulations. If the screen slots and pore spaces have been filled, then remedies proposed may have little impact on well productivity.

Limitations

The data and interpretations for this study were limited in the following ways:

1. Only three well pairs were sampled for water quality. Those wells were selected to represent the range of site conditions that result in frequent and infrequent pump replacement. However, conditions that were not sampled may also cause frequent pump failure at the CDF and potential mitigating solutions may not be applicable to wells at those sites. Examination of more wells might be required to further generalize the results reported in this document.
2. Precipitation and evapotranspiration were not entirely constant during the investigation; therefore, the influence of precipitation and evapotranspiration on conditions observed in the wells could not be fully evaluated. For example, the decline in concentrations of some constituents that were detected in the weeks following pump inactivity in some wells could be related to the lack of pumping or might be related to rain events during the time of pump inactivity. A repeat of the pumping regime tests during a shorter, more-constant weather period might be required to explain the lower constituent concentrations.
3. Solid-phase samples were collected as pumps were being serviced; however, the samples were not necessarily from the same wells as those sampled for water quality and bacterial activity. As a result, direct comparisons between aqueous, microbiological, and solid phases are inferential. Sets of water-quality and solid-phase samples from identical wells would be required to directly corroborate some of the suppositions made in this report. For example, supersaturated conditions in one well were correlated with the presence of minerals identified with X-ray diffraction in a nearby well but without identifying the presence of the minerals in the same well that produced the groundwater; the conclusion is only inferential.
4. Equipment blanks identified small quantities of constituent carryover from imperfect equipment cleaning. These concentrations were miniscule in comparison to the concentrations detected in environmental samples but should be recognized.
5. Groundwater samples for chemical analysis were only collected from the screened interval of the extraction wells. As a result, proposed mitigation strategies that assume increasing concentrations of water-quality constituents and decreasing redox with greater depth in the aquifer are based on observations at other sites and may not apply to the CDF. Sampling from multiple depths in the permeable aquifer material would be needed to confirm assumed water-quality stratification.
6. Proposed mitigation strategies are based on disrupting bacterial and geochemical processes that were observed in wells that require frequent pump replacement but that are not observed in wells without frequent pump replacement, strategies that have been applied to other sites, or strategies evaluated in the literature using theoretical or microcosm studies. To fully evaluate if the strategies apply to the CDF, the strategies would need pilot scale testing or trial and error evaluations.

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Appendix 1. Driller's Records for Wells at the Confined Disposal Facility used by this Study

Well records do not have an accompanying Extraction Well Construction Report as indicated in the REMARKS section.



Shaw Environmental, Inc.

BORING NO.: EW-4B

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT: US Army Corps of Engineers

LOGGED BY: B. Squire

TOTAL DEPTH: 37 ft.

DATE BEGAN: 06-13-08

DATE ENDED: 06-13-08

TIME BEGAN:

TIME ENDED:

SITE LOCATION: East Chicago, IN

BORING LOCATION: STA. 89 + 64.30

SHEET 1 OF 2

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
0		Brown CLAY FILL, little fine to coarse sand (>10%, rounded to subrounded) trace fine gravel (<10%, subrounded), medium stiff, low plasticity, moist (FILL)	FILL	SS-1 0.0'-2.0' REC=1.2'	5		0	Datum = 589.0
1					5			Soil samples obtained using 2-in. O.D. x 30-in long split-spoon sampler.
2					7			
3		Black fine to coarse SAND (rounded to subrounded), some fine gravel (>20%, subrounded), little silt (>10%), medium dense, moist to saturated (lacustrine)	SM	SS-2 2.0'-4.0' REC=1.7'	6		13	
4					3			
5					6			SS-3: no recovery, water on split-spoon sampler.
6					16			
7		Gray-brown fine to coarse SAND (rounded to subrounded), trace fine gravel (<10%, subrounded), trace silt (<10%), dense, saturated (lacustrine)	SW	SS-3 4.0'-6.0' REC=0.0'	12			
8					11			
9					10			
10					16			
11					3			
12					9		228	Shell fragments in SS-4.
13		Gray fine SAND, trace silt (<10%), medium dense to dense, saturated (lacustrine)	SW	SS-4 6.0'-8.0' REC=1.6'	14			
14					23			
15					4			
16					7		182	
17					7			
18					12			
19					2		43	
20					4			
21					17			
22					18			
23					3		84	
24					5			
25					10			
26					17			
27					7		13	
28					12			
29					14			
30					16			
31					5		2	
32					7			
33					12			
34					22		8	
35					3			
36					8			
37					14			
38					20			

DRILLING INFORMATION

DRILLING CONTRACTOR: DNP (Jennings)

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-50

WATER LEVEL (ft)

TIME: W.D. LEVEL: 4

TIME: LEVEL:

TIME: LEVEL:

REMARKS

See Extraction Well Construction Report

01-27-2009 Z:\PROJECTS\Dye\Gradient Control\Boring Logs\EW-4A thru EW-4D\EW-4B.bor



Shaw Environmental, Inc.

BORING NO.: EW-4B

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT: US Army Corps of Engineers

LOGGED BY: B. Squire

TOTAL DEPTH: 37 ft.

DATE BEGAN: 06-13-08

DATE ENDED: 06-13-08

TIME BEGAN:

TIME ENDED:

SHEET 2 OF 2

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
20		Gray fine SAND, little silt (>10%), dense, saturated (lacustrine)			8			
21				SS-11 20.0'-22.0' REC=1.3'	10		2	
22					11			
23				SS-12 22.0'-24.0' REC=1.0'	23		0	
24					5			
25				SS-13 24.0'-26.0' REC=1.2'	12			
26					15		0	
27				SS-14 26.0'-28.0' REC=1.4'	23			
28					6			
29				SS-15 28.0'-30.0' REC=1.6'	12		0	
30		some silt (>20%) at 30 ft.			14			
31				SS-16 30.0'-32.0' REC=1.4'	20		0	
32					9			
33		Gray fine to coarse SAND (rounded to subrounded), trace fine to medium gravel (>10%, subrounded) trace silt (<10%), medium dense, saturated (lacustrine)	SM	SS-17 32.0'-34.0' REC=1.3'	9		0	
34			SW		11			
35		Brown-gray CLAY, trace fine sand (<10%), soft to medium stiff, high plasticity, moist (lacustrine)	CL	SS-18 34.0'-36.0' REC=1.3'	1		0	
36				SS-19 36.0'-37.0' REC=1.0'	4			
37		End of boring at 37 ft.			4			
38					8			
39					5			
40					6			
41								

Sieve analysis (30 ft - 33 ft):
Gravel = 0.0%
Sand = 75.5%
Fines = 24.5%

DRILLING INFORMATION

DRILLING CONTRACTOR: RDNP (Jennings)

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-50

WATER LEVEL (ft)

TIME: W.D. LEVEL: 4

TIME: LEVEL:

TIME: LEVEL:

REMARKS

See Extraction Well Construction Report

01-27-2008 Z:\PROJECTS\IDY\en\Gradient Control\Boring Logs\EW-4A thru EW-4D\EW-4B.bor

SHEET 1 OF 2



Shaw Environmental, Inc.

BORING NO.: EW-11B

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT:

US Army Corps of Engineers

LOGGED BY: S. McGinnis

-TOTAL DEPTH:

38 ft.

DATE BEGAN: 06-18-08

DATE ENDED:

06-18-08

TIME BEGAN: 10:30

TIME ENDED:

14:00

SITE LOCATION: East Chicago, IN

BORING LOCATION: STA. 55 + 51.45

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
0		Brown CLAY FILL, little fine to coarse sand (>10%, rounded to subrounded), trace fine to coarse gravel (<10%, subangular), medium stiff, low plasticity, moist (FILL)	FILL	SS-1 0.0'-2.0' REC=1.6'	9			Datum = 590.2
1					9			Soil samples obtained using 2-in O.D. x 30-in long split-spoon sampler.
2					11			
3		Black fine to coarse SAND (rounded to subrounded), little fine to coarse gravel (>10%, subrounded), trace silt (<10%), medium dense, saturated (lacustrine)	SW	SS-2 2.0'-4.0' REC=1.6'	8			Petroleum staining, odor, free product (oil) in samples 3 ft. to 12 ft.
4					19			
5					8		502	
6					8			
7					4			
8		Black fine GRAVEL (subrounded), and fine to coarse sand (>30%, rounded to subrounded), trace silt (<10%), medium dense, saturated (lacustrine)	GW	SS-3 4.0'-6.0' REC=1.8'	8			
9					8			
10					6		754	
11					7			
12					6			
13					6			
14					13		566	
15					12			
16					5			
17					4			
18		Black fine to coarse SAND (rounded to subrounded), trace fine gravel (<10%, subrounded), trace silt (<10%), medium dense, saturated (lacustrine)	SW	SS-4 6.0'-8.0' REC=1.3'	3		45	
19					3			
20					6			
21					2			
22					2		85	
23					4			
24					6			
25					5		44	
26					8			
27					7			
28					8		196	
29					17			
30		some fine gravel (>20%, subrounded) 18 ft. to 18.8 ft.			22			
31					13			
32					13		86	Shell fragments in samples 18 ft. to 36 ft.
33					12			
34					13			
35					3			
36					4			
37					4			
38					9			
39					5			
40					5			
41					11			
42					13			

DRILLING INFORMATION

DRILLING CONTRACTOR: RDNF (Mooney)

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-50

WATER LEVEL (ft)

TIME: W.D. LEVEL: 3

TIME: LEVEL:

TIME: LEVEL:

REMARKS

See Extraction Well Construction Report

01-29-2009 Z:\PROJECTS\Dynamic\Gradient Control\Boring Logs\EW-11A thru EW-11D\EW-11B.bor



Shaw Environmental, Inc.

BORING NO.: EW-11B

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT:

US Army Corps of Engineers

LOGGED BY: S. McGinn

TOTAL DEPTH:

38 ft.

DATE BEGAN: 06-18-08

DATE ENDED:

06-18-08

TIME BEGAN: 10:30

TIME ENDED:

14:00

SHEET 2 OF 2

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
24		Gray fine to coarse SAND (rounded to subrounded), trace fine gravel (<10%, subrounded), trace silt (<10%), medium dense, saturated (lacustrine)	SP-SM	SS-13 24.0'-28.0' REC=2.0'	8		23	Sieve analysis (22 ft. - 26 ft.): Gravel = 0.3% Sand = 94.4% Fines = 5.3%
25					9			
26				13				
27				SS-14 26.0'-28.0' REC=2.0	16			
					6			
28				9				
29				11				
30				14				
31				SS-15 28.0'-30.0' REC=2.0'	7			
					9			
32	11							
33	14							
34	SS-16 30.0'-32.0' REC=2.0'	5						
		7						
35	9							
36	11							
37	SS-17 32.0'-34.0' REC=2.0'	14						
		5						
38	7							
39	SS-18 34.0'-36.0' REC=2.0'	9						
		11						
40	13							
41	6							
42	8							
43	SS-19 36.0'-38.0' REC=2.0'	7						
		8						
44	2							
45	2							
46	3							
47	3							
48								
49								
End of boring at 38 ft.								
39								
40								
41								
42								
43								
44								
45								
46								
47								
48								
49								
DRILLING INFORMATION			WATER LEVEL (ft)		REMARKS			
DRILLING CONTRACTOR: RDNP (Mooney)			TIME: W.D. LEVEL: 3		See Extraction Well Construction Report			
DRILLING METHOD: 8.25-in. I.D. HSA			TIME: LEVEL:					
DRILLING EQUIPMENT: Diedrich D-50			TIME: LEVEL:					

01-29-2008 Z:\PROJECTS\DYer\Gradient Control\Boring Logs\EW-11A thru EW-11D\EW-11B.bor

SHEET 1 OF 2



Shaw Environmental, Inc.

BORING NO. EW-14A

MONITORING WELL NO. N/A

PROJECT. Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO. 111982

CLIENT:

US Army Corps of Engineers

LOGGED BY. S. McGinn

TOTAL DEPTH

36 ft.

DATE BEGAN: 06-04-08

DATE ENDED:

06-05-08

TIME BEGAN: 14 05

TIME ENDED:

11:30

SITE LOCATION: East Chicago, IN

BORING LOCATION: STA. 42 + 23.67

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
0	Brown and black fine to coarse SAND FILL, little fine to coarse gravel (>10%, subangular), brick fragments, dense, dry (FILL)	Brown CLAY FILL, trace fine to coarse sand (<10%, subrounded), trace fine gravel (<10%, subrounded), medium stiff, low plasticity, moist (FILL)	FILL	SS-1 0.0'-2.0' REC=1.5'	9			Datum = 590.4 Soil samples obtained using 2-in O.D. x 30-in long split-spoon sampler.
1					12			
2					15			
3	Black fine to coarse SAND FILL (subrounded), little fine to coarse gravel (>10%, subangular), little silt (>10%), yellow brick fragments, dense, saturated (FILL)	FILL	FILL	SS-2 2.0'-4.0' REC=1.4'	16			Petroleum staining, free product (oil) in samples 6 ft. to 10 ft.
4					9			
5					7			
6	Black fine to coarse SAND (rounded to subrounded), little fine to coarse gravel (>10%, subrounded), trace silt (<10%), medium dense, saturated (lacustrine)	SW	SW	SS-3 4.0'-6.0' REC=1.3'	7			
7					14			
8					5			
9	Gray fine to medium SAND (rounded to subrounded), little silt (>10%), trace fine gravel (<10%, rounded), medium dense, saturated (lacustrine)	SM	SM	SS-4 6.0'-8.0' REC=1.6'	9			
10					10			
11					10			
12	Gray fine SAND, and silt (>30%), medium dense to dense, saturated (lacustrine)	SM	SM	SS-5 8.0'-10.0' REC=2.0'	12			Ceased drilling at 20 ft. on 6/4/08. Resumed drilling/sampling at 20 ft. on 6/5/08.
13					4			
14					5			
15				SS-6 10.0'-12.0' REC=1.4'	6			
16					5			
17					8			
18				SS-7 12.0'-14.0' REC=1.1'	10			
19					12			
20					4			
				SS-8 14.0'-16.0' REC=2.0'	4			
					5			
					7			
				SS-9 16.0'-18.0' REC=2.0'	5			
					6			
					9			
				SS-10 18.0'-20.0' REC=2.0'	2			
					3			
					3			
					4			
					3			
					5			
					7			
					9			

DRILLING INFORMATION

DRILLING CONTRACTOR: RDNP (Kris)

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-120

WATER LEVEL (ft)

TIME: W.D. LEVEL: 3.5

TIME: LEVEL:

TIME: LEVEL:

REMARKS


See Extraction Well Construction Report

02-02-2009 Z:\PROJECTS\Dyer\Gradient\Control\Boring Logs\EW-14A thru EW-14D\EW-14A.bor

Shaw Shaw Environmental, Inc.
 BORING NO.: EW-14A
 MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility
 PROJECT NO. 111982 CLIENT: US Army Corps of Engineers
 LOGGED BY: S. McGinn TOTAL DEPTH: 36 ft.
 DATE BEGAN: 06-04-08 DATE ENDED: 06-05-08
 TIME BEGAN: 14:05 TIME ENDED: 11:30

SHEET 2 OF 2

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
20		Gray fine SAND, and silt (>30%), medium dense to dense, saturated (lacustrine)	SM	SS-11 20.0'-22.0' REC=2.0'	12			Missed sample interval SS-12, inadvertently over-drilled 20 ft. to 24 ft. Resumed sampling at 24 ft. (SS-13).

02-02-2008 Z:\PROJECTS\Dyer\Gradient Control\Boring Logs\EW-14A thru EW-14DEW-14A.bor

SHEET 1 OF 2



Shaw Environmental, Inc.

BORING NO.: EW-20A

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT:

US Army Corps of Engineers

LOGGED BY: M. Giles

TOTAL DEPTH:

32' bgs

DATE BEGAN: 07-14-08

DATE ENDED:

07-14-08

TIME BEGAN: 08:00

TIME ENDED:

09:25

SITE LOCATION: East Chicago, IN

BORING LOCATION: STA. 13 + 11.82

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
0		(Logged from auger cuttings 0 - 10 ft.)						
1		Brown CLAY FILL, and fine to coarse sand (>30%, subrounded), and fine to coarse gravel (>30%, subangular), concrete rubble, low plasticity, moist to saturated (FILL)		SS-1 0.0'-2.0' REC=0	-		-	
2					-		-	
3				SS-2 2.0'-4.0' REC=0	-		-	
4					-		-	
5				SS-3 4.0'-6.0' REC=0	-		-	
6					-		-	
7				SS-4 6.0'-8.0' REC=0	-		-	
8					-		-	
9				SS-5 8.0'-10.0' REC=0	-		-	
10		Gray fine to medium SAND (rounded to subrounded), trace silt (<10%), medium dense, saturated (lacustrine)			3		0.2	
11				SS-6 10.0'-12.0' REC=0.7'	5			
12					7			
13				SS-7 12.0'-14.0' REC=1.2'	8		0	
14					3			
15				SS-8 14.0'-16.0' REC=0.7'	4			
16					6		0	
17				SS-9 16.0'-18.0' REC=0.6'	11			
18		Brown-gray fine to medium SAND (rounded to subrounded), little silt (>10%), medium dense, saturated (lacustrine)			14		0	
19					3			
20				SS-10 18.0'-20.0' REC=0.8'	4		0	
					7			
					5			
					9			
					13			
					14			

Datum = 589.0
Soil samples obtained using 2-in O.D. x 30-in long split-spoon sampler
Split-spoon refusal 2 ft to 8 ft. due to buried concrete debris. Blind drill to 10 ft. to clear obstructions.
Began sampling at 10 ft.

DRILLING INFORMATION

DRILLING CONTRACTOR: RDNP

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-120

WATER LEVEL (ft)

TIME: W.D. LEVEL: 5

TIME: LEVEL:

TIME: LEVEL:

REMARKS

See Extraction Well Construction Report

02-08-2008 Z:\PROJECTS\Dye\Gradiant\Control\Boring_Log\EW-20A thru EW-20D\NEW_20A.bor



Shaw Environmental, Inc.

BORING NO.: EW-20A

MONITORING WELL NO.: N/A

PROJECT: Indiana Harbor & Canal - Confined Disposal Facility

PROJECT NO: 111982

CLIENT:

US Army Corps of Engineers

LOGGED BY: M. Giles

TOTAL DEPTH:

32' bgs

DATE BEGAN: 07-14-08

DATE ENDED:

07-14-08

TIME BEGAN: 08:00

TIME ENDED:

09:25

SHEET 2 OF 2

Depth (ft)	Strata	DESCRIPTION	USCS	Sample Type & No. Depth (ft) Recovery (ft)	Blow Count	UCS (tsf)	PID Reading (ppm)	REMARKS
20		Brown-gray fine to medium SAND (rounded to subrounded), little silt (>10%), medium dense, saturated (lacustrine) and silt (>30%) after 24 ft.	SM	SS-11 20.0'-22.0' REC=0.7'	4			Sieve analysis (21 ft. - 26 ft.): Gravel = 0.0% Sand = 86.4% Fines = 13.6%
21					5			
22					8		0	
23					11			
24				SS-12 22.0'-24.0' REC=0.9'	5			
25					7		0	
26					11			
27					13			
28				SS-13 24.0'-26.0' REC=0.9'	5			
29					8		0	
30		Gray SILT, and fine sand (>30%), medium dense, wet (lacustrine)	ML	SS-14 26.0'-28.0' REC=1.0'	11			
31					14			
32				SS-15 28.0'-30.0' REC=0.9'	6		0	
33		Gray CLAY, trace fine sand (<10%), soft, high plasticity, moist (lacustrine)	CL	SS-16 30.0'-32.0' REC=1.0'	8			
34					10		0	
35		End of boring at 32 ft.			4			
36								
37								
38								
39								
40								
41								

DRILLING INFORMATION

DRILLING CONTRACTOR: RDNF

DRILLING METHOD: 8.25-in. I.D. HSA

DRILLING EQUIPMENT: Diedrich D-120

WATER LEVEL (ft)

TIME: W.D. LEVEL: S

TIME: LEVEL:

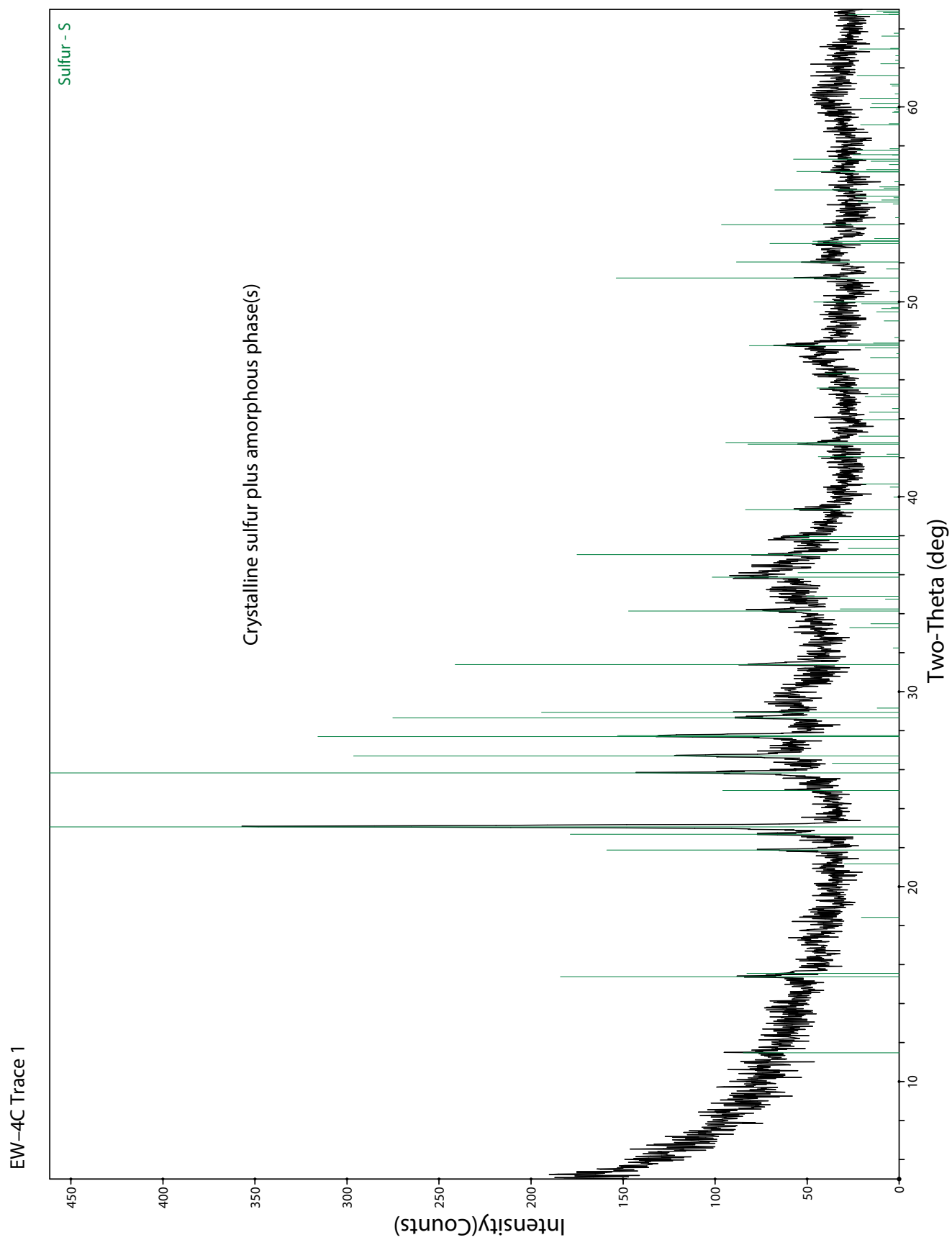
TIME: LEVEL:

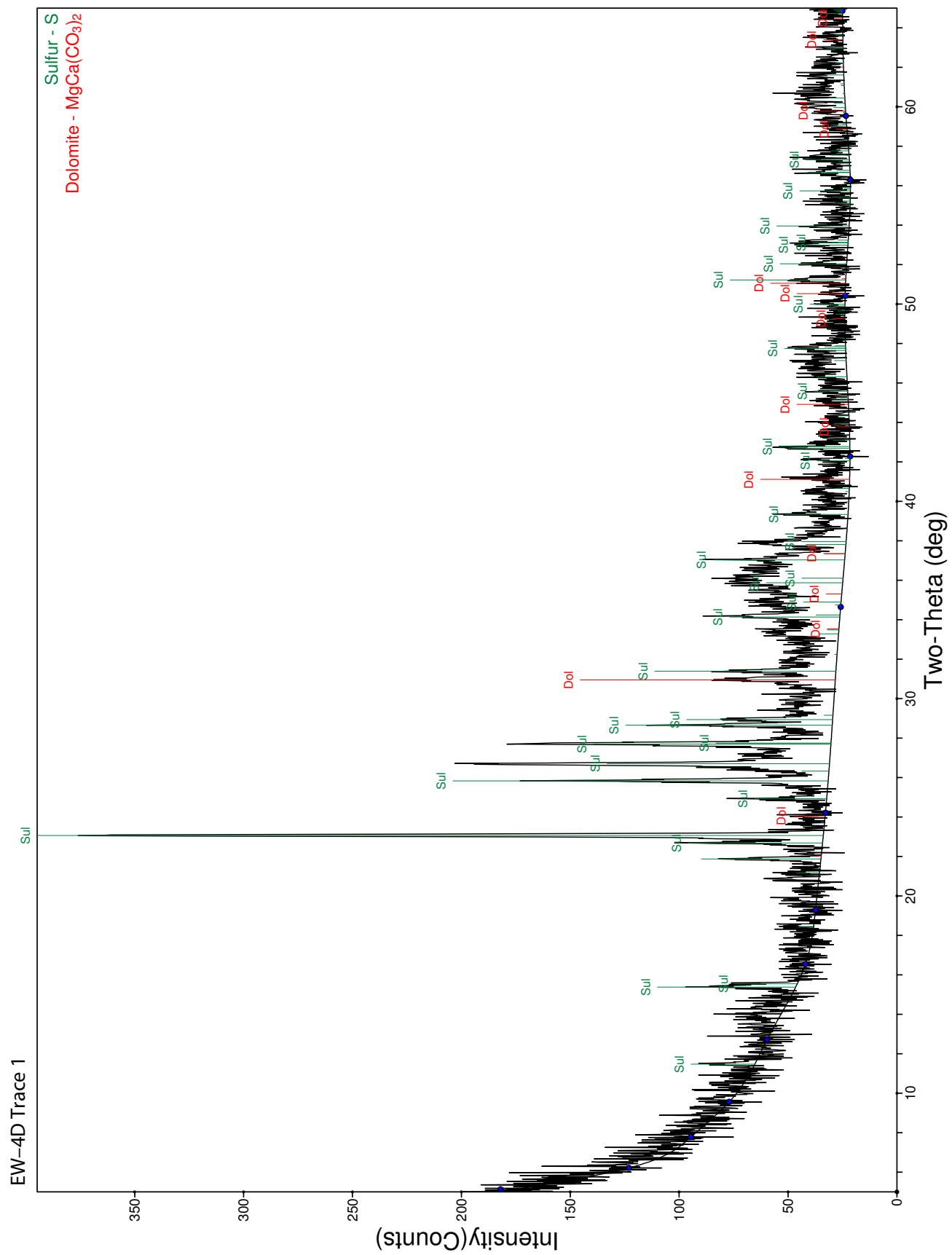
REMARKS

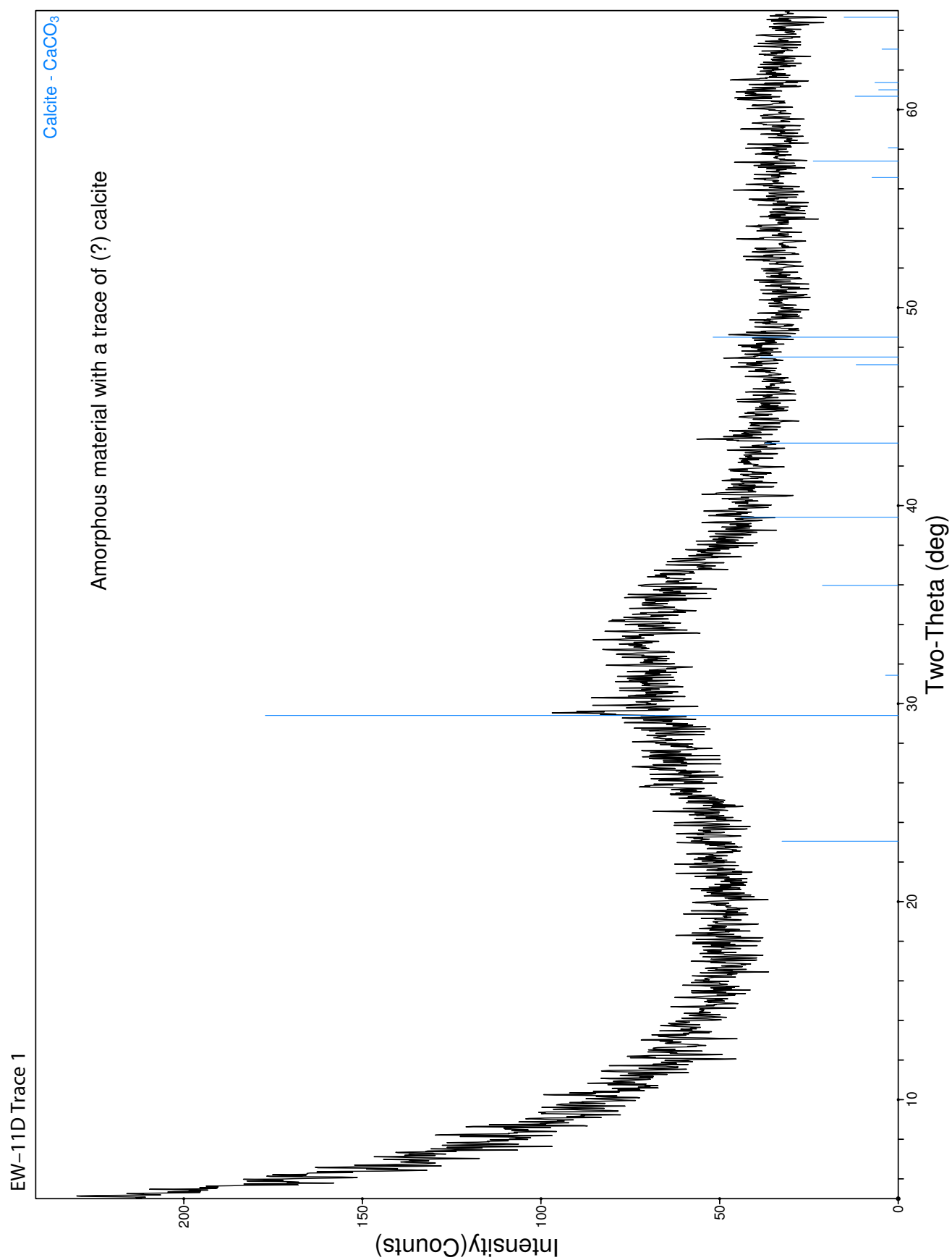
See Extraction Well Construction Report

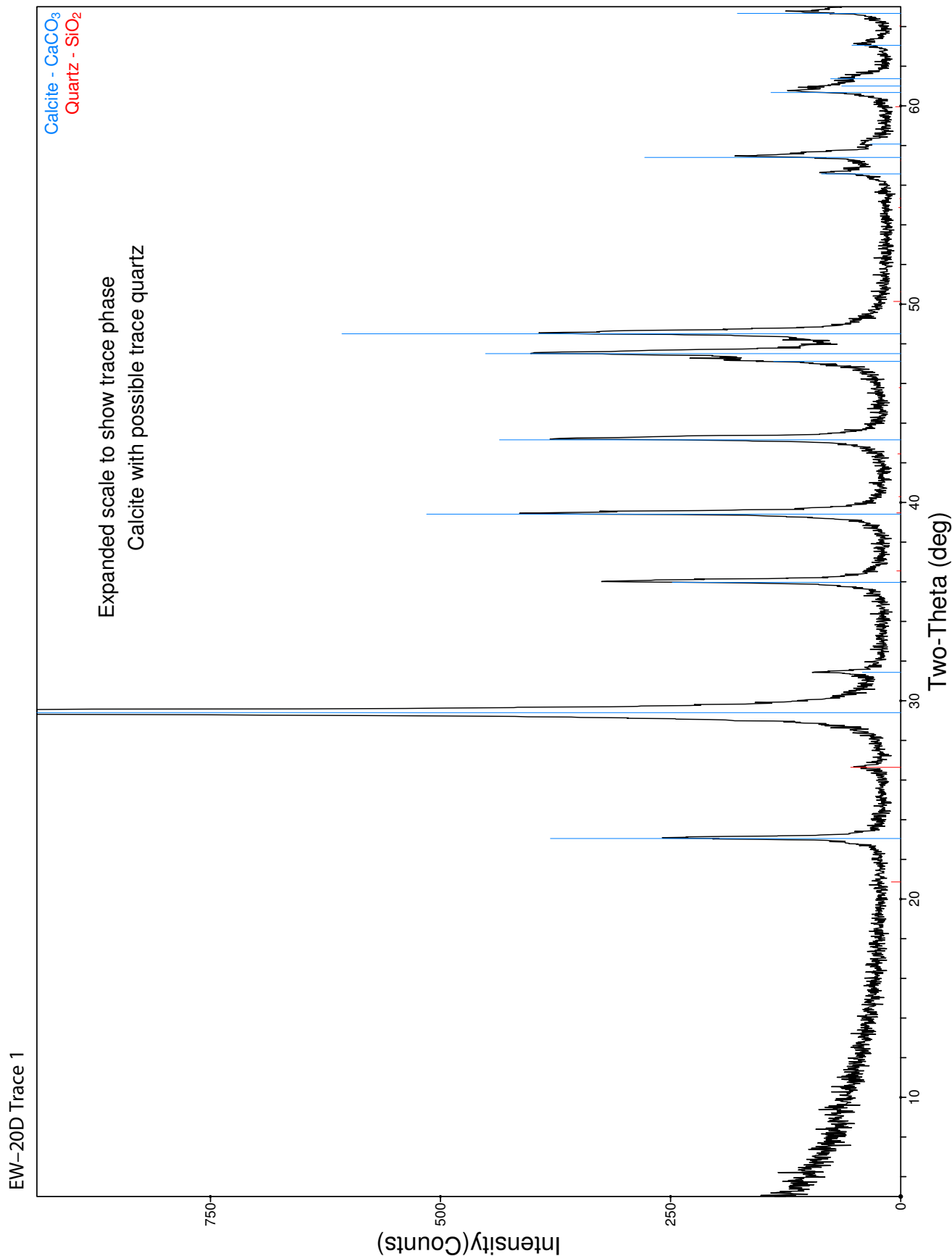
02-09-2008 Z:\PROJECTS\Dyer\Gradient Control\Boring Logs\EW-20A Inu EW-200\EW-20A.bor

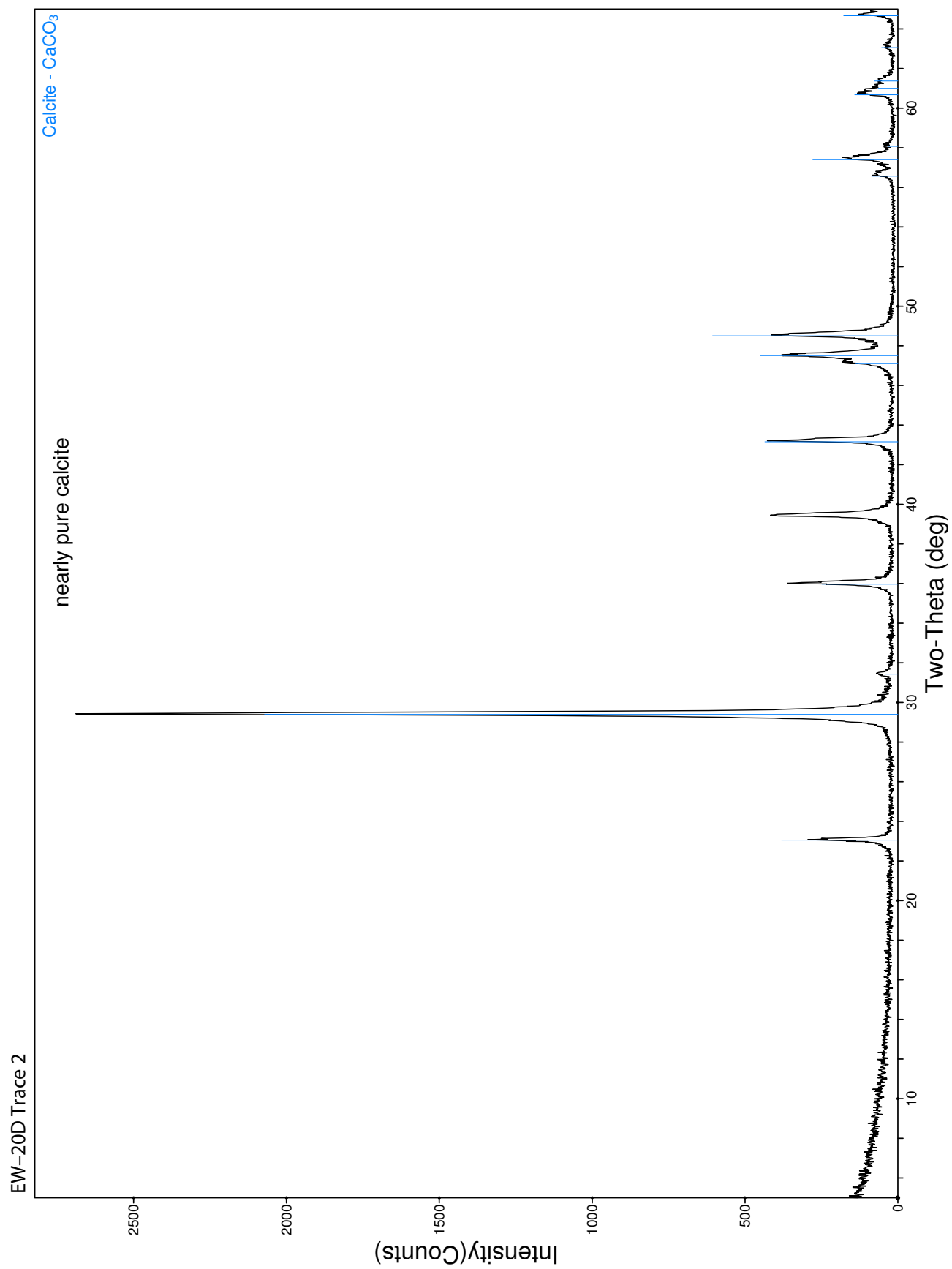
Appendix 2. X-Ray Diffractograms of Solids Collected on Filter with 0.45-Micron Pore Size during Water-Quality Sampling or from Suspended Sediment in Groundwater Samples Collected at the Confined Disposal Facility

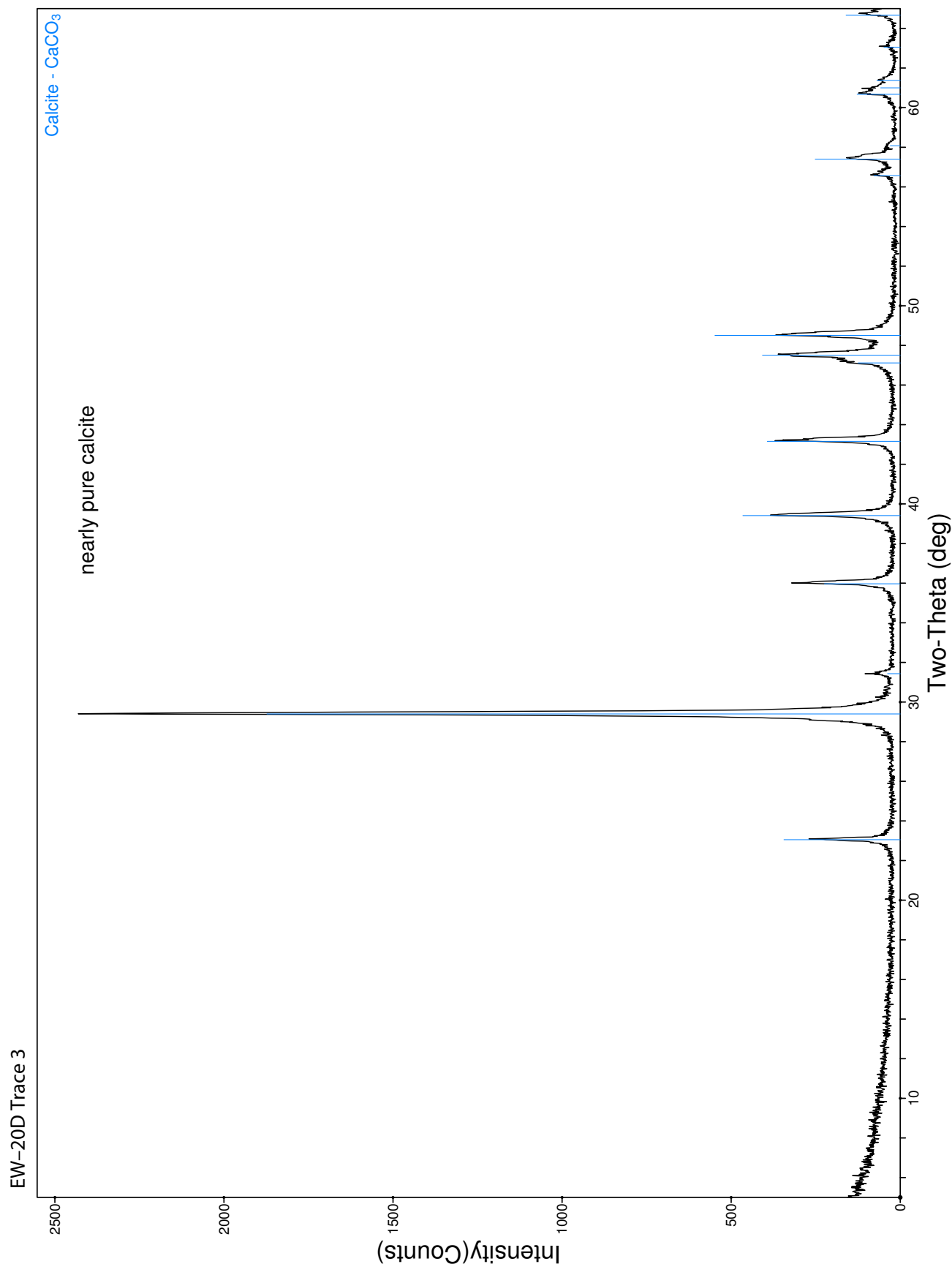


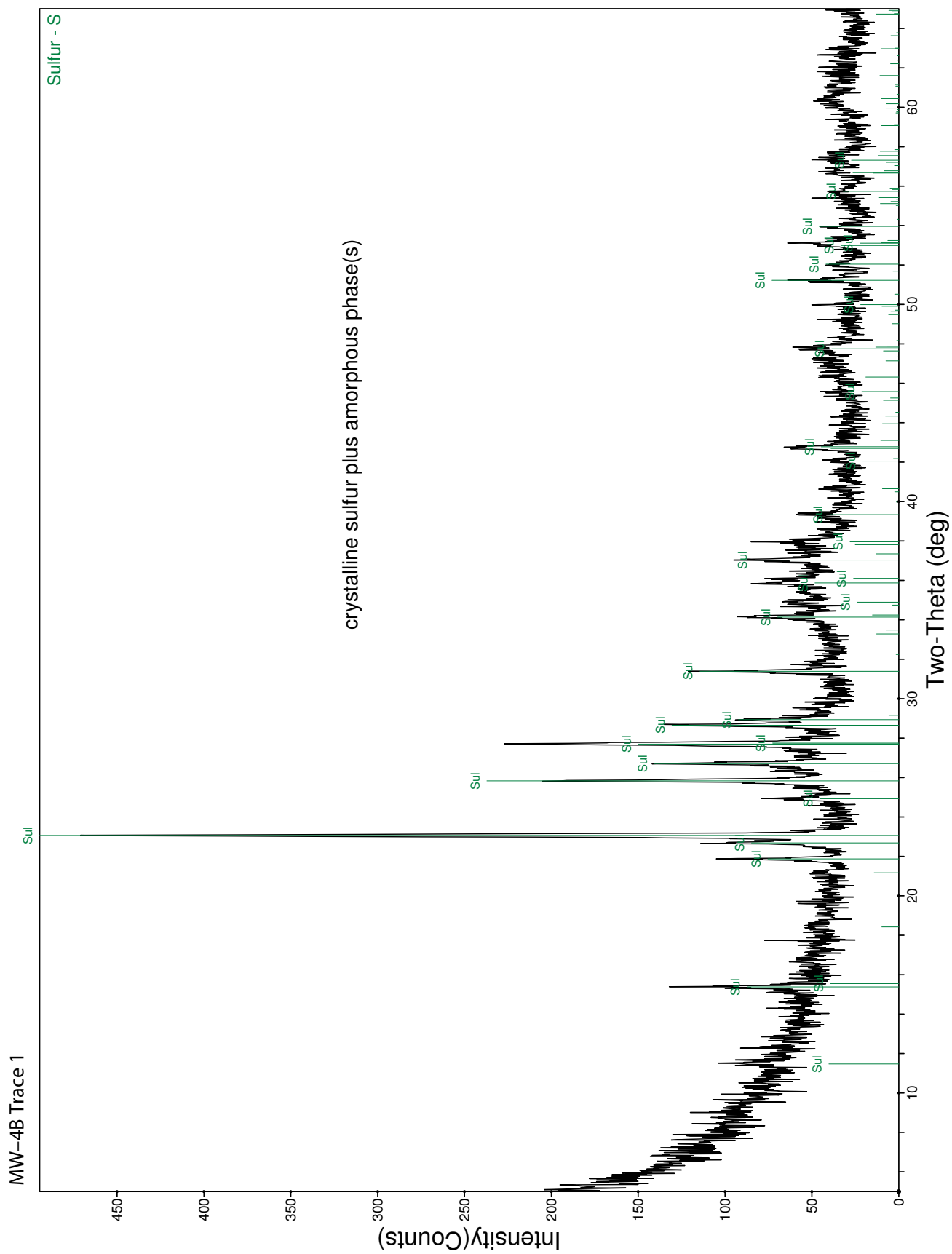


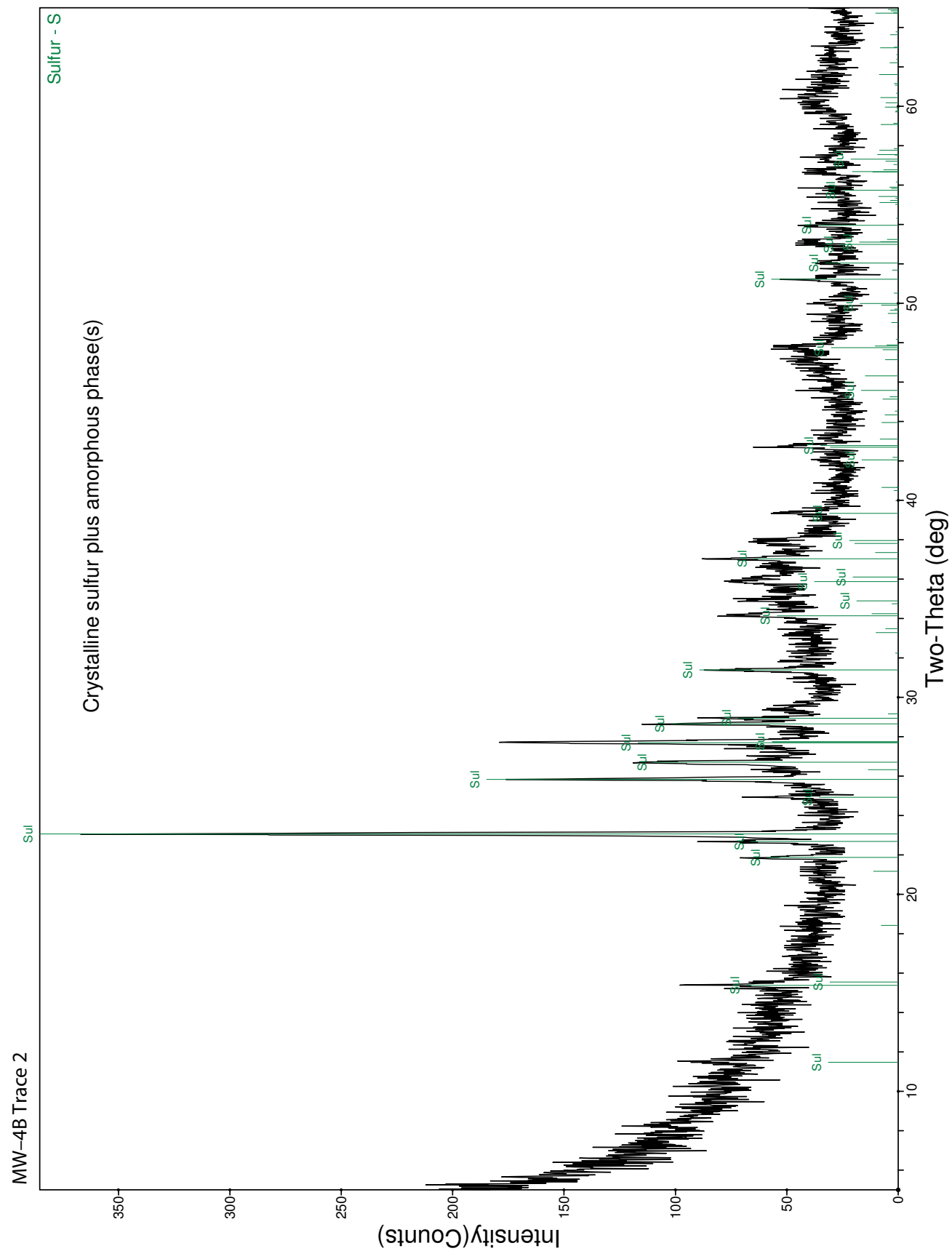






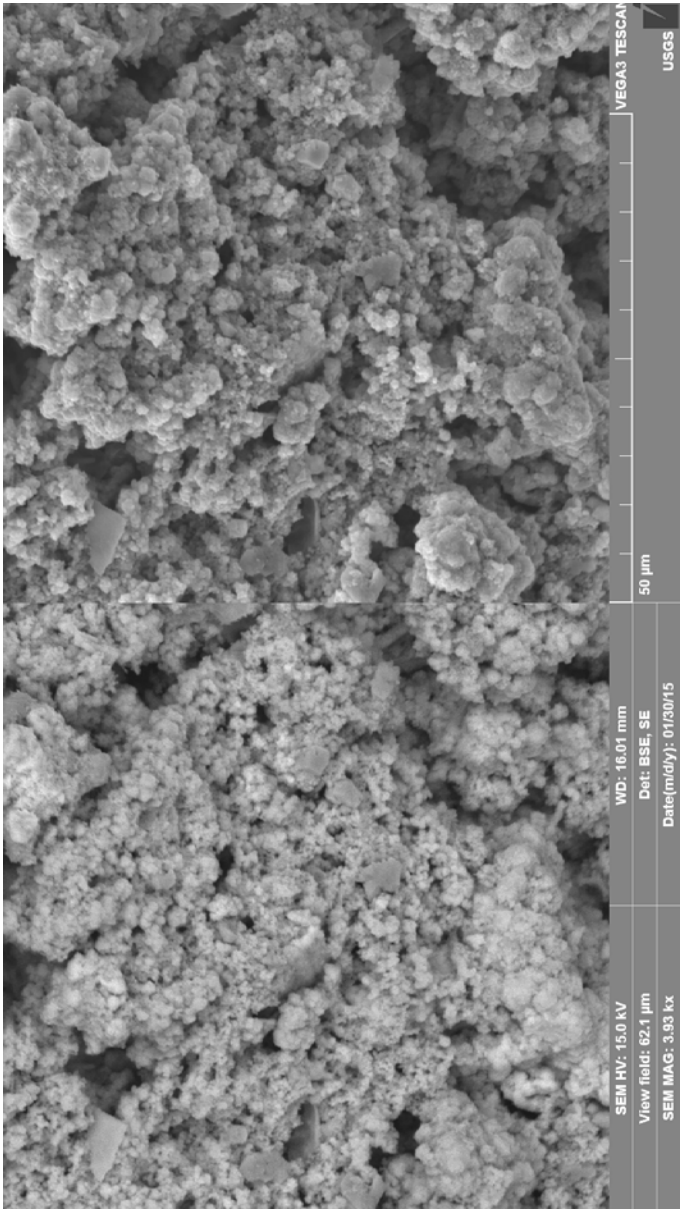
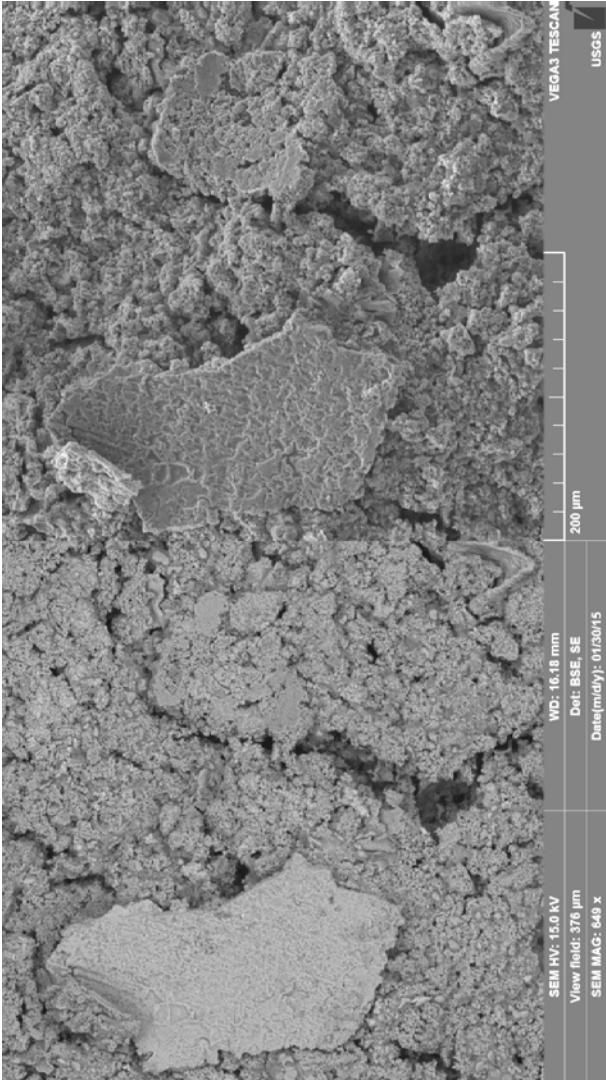






Appendix 3. Scanning Electron Micrographs of Solid Samples Collected on Filter with 0.45-Micron Pore Size during Water-Quality Sampling or from Suspended Sediment in Groundwater Samples Collected at the Confined Disposal Facility

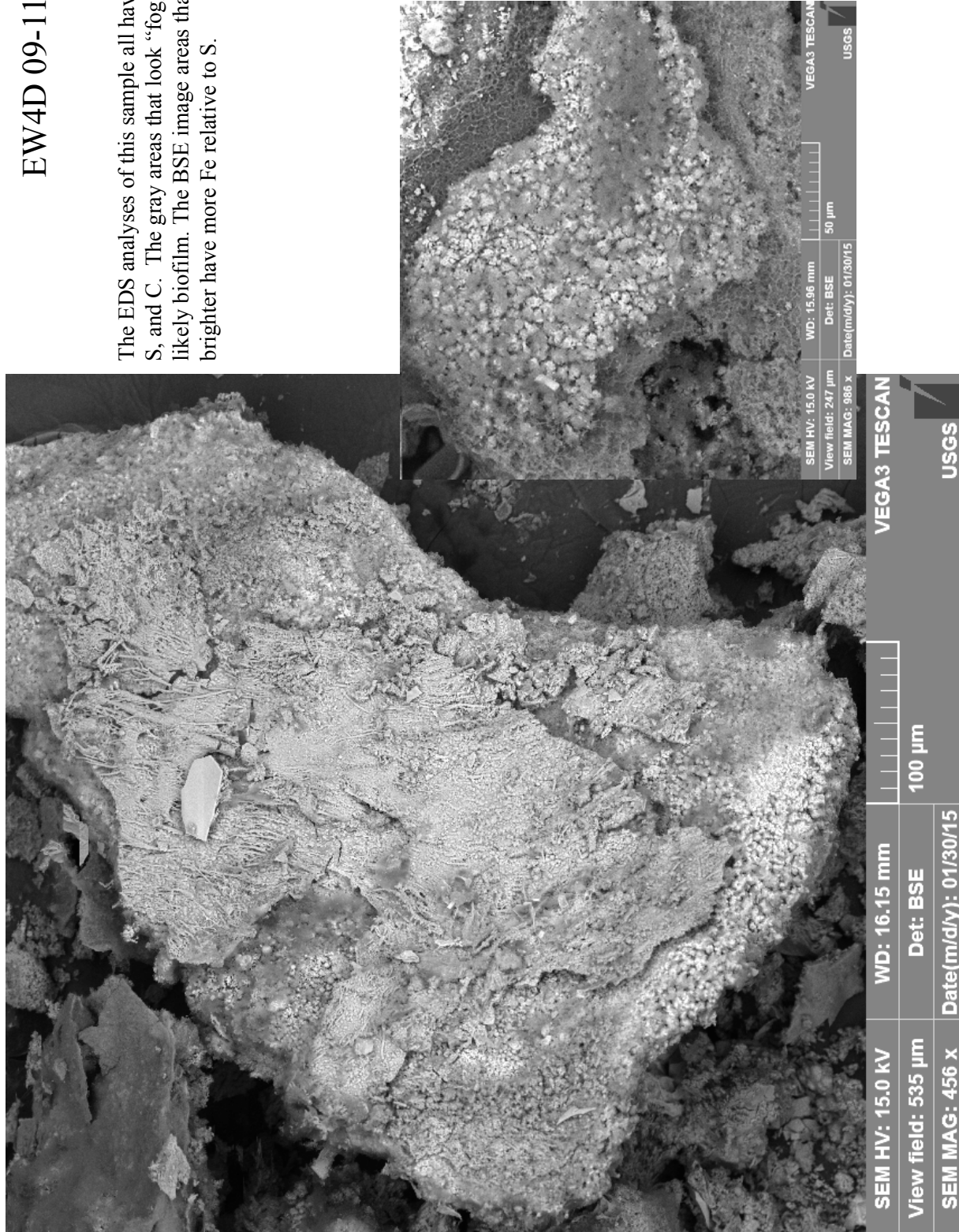
EW4C 10-23-14
EDS analyses of the sample matrix reveals
Fe, S, Ca, and C and in some spots Mg.
Flat piece Fe and S with C.

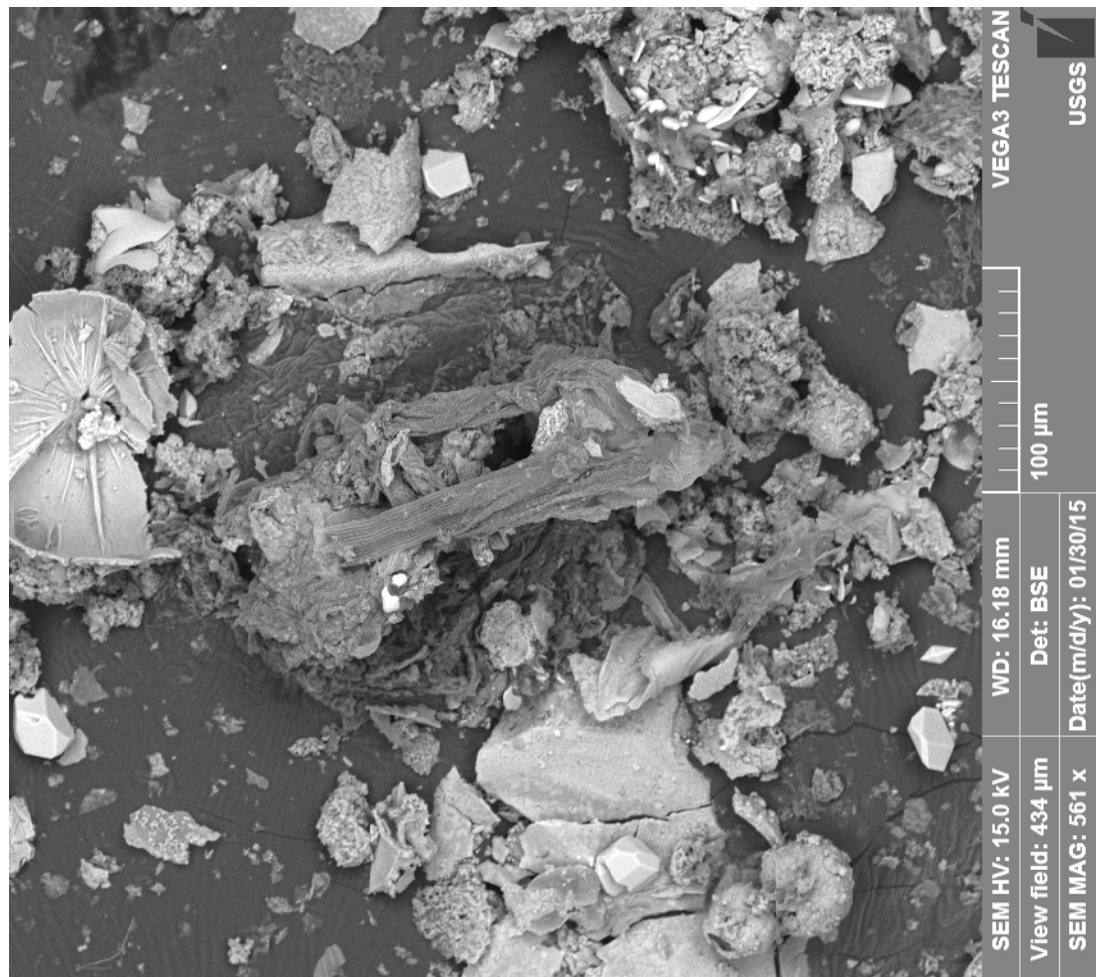
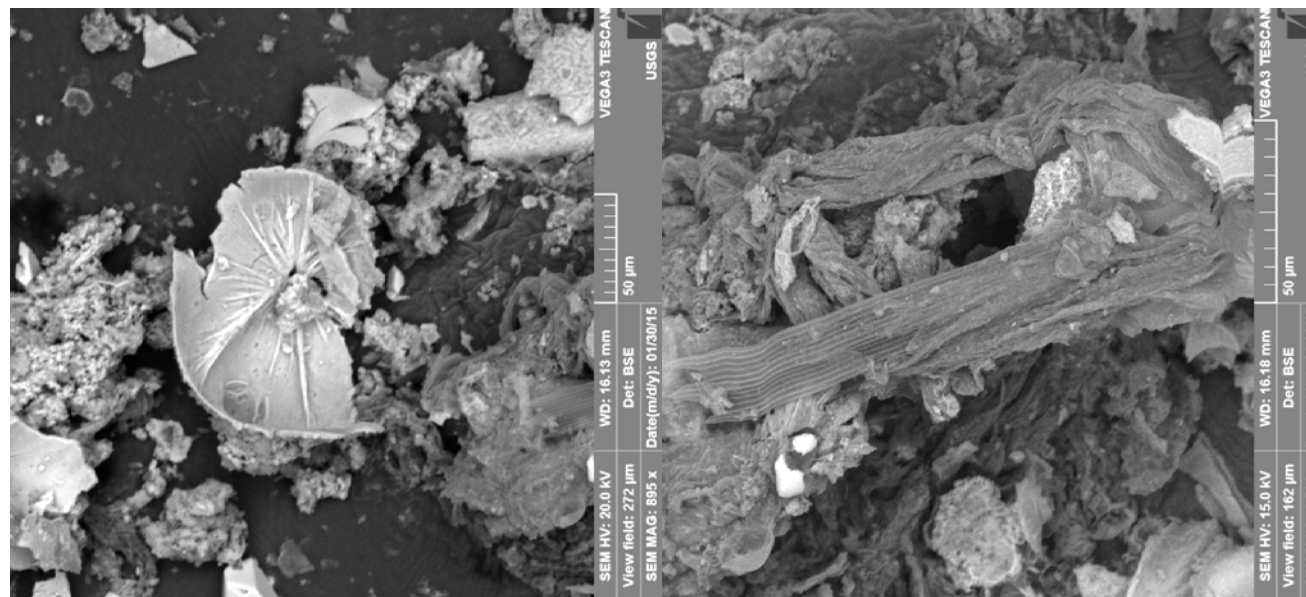


EW4C 10-23-14 C

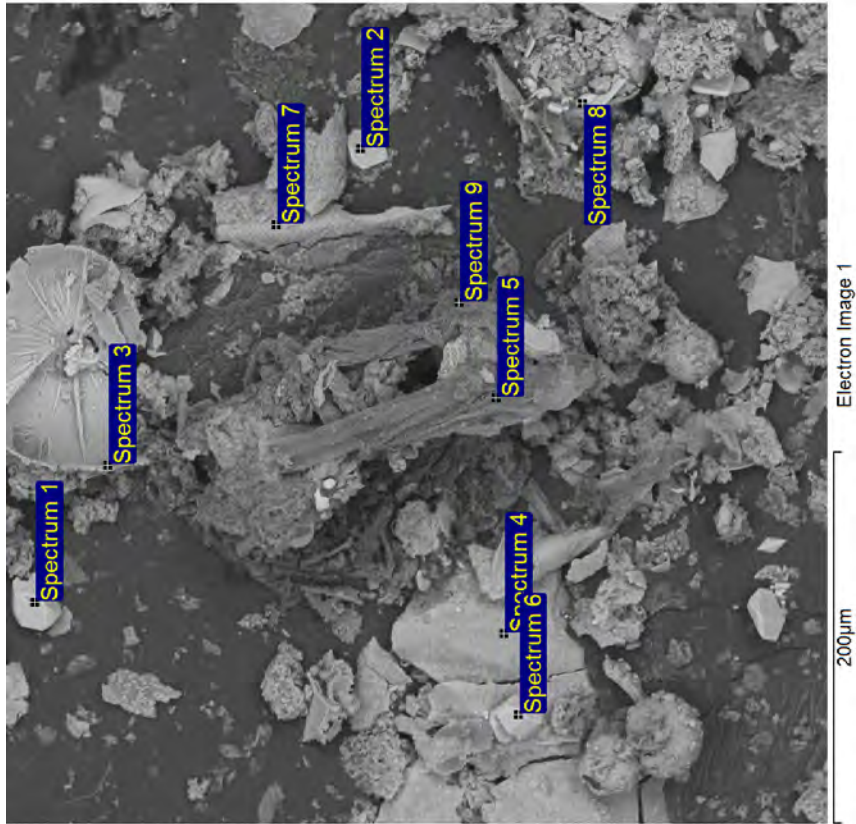
EW4D 09-11-14 D

The EDS analyses of this sample all have Fe, S, and C. The gray areas that look “foggy” are likely biofilm. The BSE image areas that are brighter have more Fe relative to S.



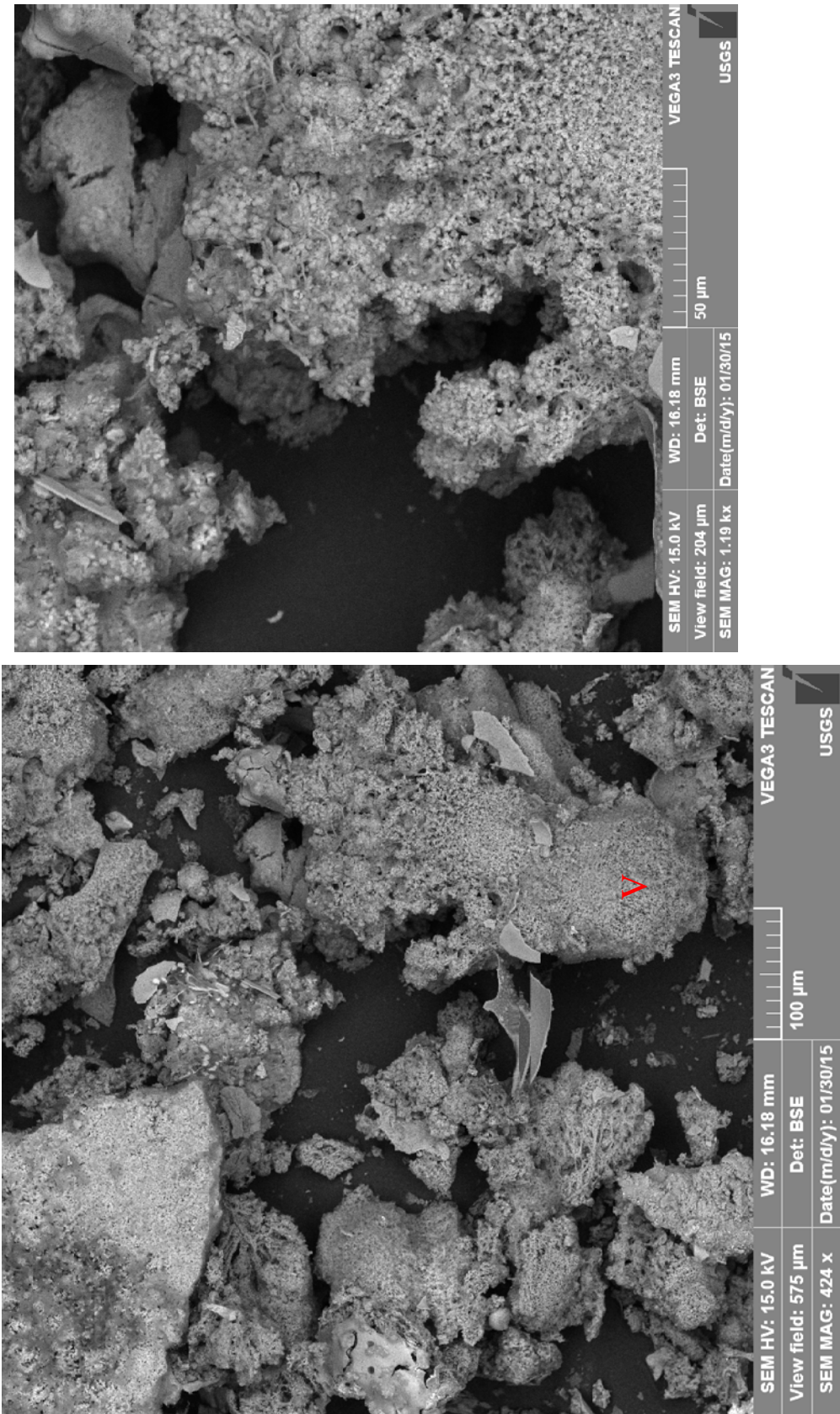


See next page for analyses.



Spectrum	C	Al	Si	S	Ca	Fe	O	Total
Spectrum 1	5.74			31.63			62.63	100
Spectrum 2	7.98			28.34			63.68	100
Spectrum 3	15.16			3.97		26.86	54.02	100
Spectrum 4	17.07			5.4		18.64	58.89	100
Spectrum 5		6.49	17.2	16.3		7.96	52.05	100
Spectrum 6	6.35			30.73			62.92	100
Spectrum 7	14.95			4.91		25.61	54.53	100
Spectrum 8	10.75			24.28			64.97	100
Spectrum 9	20.01	0.69	1.64	4.19	1.43	7.31	64.73	100

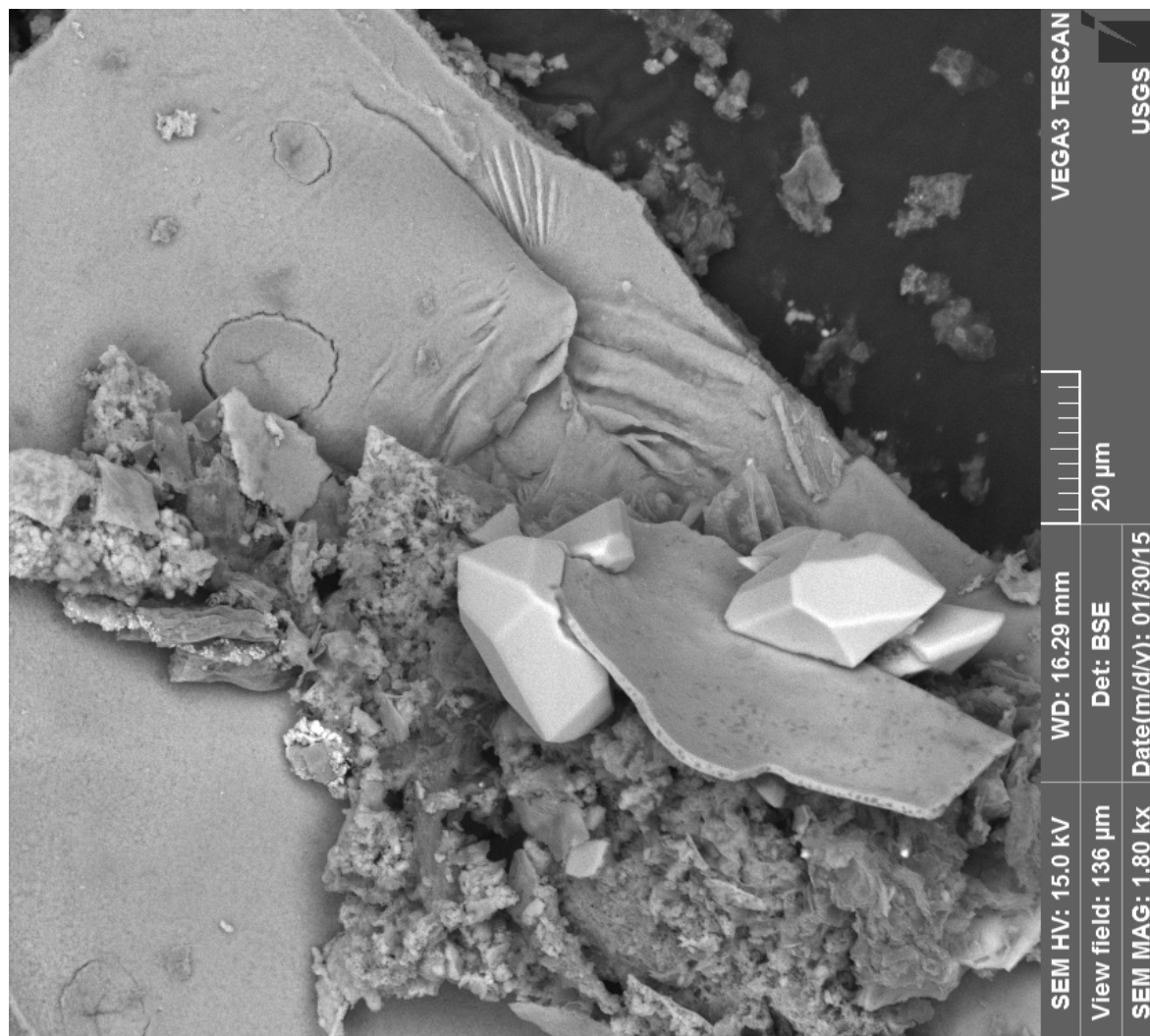
Here is an image with spectra analysis points indicated. These data are not quantitative. The results can be used to say something about concentrations relative to each point, but the results cannot be used as quantitative concentrations of elements.

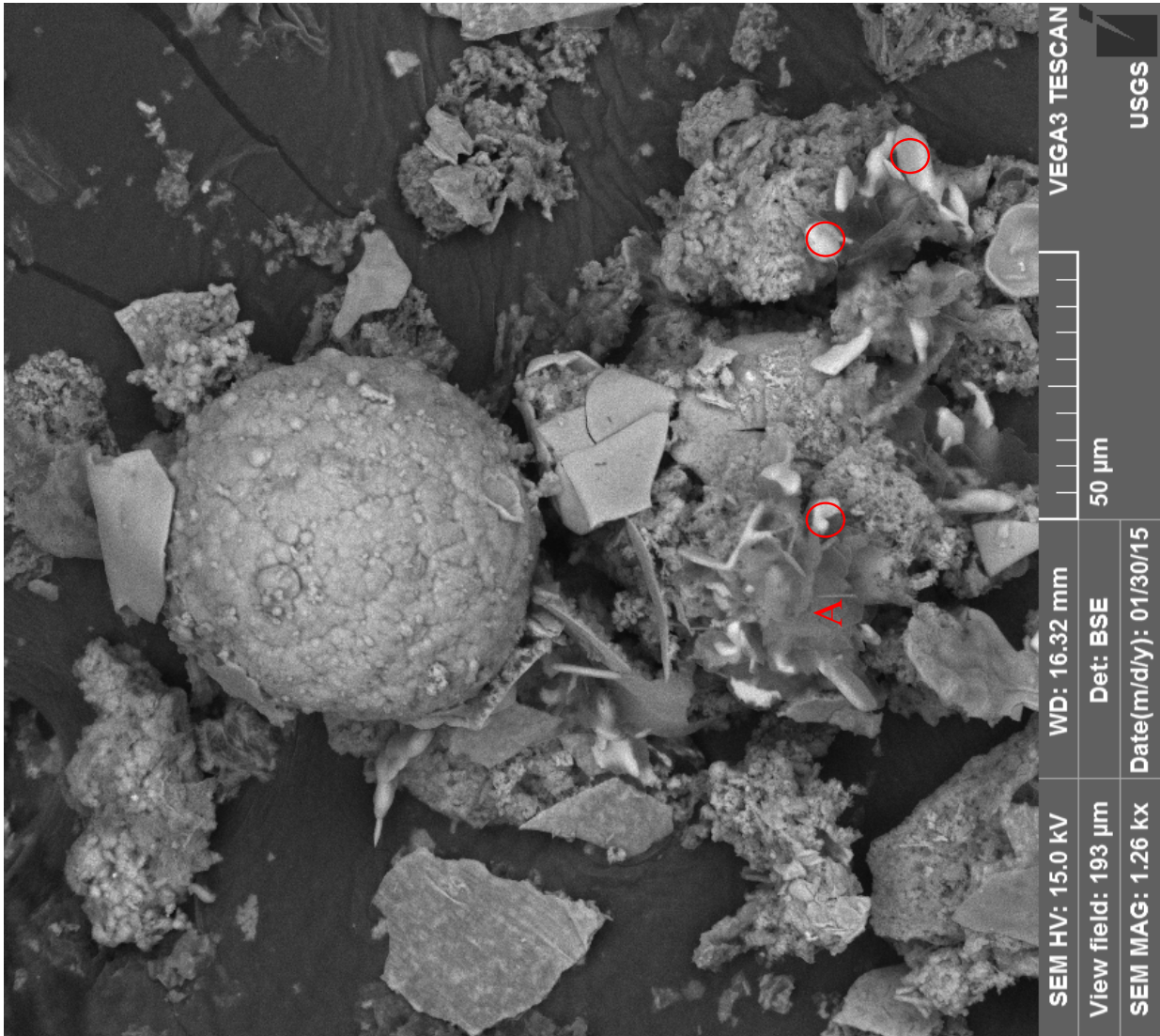


Presumably the spherical object “V” is a whole vacuole. There are mineralized biostructures extending off the vacuole; enlarged on the right. EDS indicate Fe, S, and C.

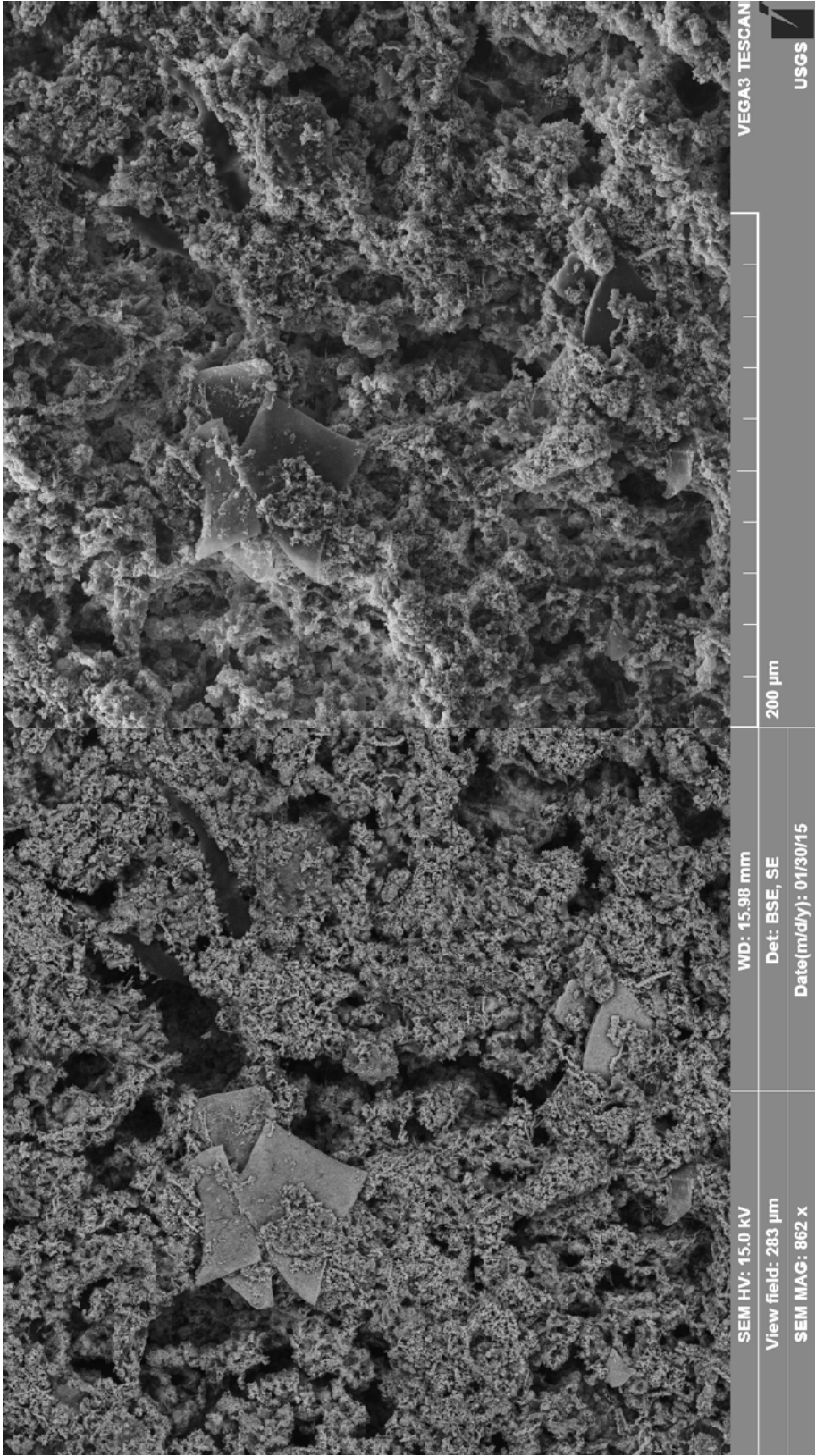
EW4D 09-11-14 D

The EDS analyses of this sample all have Fe, S, and C; except the sulfur crystals (on a broken vacuole plate).





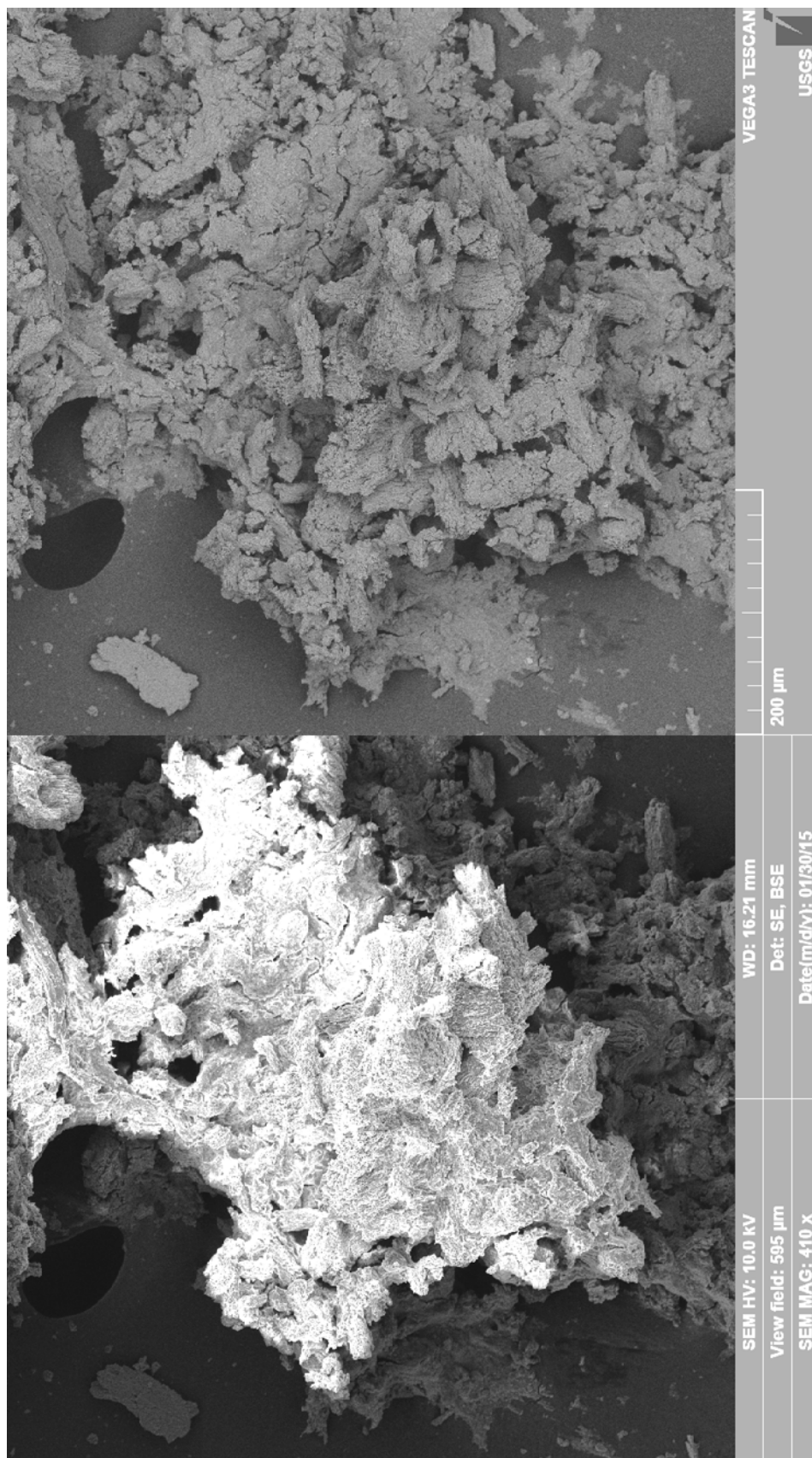
The areas circled in red are S crystals.
Presumably the spherical object is a whole vacuole. The area labeled “A” is likely carbon biofilm.



EW6C 11-6-14

This sample has a relatively homogeneous matrix with tubular feature as imaged here. EDS analysis of the matrix is Fe, Ca, P, Si, and C. The platy structures are Fe > Ca > P > Si > C.

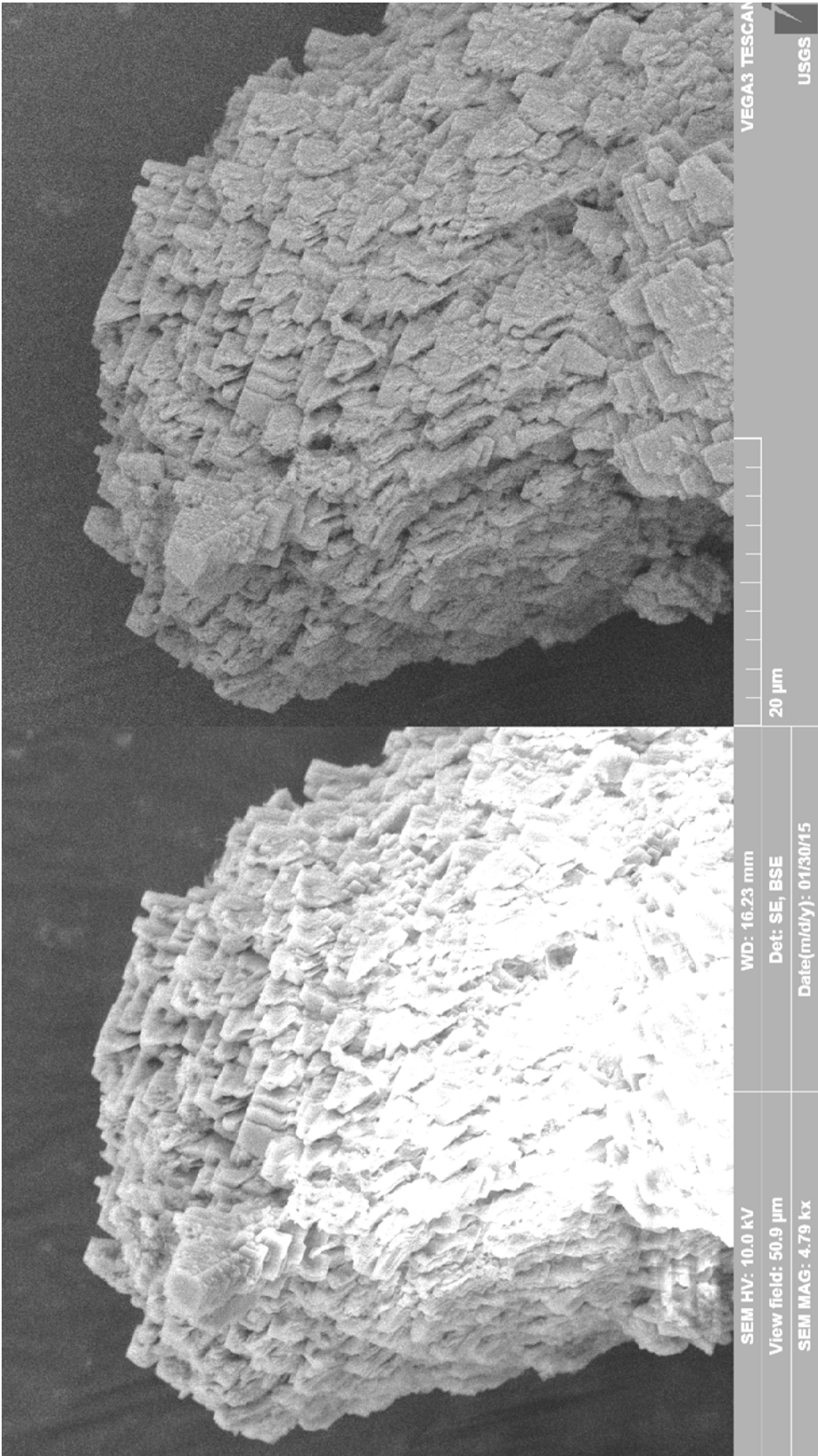
EW6C 11-6-14 B



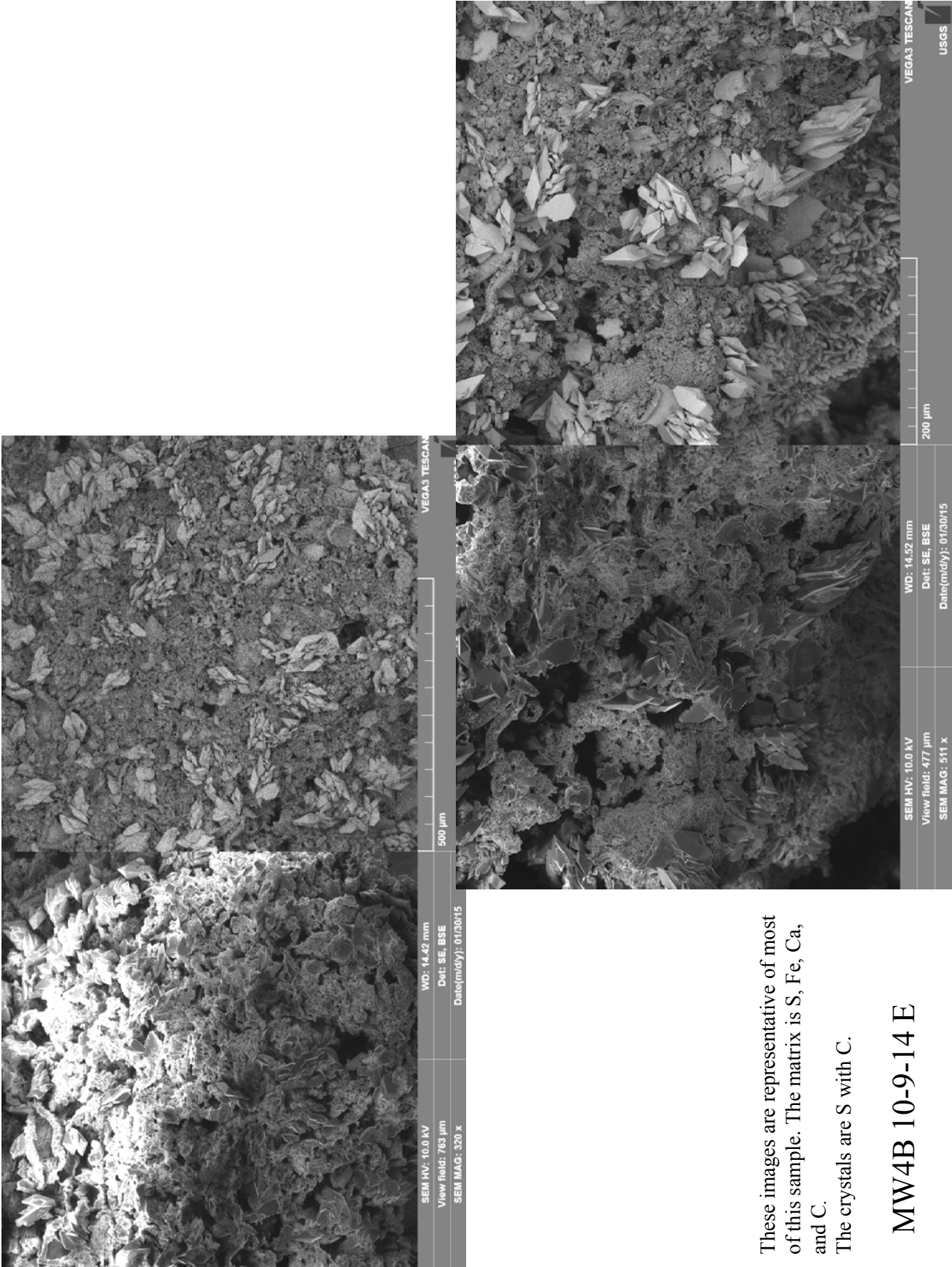
This sample is in a homogeneous matrix as demonstrated by the uniform gray color in the right image (back-scatter electrons). Energy Dispersive X-Ray Spectroscopy (EDS) analyses (not shown) indicate the sample is Ca and C. From the crystal structure the sample is likely calcite, CaCO_3 . The crystalline material is held together by an amorphous matrix or biofilm as indicated by desiccation cracks. The bright area in the left image (secondary electron image) shows that the sample was not well grounded.

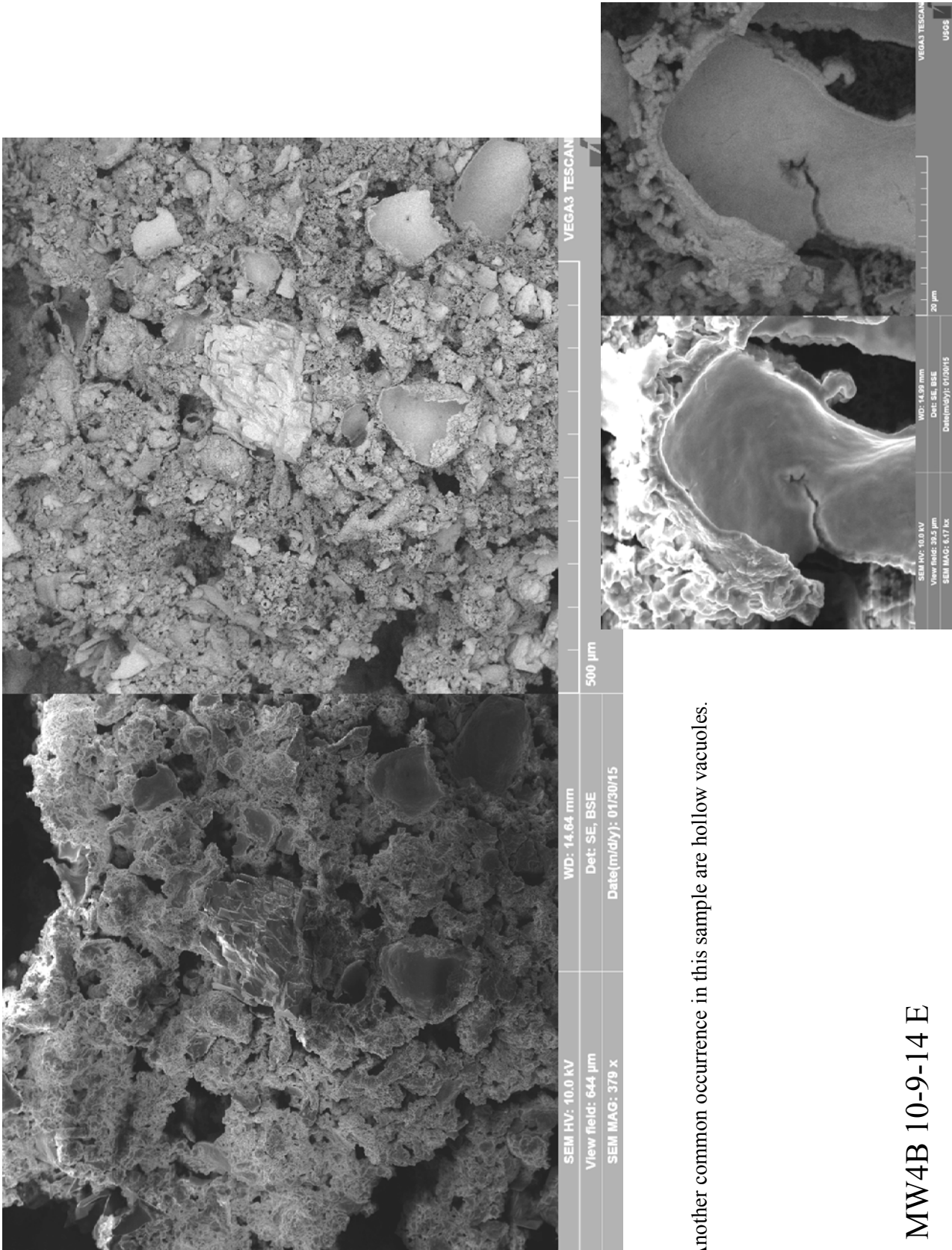
EW20D 10-23-14 I

EW20D 10-23-14 I



Enlargement of the CaCO₃ precipitate.

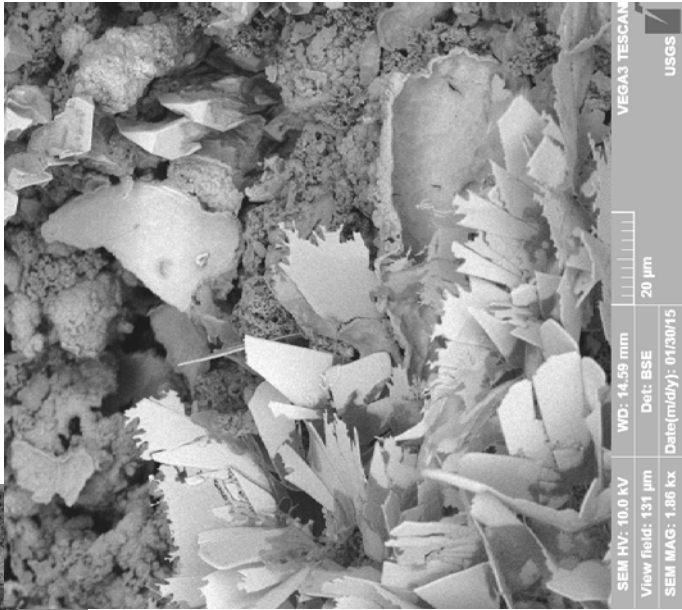
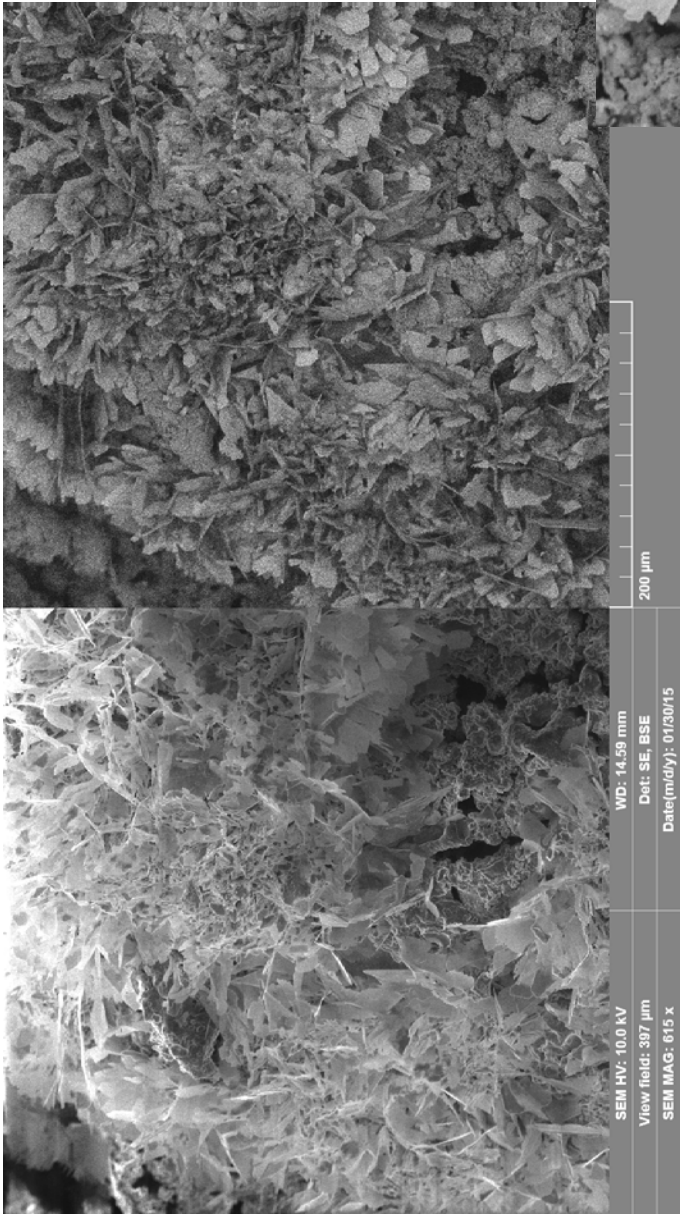




Another common occurrence in this sample are hollow vacuoles.

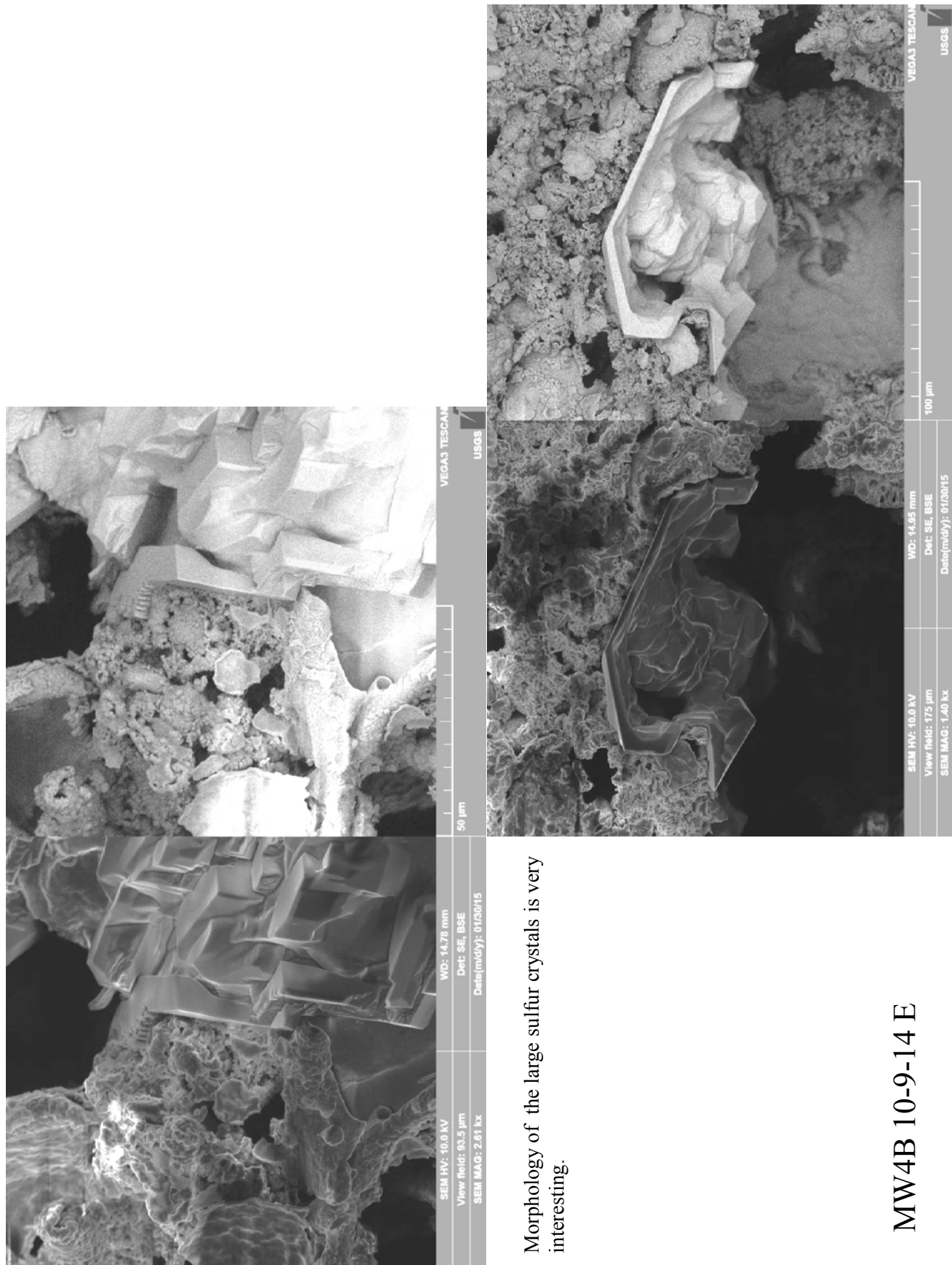
MW4B 10-9-14 E

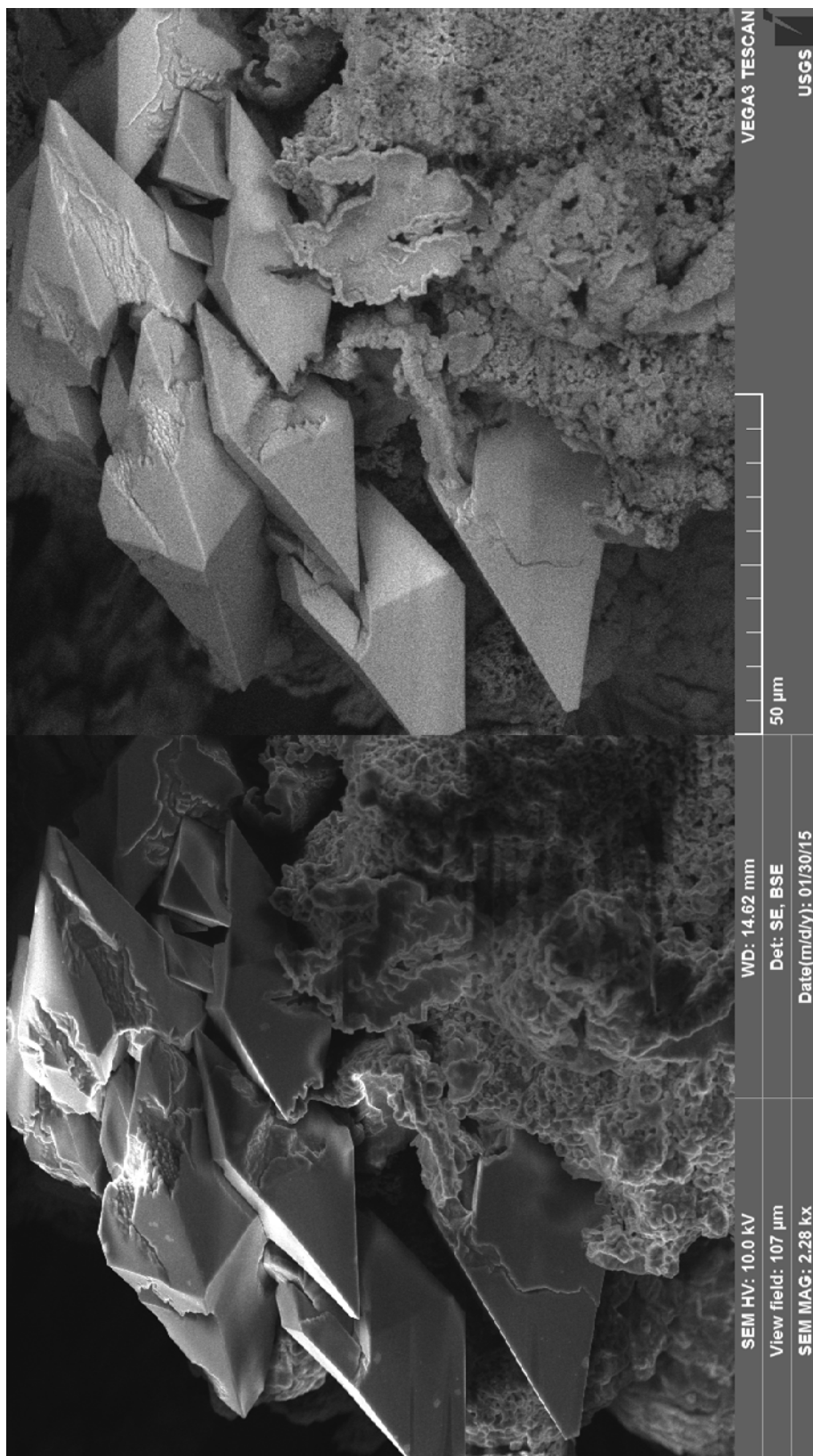
MW4B 10-9-14 E



The area circled in red below is imaged here. The buff colored precipitate appeared as the sample dried on the SEM stub. These are crystals of sulfur, the frilled upper edge of the crystals is due to evaporative precipitation.

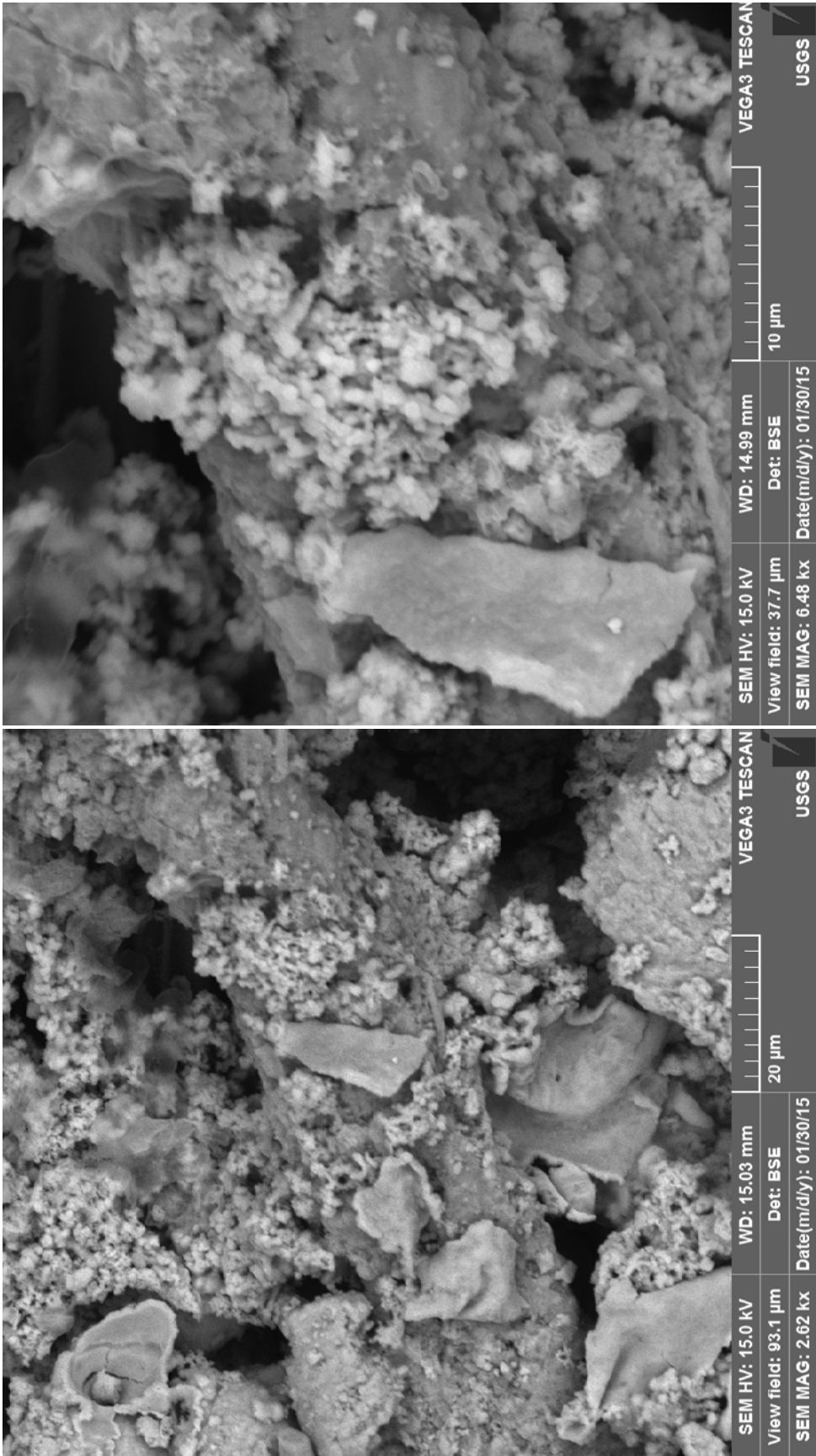




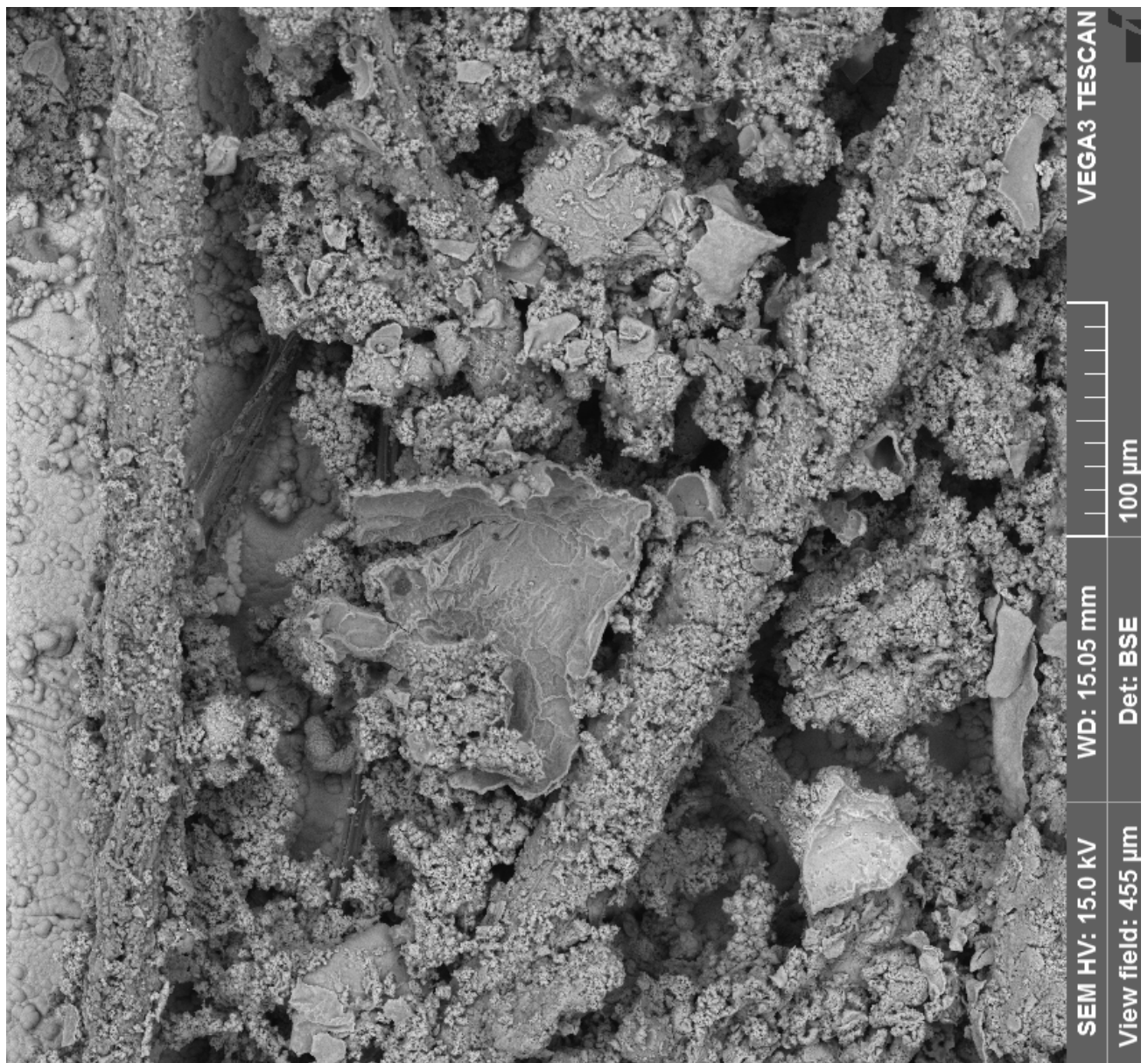


A cluster of sulfur crystals.

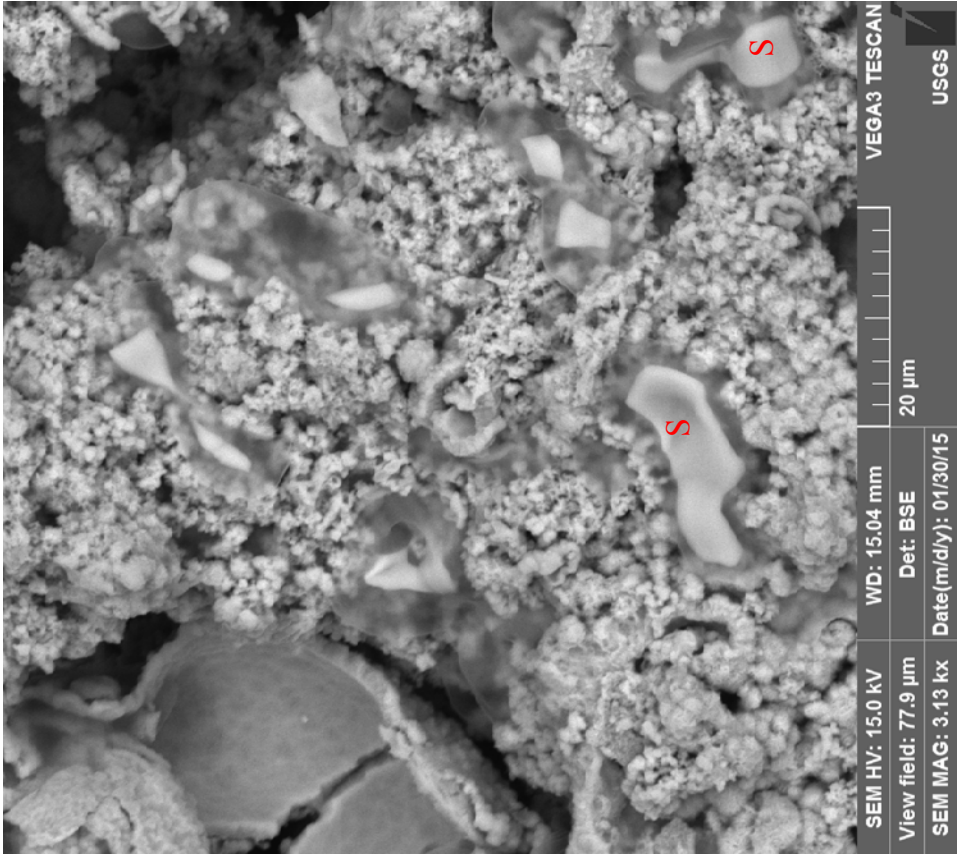
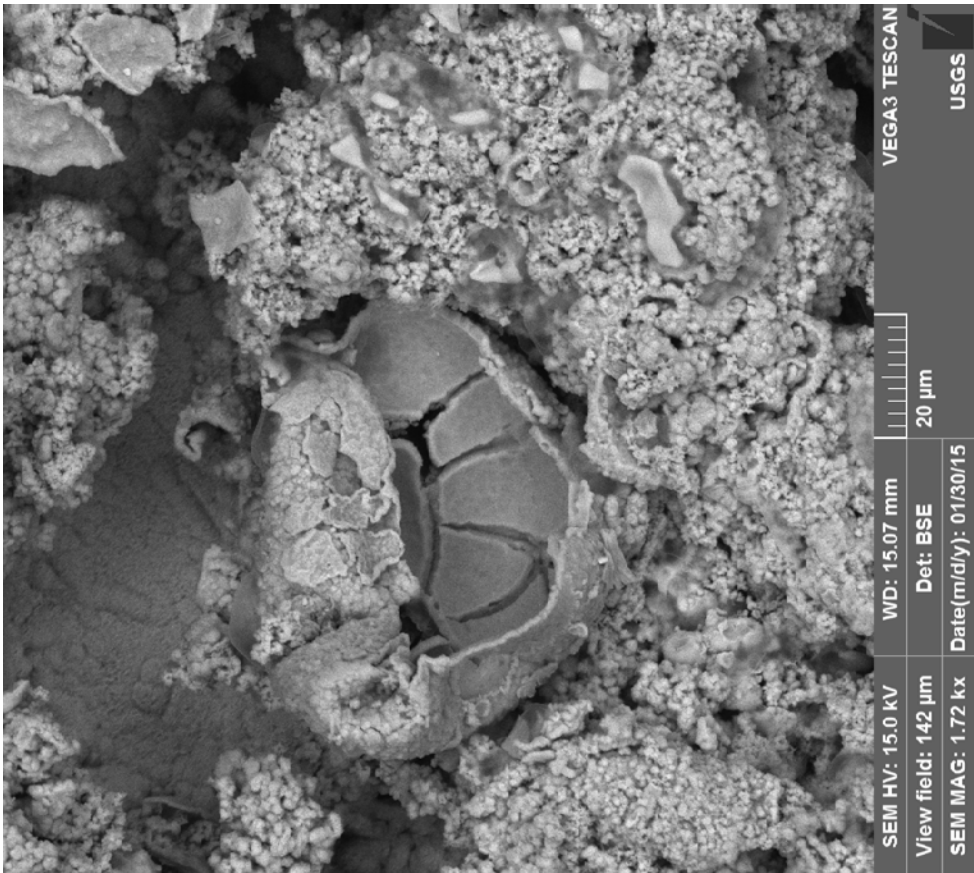
MW4B 10-9-14 E



This sample had strings of biofilm, one crosses the left image above. The string was high C with S, Fe, and traces of Ca and Mg. Matrix EDS analyses detected Fe, S, Ca, and C with minor Mg and Si.



The sulfur crystals (S) are surrounded by biofilm. Vacuole and matrix Fe, S₂ and C with minor Ca and Mg.



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