Prepared in cooperation with the Lahontan Regional Water Quality Control Board

Groundwater Chemistry and Hexavalent Chromium

Chapter E of

Natural and Anthropogenic (Human-Made) Hexavalent Chromium, Cr(VI), in Groundwater near a Mapped Plume, Hinkley, California

Professional Paper 1885-E

U.S. Department of the Interior
U.S. Geological Survey

Front cover

Boxplots showing hexavalent chromium concentrations in water.

Hexavalent chromium concentrations in water (U.S. Geological Survey data), March 2015 through November 2017.

Background photograph: Pacific Gas and Electric Company (PG&E) compressor station, Hinkley, California, March 2009. Photograph by Steven Perry, ARCADIS, Inc., courtesy of PG&E.

Redox potential as a function of pH for wells sampled by the U.S. Geological Survey.

Specific conductance in water from wells sampled by the Pacific Gas and Electric Company.

Hexavalent chromium concentrations in water (Pacific Gas and Electric Company data), October–December 2015.

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This study was developed by the U.S. Geological Survey (USGS) with input from a technical working group (TWG) composed of community members, the Lahontan Regional Water Quality Control Board (RWQCB), the Independent Review Panel Manager (Project Navigator, Ltd.), Pacific Gas and Electric Company (PG&E), and consultants for PG&E. The study was funded cooperatively under an agreement between the Lahontan RWQCB and the USGS. Funding for the study was provided by PG&E to the Lahontan RWQCB. Logistical support for field work, including access to wells, was provided by PG&E. The TWG met approximately quarterly during the study to provide input to the study, and the Hinkley community was updated annually on study progress.

The authors thank the many people involved in the design and implementation of this study including the staff of the Lahontan RWQCB, the staff of PG&E and their consultants, and the staff of Project Navigator, Ltd. The authors also acknowledge and thank the many involved community members who allowed access to their properties for sample collection, and who collectively donated thousands of hours on behalf of the local community in support of this project and for resolution of other issues related to anthropogenic hexavalent chromium, Cr(VI), within the Hinkley area.

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)

International System of Units to U.S. customary units

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
micrometer (µm)	0.00003937	inch (in.)
Volume		
liter (L)	33.81402	ounce, fluid (fl. oz)
milliliter (mL)	0.033814	ounce, fluid (fl. oz)
	Mass	
microgram (µg)	0.00000003527	ounce, avoirdupois (oz)
milligram (g)	0.00003527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Datum

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

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

Below land surface (bls) is the datum used to describe depth.

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

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Concentrations of chemical constituents in rock or unconsolidated solids are given in milligrams per kilogram (mg/kg).

Redox, a combination of the words reduction and oxidation, refers to chemical processes in which one substance or molecule gains an electron (is reduced and its oxidation state is decreased) and another loses an electron (is oxidized and its oxidation state is increased). The processes of oxidation and reduction occur simultaneously and cannot occur independently.

Abbreviations

BD-90/90	binomial distribution 90/90
Ca^{2+}	calcium ion
Cl^{1-}	chloride ion
CO_3^{2-}	carbonate ion
Cr(III)	trivalent chromium having an oxidation state of +3
$Cr(OH)_3$	chromium hydroxide solid
$Cr(OH)_3^0{}_{(aq)}$	chromium hydroxide ion
Cr(t)	total dissolved chromium
Cr(VI)	hexavalent chromium having an oxidation state of +6
CrO_4^{2-}	chromate ion
Eh	redox potential
EPA	U.S. Environmental Protection Agency
Fe	iron
Fe(II)	ferrous iron having an oxidation state of +2
Fe(III)	ferric iron having an oxidation state of +3
GAMA	Groundwater Ambient Monitoring and Assessment
GFAAS	graphite furnace atomic absorption spectroscopy
HCO_3^{1-}	bicarbonate ion
$HCrO_4^{1-}$	hydrogen chromate ion
ICP-MS	inductively coupled plasma-mass spectrometry
IRP	Independent Review Panel
K^{1+}	potassium ion
LRL	laboratory reporting level
LTU	land treatment unit

MCL	maximum contaminant level
Mg^{2+}	magnesium ion
Mn	manganese
Mn(III)	manganese having an oxidation state of +3
Mn(III/IV)	manganese oxide with some manganese having an oxidation state of +3 and some having an oxidation state of +4
Mn(IV)	manganese having an oxidation state of +4
MSE	mean square error
N	nitrogen
Na^{1+}	sodium ion
$NaCrO_4^{1-}$	Sodium chromate ion
NIST	National Institute of Standards and Technology
NL	notification level
NO_3^{1-}	nitrate
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
ORP	oxidation reduction potential
PCA	principal component analysis
PG&E	Pacific Gas and Electric Company
psi	pounds per square inch
p-value	probability value
Q4 2015	October–December 2015
R^2	coefficient of determination
RMSD	root mean square difference
RSIL	Reston Stable Isotope Laboratory
RWQCB	Regional Water Quality Control Board
SAS	Statistical Analysis System
SO_4^{2-}	sulfate ion
SRL	study reporting level
SSA	summative-scale analysis
SSRL	Stanford Synchrotron Radiation Lightsource
TWG	technical working group
USGS	U.S. Geological Survey
XANES	X-ray absorption near-edge structure
$\delta^{18}O$	delta oxygen-18
δD	delta deuterium isotope data

Groundwater Chemistry and Hexavalent Chromium

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Abstract

Water samples collected by the U.S. Geological Survey from more than 100 wells between March 2015 and November 2017 in Hinkley and Water Valleys, in the Mojave Desert 80 miles northeast of Los Angeles, California, were analyzed for field parameters, major ions, nutrients, and selected trace elements, including hexavalent chromium, Cr(VI). Water from most wells was alkaline and oxic. The pH ranged from 6.9 in water-table wells near recharge areas along the Mojave River to 9.4 in deeper wells farther downgradient in the northern subarea.

Hexavalent chromium concentrations measured by ion chromatography using U.S. Environmental Protection Agency Method 218.6 and a version of that method used for detection of Cr(VI) concentrations as low as 0.06 micrograms per liter (μg/L), produced results comparable to field speciation with subsequent analyses by graphite furnace atomic absorption spectroscopy (coefficient of determination, R^2, of 0.97). Hexavalent chromium concentrations ranged from less than the study reporting level of 0.10 to 2,500 μg/L. The highest concentrations were within the October–December 2015 (Q4 2015) regulatory Cr(VI) plume downgradient from the Hinkley compressor station. Hexavalent chromium concentrations outside the Q4 2015 regulatory Cr(VI) plume were as high as 11 μg/L. Hexavalent chromium concentrations in water from most wells were distributed in a narrow redox potential and pH band within the overlapping chromate ion, $CrO_4^{2-}{}_{(aqueous)}$, and manganese-3, $Mn(III)_{(solid)}$, stability fields. The redox potential of water from some wells completed in carbonate-rich mudflat/playa deposits approached the more oxic manganese-4, $Mn(IV)_{(solid)}$, stability field. However, Cr(VI) concentrations in porewater pressure-extracted from Mn(IV)-containing deposits in the eastern subarea did not exceed 3.3 μg/L, and porewater does not appear to be a source of Cr(VI) concentrations greater than this concentration in water from wells in the eastern subarea.

On the basis of comparison with California-wide data, Cr(VI) concentrations at the measured pH were higher than expected for uncontaminated water from wells (1) within the Q4 2015 regulatory Cr(VI) plume, (2) within the eastern subarea nominally crossgradient from the Hinkley compressor station and upgradient from the Q4 2015 regulatory Cr(VI) plume, and (3) from shallow wells in the northern subarea downgradient from the leading edge of the Q4 2015 regulatory Cr(VI) plume. Hexavalent chromium concentrations in alkaline water from wells in the northern subarea of Hinkley Valley and in Water Valley were within ranges expected for uncontaminated water elsewhere in California given their pH and trace-element composition. Hexavalent chromium concentrations were higher than expected on the basis of selected trace-element concentrations that co-occur with Cr(VI) in water from wells within the Q4 2015 regulatory Cr(VI) plume and from wells in the eastern and northern subareas near the plume margins. Hexavalent chromium concentrations did not exceed 4 μg/L in water from domestic wells sampled in Hinkley and Water Valleys and were generally within ranges expected for uncontaminated groundwater given their pH and trace-element composition.

Interpretations derived from Cr(VI) and pH, and from Cr(VI) and selected trace-element concentrations collected between March 2015 and November 2017 were used within a summative-scale analysis to determine the Cr(VI) plume extent (chapter G). However, Cr(VI) background concentrations (chapter G) were calculated from regulatory data collected from selected wells between April 2017 and January 2018.

E.1. Introduction

The Pacific Gas and Electric Company (PG&E) Hinkley compressor station is used to compress natural gas as it is transported through a pipeline from Texas to California. Between 1952 and 1964, cooling water used at the Hinkley compressor station was treated with a compound containing hexavalent chromium, Cr(VI), to prevent corrosion of machinery within the compressor station. Cooling-tower water was discharged to unlined ponds, releasing Cr(VI) into groundwater in the underlying unconsolidated aquifer (Lahontan Regional Water Quality Control Board, 2013a). The U.S. Geological Survey (USGS) was requested by the Lahontan Regional Water Quality Control Board (RWQCB) to complete an updated background study of Cr(VI) concentrations in Hinkley and Water Valleys.

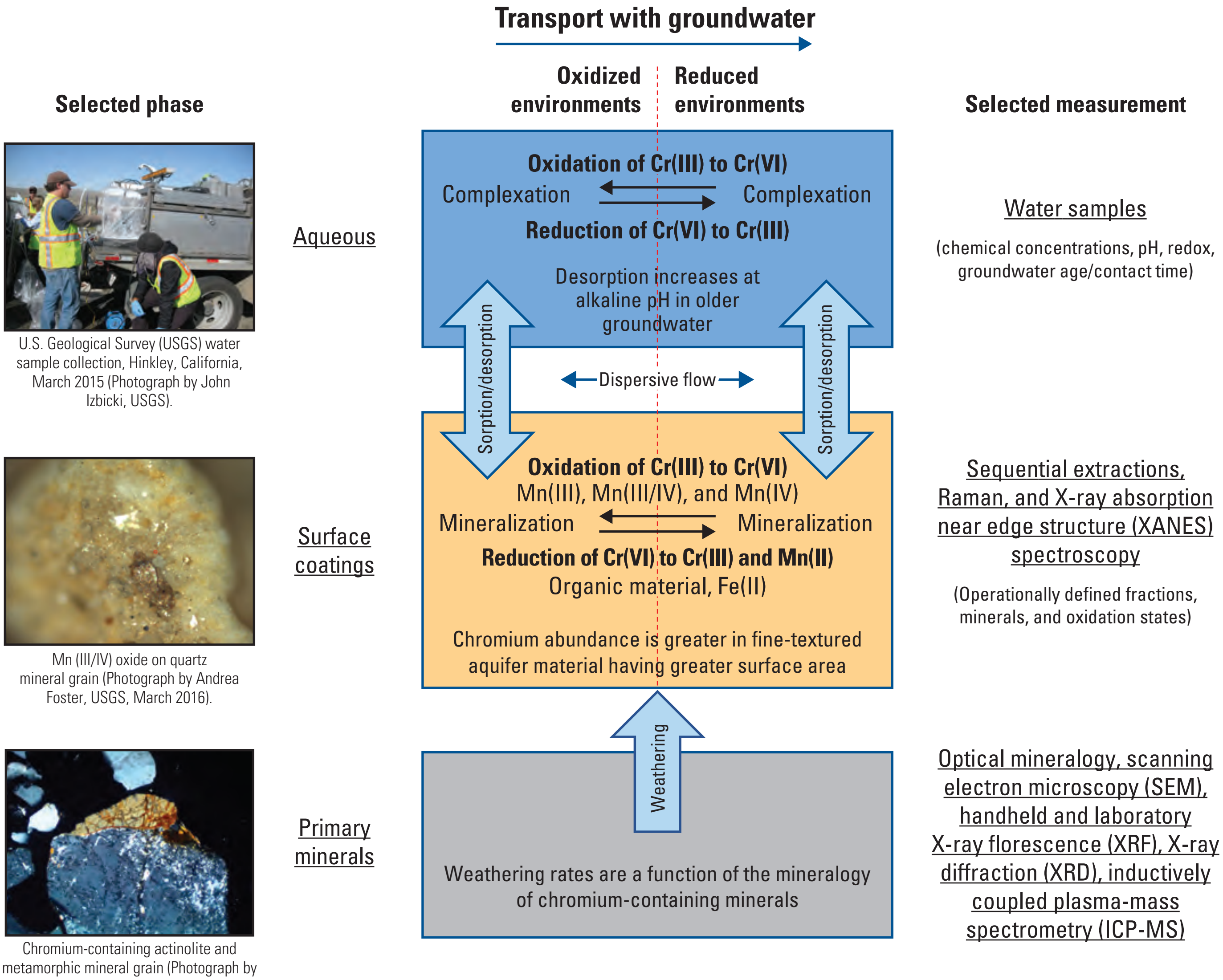
E.1.1. Chromium Geochemistry

Chromium may be present naturally in groundwater as reduced trivalent chromium, Cr(III), or as oxidized Cr(VI); Rai and Zachara, 1984; Guertin and others, 2004). Trivalent chromium is the predominate form of chromium in acidic, reduced (oxygen absent) groundwater (Rai and Zachara, 1984; Ball and Nordstrom, 1998), and Cr(III) concentrations can exceed several hundred micrograms per liter (µg/L) in reduced geothermal water (Stefánsson and others, 2015; Kaasalainen and others, 2015). However, for the chemical conditions found in most uncontaminated surface and groundwater, Cr(III) concentrations are limited by dissolution of chromite, $Cr(OH)_3$, which has low solubility (Ball and Nordstrom, 1998). Hexavalent chromium is not present in reduced groundwater, but is the predominate form of chromium in alkaline, oxic (oxygen present) groundwater (Rai and Zachara, 1984; Ball and Nordstrom, 1998).

In the past, Cr(VI) in groundwater was considered evidence of an anthropogenic (human-made) source (Hem, 1985), but Cr(VI) has recently been recognized as naturally occurring in alkaline, oxic groundwater (Robertson 1975, 1991; Ball and Izbicki, 2004; Izbicki and others, 2008a). Hexavalent chromium concentrations in alkaline, oxic groundwater are commonly controlled by pH-dependent sorption (Rai and Zachara, 1984; Ball and Nordstrom, 1998; Izbicki and others, 2015; Xie and others, 2015), and natural Cr(VI) concentrations in saline groundwater in arid regions can exceed 1,000 µg/L (Eriksen, 1983).

Trivalent chromium is an essential micronutrient. Hexavalent chromium is a carcinogen if inhaled (Daugherty, 1992; Agency for Toxic Substances and Disease Registry, 2012) and may be a carcinogen if ingested (Sedman and others, 2006; Beaumont and others, 2008). The U.S. Environmental Protection Agency (EPA; U.S. Environmental Protection Agency, 2019) does not have a maximum contaminant level (MCL) for Cr(VI) in drinking water but does have an MCL for total dissolved chromium, Cr(t), of 100 µg/L. The California MCL for Cr(t) is 50 µg/L (State Water Resources Control Board, 2018a). In 2014, California established an MCL for Cr(VI) of 10 µg/L (State Water Resources Control Board, 2017). The cost of treatment prior to use as a source of public supply was not considered during development of the 2014 California MCL for Cr(VI), and the MCL was withdrawn in August 2017. The California MCL for Cr(t) is being used for regulation of drinking water supplies until a new California MCL for Cr(VI) is developed (State Water Resources Control Board, 2017).

Natural Cr(VI) concentrations in alkaline, oxic groundwater pumped for public supply can exceed MCLs developed for the protection of public health in some geologic and hydrologic settings within California (Chung and others, 2001; Ball and Izbicki, 2004; Dawson and others, 2008; Izbicki and others, 2008a, 2012, 2015; Morrison and others, 2009; Mills and others 2011; Manning and others, 2015; McClain and others, 2016; Hausladen and others, 2018), the southwestern United States (Robertson, 1975, 1991), and elsewhere in the world (Oze and others, 2007; Kazakis and others, 2015) where chromium abundance in rock and soils is high. In addition to chromium abundance in geologic material, natural Cr(VI) concentrations in groundwater are influenced by a combination of processes, including (1) the mineralogy and weathering rates of chromium-containing minerals, (2) accumulation of chromium weathered from minerals within surface coatings on mineral grains, (3) oxidation of accumulated Cr(III) associated with the surface coatings on mineral grains to Cr(VI), and (4) pH-dependent desorption of chromium from coatings on the surfaces of mineral grains into groundwater under suitable aqueous geochemical conditions (Richard and Bourg, 1991; Kotaś and Stasicka, 2000; Izbicki and others, 2008a; Ščančar and Milačič, 2014; fig. E.1). After chromium has weathered from mineral grains, it typically must oxidize to Cr(VI) before it can desorb and enter groundwater. During natural conditions, chromium oxidation commonly occurs in the presence of manganese oxides (Mn oxides), including Mn(III) (Nico and Zasoski, 2000), Mn(III)/(IV) (Oze and others, 2007), and Mn(IV) oxides (Schroeder and Lee, 1975). Oxidation of Cr(III) to Cr(VI) in the presence of Mn oxides reaches a maximum near pH 5.6, and rates decrease as pH increases (Oze and others, 2007), although oxidation persists in alkaline water (pH greater than 7.0). Oxidation of Cr(III) to Cr(VI) is enhanced in fine-textured aquifer material and in older, slow-moving groundwater, where diffusive transport of reactants facilitates oxidation (Hausladen and others, 2019). In the absence of Mn oxides, oxidation of Cr(III) to Cr(VI) also can occur at slower rates in the presence of dissolved oxygen (Schroeder and Lee, 1975) or in the presence of peroxide during serpentinization (Oze and others, 2016).



U.S. Geological Survey (USGS) water sample collection, Hinkley, California, March 2015 (Photograph by John Izbicki, USGS).

Mn (III/IV) oxide on quartz mineral grain (Photograph by Andrea Foster, USGS, March 2016).

Chromium-containing actinolite and metamorphic mineral grain (Photograph by Krishangi Groover, USGS, January 2017).

Modified from Izbicki and others (2008) and Ščančar and Milačič (2014).

[Cr(III), trivalent chromium; Cr(VI), hevavalent chromium; Fe(II), ferrous iron; Mn(II), manganese-2 oxide; Mn(III), manganese-3 oxide; Mn(IV), manganese-4 oxide; Mn(III/IV), mixed manganese-3 and manganese-4 oxide]

Figure E.1. Conceptual model of processes controlling mineral weathering and hexavalent chromium, Cr(VI), concentrations in groundwater in the presence of oxide coatings on the surfaces of mineral grains.

Once oxidized, Cr(VI) on the surfaces of mineral grains is potentially mobile into oxic groundwater under alkaline pH. Desorption of Cr(VI) from mineral grains increases in alkaline water until pH 9.0, when almost all Cr(VI) is desorbed (Xie and others, 2015). In settings having an abundance of easily weathered chromium-containing minerals and reactive Mn oxides, Cr(VI) may occur naturally in groundwater at concentrations of concern for public health (Izbicki and others, 2008a; Morrison and others, 2009; Mills and others, 2011). In areas having comparatively low geologic abundance of chromium or chromium-containing minerals that are resistive to weathering, Cr(VI) may be present in groundwater at concentrations of concern as contact time with aquifer materials, weathering of minerals within those materials, oxidation of Cr(III) to Cr(VI), and pH increases along groundwater-flow paths—as long as oxic conditions persist within groundwater (Izbicki and others, 2008a, 2015; Manning and others, 2015).

Microbially mediated reduction of Cr(VI) to Cr(III) may occur in the presence of organic material (Oze and others, 2007) and may be inhibited in the presence of nitrate (Izbicki and others, 2008b). Abiotic reduction of Cr(VI) to Cr(III) also can occur in the presence of ferrous iron, Fe(II), at a pH greater than 5.6, or in the presence of hydrogen sulfide (Fendorf and others, 2000).

E.1.2. Problem and Approach

The Pacific Gas and Electric Company Hinkley compressor station, in the Mojave Desert about 80 miles (mi) northeast of Los Angeles, California, is used to compress natural gas as it is transported through a pipeline from Texas to California. Between 1952 and 1964, cooling water used at the Hinkley compressor station was treated with a compound containing Cr(VI) to prevent corrosion of machinery within the compressor station. Cooling wastewater was discharged to unlined ponds resulting in release to soil and groundwater in the underlying unconsolidated aquifer (Lahontan Regional Water Quality Control Board, 2013a). Although regulatory data have been collected at the site since the late 1980s (Ecology and Environment, Inc., 1988), the extent of anthropogenic Cr(VI) in groundwater downgradient from the Hinkley compressor station remains uncertain, in part because of uncertainty regarding background Cr(VI) concentrations in groundwater in the area. This uncertainty was not resolved by a previous background Cr(VI) study (CH2M Hill, 2007), and the USGS was requested to complete an updated Cr(VI) background study in Hinkley and Water Valleys beginning in January 2015 (Izbicki and Groover, 2016, 2018).

Between March 2015 and November 2017, the USGS collected water samples for analyses of chemical constituents (table E.1) from more than 100 wells in Hinkley and Water Valleys, California (fig. E.2). Most sampled wells were selected from monitoring wells installed by PG&E for regulatory purposes near the margins of the October–December 2015 (Q4 2015) regulatory Cr(VI) plume. Samples also were collected from (1) 12 monitoring wells installed by PG&E at 6 locations upgradient from the Hinkley compressor station as part of the USGS Cr(VI) background study, (2) 7 domestic wells in areas where monitoring wells were not available, and (3) 5 selected production wells. Chemical analyses of water from the surface discharge of temporary pumps installed within the production wells are presented in this chapter; unpumped and pumped well-bore flow data from those production wells and depth-specific water chemistry and isotopic data collected during pumping conditions are discussed in chapter H within this professional paper. Water from sampled wells was analyzed for chemical constituents (table E.1) and for isotopic and age-dating constituents are discussed in chapter F within this professional paper. Additional data, collected in areas where monitoring wells were not available, were collected from more than 70 domestic wells sampled between January 25 and 31, 2016; these samples were analyzed for a smaller number of constituents that included field parameters (pH, specific conductance, and dissolved oxygen) and selected trace elements including Cr(VI) and Cr(t). Porewater samples were collected at 11 locations in Hinkley Valley to evaluate Cr(VI) and selected trace-element concentrations in porewater within fine-grained materials that do not contribute water freely to wells. Water chemistry and isotopic data are available in appendix E.1 (table E.1.1) and also from the USGS National Water Information System (NWIS) online database (U.S. Geological Survey, 2021).

Sampled wells were selected by the USGS in collaboration with a technical working group (TWG) composed of Hinkley community members, the Independent Review Panel (IRP) Manager (Project Navigator, Ltd.), the Lahontan RWQCB, PG&E, and consultants for PG&E. The selected wells represent a mutually agreed upon, spatially distributed set of wells covering a range of geologic, hydrologic, and geochemical settings within and near the regulatory Cr(VI) plume. Most data were collected in three sample rounds between March 2015 and March 2017 to allow preliminary interpretation of earlier data that guided the collection of later data. An additional four wells were sampled in November 2017 to fill data gaps. Collectively, wells sampled as part of this study represent the most complete, non-regulatory set of water-quality data available near the Cr(VI) plume.

E.1.3. Site Description

Most geologic materials in Hinkley and Water Valleys are low in chromium (Smith and others, 2014), although chromium is locally present in hornblende diorite in Iron Mountain, in basalt in Water Valley, and in local alluvium eroded from those materials (chapter B). Chromium concentrations in unconsolidated materials are higher in fine-textured silt and clay and lower in coarse-textured sand and gravel (chapter B). Chromite is not present, and most chromium is substituted within magnetite, which is relatively resistant to weathering. Some more easily weathered chromium-containing minerals also are present, including actinolite in older alluvium deposited by the ancestral Mojave River, hornblende in weathered bedrock, and local alluvium eroded from Iron Mountain (chapter C).

Hinkley Valley is about 62 square miles (mi^2) and contains about 36 mi^2 of unconsolidated deposits that were saturated under predevelopment (pre-1930) conditions. Aquifers of interest in Hinkley and Water Valleys are composed primarily of unconsolidated deposits consisting of alluvium and lake-margin deposits sourced from the Mojave River (Miller and others, 2018, 2020), and are referred to as “Mojave-type” deposits (chapter A, table A.1). Locally derived alluvium, lacustrine deposits, and weathered bedrock also are important aquifers in some areas.

On the basis of differences in geology and hydrology, the study area was divided into eastern, western, and northern subareas within Hinkley Valley and Water Valley (fig. E.2). The eastern subarea is closest to recharge areas along the Mojave River. Mojave-type deposits in this area compose the upper aquifer, which overlies fine-textured lacustrine (lake) deposits generally described as “blue clay” at a depth of about 160 feet (ft) below land surface (bls; ARCADIS and CH2M Hill, 2011; Jacobs Engineering Group, Inc., 2019).

Table E.1. Chemical constituents analyzed in water from sampled wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in U.S. Geological Survey (2021) and appendix E.1 (table E.1.1).

[All constituents, except field measurements, filtered through 0.45-millimeter pore-sized filter. Constituents analyzed at the U.S. Geological Survey (USGS) National Water Quality Lab in Denver, Colorado. Redox couples analyzed at the USGS Trace Element Laboratory, Boulder, Colorado. Additional analyses for total dissolved chromium, Cr(t), and hexavalent chromium, Cr(VI), done by a commercial laboratory. Reporting level is laboratory reporting level, LRL. The USGS field measurements include water temperature, pH, dissolved oxygen, specific conductance, and alkalinity. The Pacific Gas and Electric Company field measurements include water level, pH, dissolved oxygen, oxidation reduction potential (ORP), and specific conductance. **Abbreviations**: Fe(t), total dissolved iron; Fe(II), ferrous iron; As(t), total dissolved arsenic; As(III), arsenite; Fe(III) ferric iron; As(V), arsenite; Cr(III), trivalent chromium]

Chemical constituents	Reporting level
Major ions, in milligrams per liter	
Alkalinity (bicarbonate)	4.6
Calcium	0.02
Chloride	0.02
Fluoride	0.04
Magnesium	0.01
Potassium	0.03
Silica	0.02
Sulfate	0.02
Residue on evaporation (dissolved solids)	20
Minor ions, in micrograms per liter	
Bromide	30
Iodide	1
Strontium	0.2
Nutrients, in milligrams per liter	
Ammonia, as nitrogen	0.01
Ammonia plus organic nitrogen as nitrogen	0.07
Nitrite, as nitrogen	0.001
Nitrite plus nitrate, as nitrogen[1]	0.04
Phosphorous	0.02
Orthophosphorous, as phosphorous	0.004

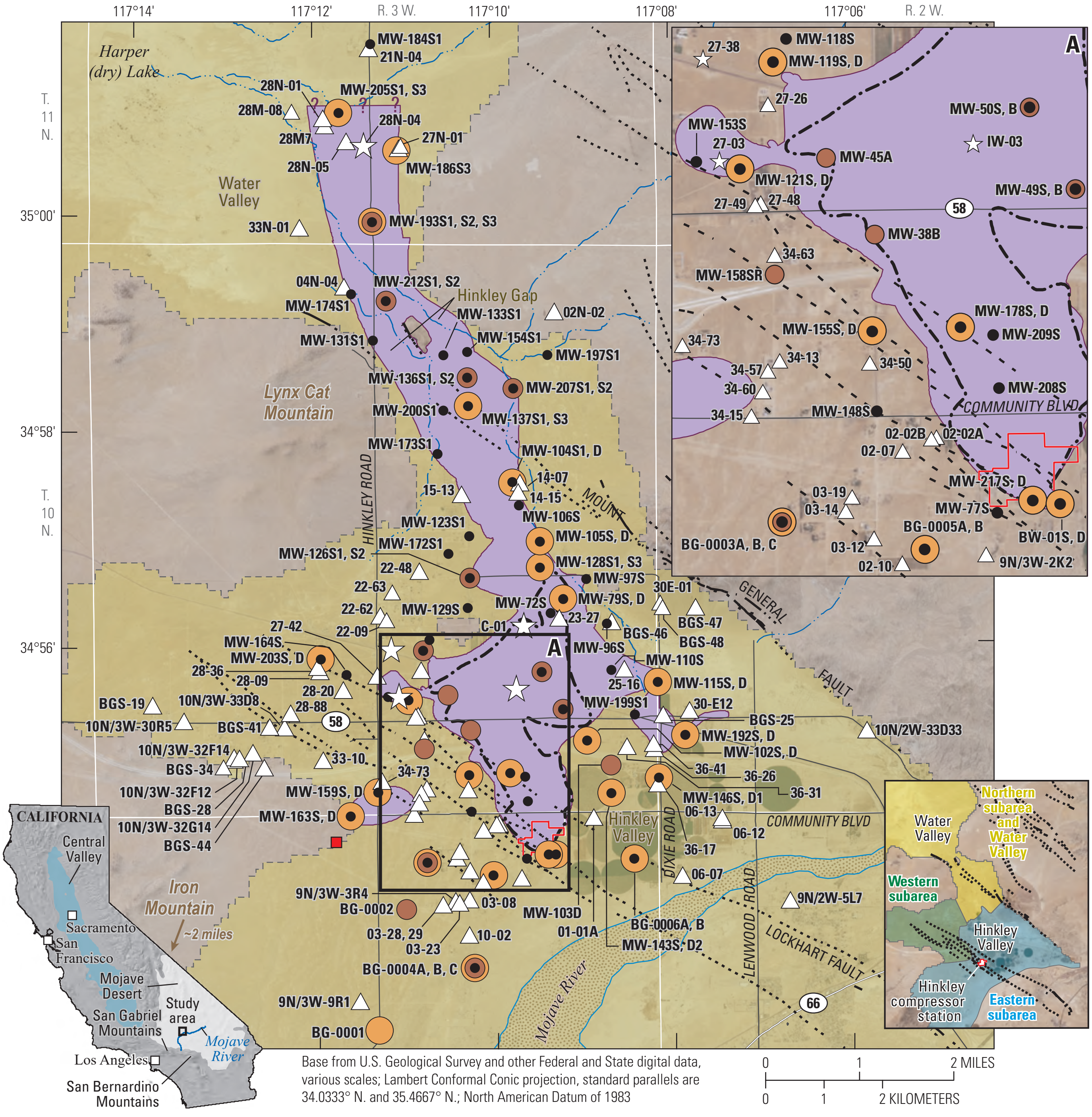
Chemical constituents	Reporting level
Trace elements, in micrograms per liter	
Antimony	0.03
Aluminum	2.2
Arsenic, As(t)	0.1
Barium	0.3
Boron	2
Cadmium	0.03
Chromium, Cr(t)	0.5
Iron, Fe(t)	5.0
Lead	0.04
Lithium	0.1
Manganese	0.1
Uranium	0.1
Vanadium	0.1
Redox couples, in micrograms per liter	
Fe(t)/Fe(II)[2]	2/2
As(t)/As(III)[2]	0.2/0.5
Cr(t)/Cr(VI)[2]	0.2/0.06

[1] Nitrate calculated by difference from nitrite and nitrite plus nitrate.

[2] Fe(III), As(V), and Cr(III) calculated by difference from their respective redox couples. Commercial laboratory reporting limit for Cr(t) was 0.2 micrograms per liter (µg/L); laboratory reporting limit for Cr(VI) ranged from 0.06 to 0.2 µg/L, depending on analytical technique.

Fine-textured deposits, generally described as “brown clay,” are interspersed throughout unconsolidated deposits, and in places, this brown clay separates the upper aquifer into shallow and deep zones (ARCADIS and CH2M Hill, 2011; Jacobs Engineering Group, Inc., 2019). Mudflat/playa deposits sourced from the Mojave River are present at land surface near Mount General and at depth within the eastern subarea, where these deposits also are commonly described as brown clay. The western subarea consists of Mojave-type deposits overlying groundwater-discharge deposits and weathered bedrock (CH2M Hill, 2013; Miller and others, 2018, 2020). The northern subarea consists of Mojave River alluvium overlying fine-textured lacustrine and mudflat/playa deposits sourced from the Mojave River and local materials (Stantec, 2013; Miller and others, 2018, 2020). Aquifers within Water Valley consist of lake-margin deposits sourced from the ancestral Mojave River along the margins of Harper (dry) Lake that overlie and interfinger with locally derived alluvium (Miller and others, 2018, 2020).

Groundwater recharge is primarily from intermittent flows in the Mojave River (fig. E.2) that occur on average once every 5–7 years (Lines, 1996; Stamos and others, 2001; Seymour, 2016). During predevelopment conditions, groundwater flow was from the Mojave River northward toward Hinkley Gap and Water Valley where groundwater discharged by evaporation along the margins of Harper (dry) Lake (Thompson, 1929). The Lockhart fault is an impediment to groundwater flow in Hinkley Valley (Stamos and others, 2001; Stantec, 2013). Predevelopment (pre-1930) and 2018 water-level maps are provided in chapter H within this professional paper (fig. H.8).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

EXPLANATION

▨ **Maximum extent of 3.1 micrograms per liter hexavalent chromium, Cr(VI), October–December 2015 (Q4 2015); queried where approximate (ARCADIS, 2016)**

Pacific Gas and Electric Company (PG&E) Hinkley compressor station

▨ **Mojave River active channel, 2005 (Mojave Water Agency, 2014)**

Q4 2015 regulatory Cr(VI) plume (ARCADIS, 2016)

Predevelopment (1930) saturated unconsolidated deposits

Fault—location accurate; dashed where approximately located or concealed (Miller and others, 2018)

🟥 **Western excavation site**

Wells sampled by U.S. Geological Survey and well identifier

● Shallow monitoring well[1]

● Middle monitoring well[1]

● Deep monitoring well[1]

△ Domestic well

☆ Production well with depth-dependent samples

[1] *Shallow monitoring well identified by suffix S, S1, or A; middle monitoring well by suffix S2; deep monitoring well by suffix S3, D, D1, D2, or B; bedrock well by suffix C; replacement well by suffix R.*

Figure E.2. Sampled wells by well type, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

Water-level declines resulting from agricultural pumping since the early 1950s, have been as much as 60 ft (Stone, 1957; California Department of Water Resources, 1967; Seymour and Izbicki, 2018). As a consequence of water-level declines, saturated alluvium in much of the western subarea downgradient (northeast) from the Lockhart fault, is a thin veneer commonly less than 10 ft thick overlying groundwater-discharge deposits and weathered bedrock (CH2M Hill, 2013; Miller and others, 2018, 2020), and saturated alluvium in much of the northern subarea is a thin veneer overlying fine-textured lacustrine and mudflat/playa deposits (Stantec, 2013; Miller and others, 2018, 2020). Many monitoring wells in the western subarea are completed partly or entirely in weathered bedrock aquifers, and many monitoring wells in the northern subarea are completed partly or entirely in fine-textured mudflat/playa or lacustrine deposits. Lake-margin deposits in much of Water Valley, formerly pumped for agricultural water supply, were largely above the water table at the time of this study (2015–18; Stamos and others, 2001; Miller and others, 2018, 2020).

The Hinkley compressor station and much of the Q4 2015 regulatory Cr(VI) plume are located in the eastern subarea of Hinkley Valley (fig. E.2). In Q4 2015, the regulatory Cr(VI) plume extended 3.0 mi downgradient from the release location within the Hinkley compressor station (ARCADIS, 2016), and the highest Cr(VI) concentrations in groundwater remained less than 3,000 ft downgradient from the release location within the Hinkley compressor station. However, the actual extent of the Cr(VI) release was uncertain and Cr(VI) concentrations greater than the interim regulatory background of 3.1 µg/L (CH2M Hill, 2007; Lahontan Regional Water Quality Control Board, 2008) were present in water from wells within Water Valley, more than 8 mi downgradient from the Hinkley compressor station (fig. E.2; ARCADIS, 2016). Remediation of Cr(VI) released from the Hinkley compressor station began in 1992, and in 2010 site cleanup was projected to require 10–95 years (Haley and Aldrich, Inc., 2010; Pacific Gas and Electric Company, 2011).

Monitoring wells installed for regulatory purposes by PG&E were commonly identified by the prefix MW, with sites numbered sequentially in the order they were drilled (ARCADIS, 2016). Shallow wells, commonly screened across or just below the water table, were identified with the suffix S or S1 (ARCADIS, 2016). Deeper wells were identified with the suffix D, D1, or D2, or with the suffix S2 or S3 if a hydrologically important clay layer was not present; older monitoring wells were identified with the suffix A or B for shallower or deeper wells, respectively (ARCADIS, 2016). The suffix C was used for wells completed in consolidated rock, and the suffix R was added if the well was a replacement for a well that was destroyed (ARCADIS, 2016). Wells installed by PG&E as part of the USGS Cr(VI) background study were identified with the prefix BG; the sites were numbered sequentially in the order they were permitted, and BG wells were identified from shallowest to deepest with the suffix A, B, or C. Although drilling methods changed through time and in response to site conditions, most monitoring wells were drilled with auger rigs. Core material, archived by PG&E, was available for most wells installed after 2011 from near the water table to below the depth of the deepest well.

E.1.4. Purpose and Scope

The purpose of this chapter is to evaluate the chemical composition and Cr(VI) concentrations in water from selected wells sampled as part of the USGS Cr(VI) background study in Hinkley and Water Valleys, California. Scope of the work included (1) evaluating the quality of PG&E and USGS data; (2) evaluating the chemistry of groundwater in Hinkley and Water Valleys, including the spatial distribution of Cr(VI); (3) evaluating geochemical controls on Cr(VI), including redox and pH-dependent sorption processes, and cooccurrence of Cr(VI) with selected trace elements; (4) evaluating Cr(VI) concentrations in porewater extracted from fine-textured material within the study area, including the impact of porewater fluids on aquifer Cr(VI) concentrations; and (5) evaluating Cr(VI) concentrations in water from domestic wells sampled within the study area.

Interpretations derived from Cr(VI), pH, and trace-element data were used within a summative-scale analysis (SSA) to determine the Cr(VI) plume extent in the upper aquifer system underlying Hinkley and Water Valleys. Although data collected as part of this study between March 2015 and November 2017 were used to define the summative scale Cr(VI) plume extent, these data were not used to calculate Cr(VI) background concentrations in chapter G within this professional paper. Instead, Cr(VI) background concentrations were calculated from regulatory data collected from selected wells between April 2017 and January 2018.

E.2. Field and Laboratory Methods and Quality-Assurance Data

Sample-collection crews contracted by PG&E worked with USGS field crews to collect samples from PG&E monitoring wells. Prior to sample collection, water from PG&E monitoring wells was purged with the same equipment and similar procedures used to collect quarterly samples for regulatory purposes. Well-purge protocols used as part of this study included (1) removing at least three casing volumes of water from the well prior to sample collection and (2) continuous monitoring of field parameters including water levels, pH, temperature, specific conductance, dissolved oxygen, and oxidation reduction potential (ORP) during purging and sample collection. Protocols were consistent with those described in the U.S. Geological Survey Field Manual (Wilde, 2006; U.S. Geological Survey, variously dated). In contrast, a modified low-flow sample collection method in which only one casing volume is commonly removed from wells prior to sample collection was used by PG&E sample collection crews for regulatory purposes (chapter D). Submersible pumps used to purge wells and collect samples were moved from well to well after cleaning and decontamination; tubing connecting the pump to the surface was dedicated to each well. Purge water, and other wastewater associated with sample collection from monitoring wells, was stored in portable tanks and disposed of at on-site treatment facilities.

Samples were collected by USGS staff after a minimum of three casing volumes was pumped from the wells and field parameters had stabilized. Samples for water chemistry were collected from dedicated plastic tubing used at each well for regulatory sample collection. Samples for dissolved-atmospheric and industrial gases (discussed in chapter F within this professional paper) were collected from copper tubing attached to the submersible pump using fittings designed for this study. Copper tubing was moved from well to well with sample pumps after cleaning and decontamination. Monitoring wells installed upgradient from the PG&E Hinkley compressor station for the purposes of this study were sampled by USGS field crews using USGS pumps and equipment without participation of PG&E contract crews. These wells were not equipped with dedicated plastic tubing. The pump, plastic tubing, and copper tubing were moved from well to well after cleaning and decontamination using procedures described in the U.S. Geological Survey Field Manual (Wilde, 2004). Purge water, and other wastewater associated with sample collection, was stored in portable tanks and disposed of at on-site treatment facilities. Domestic wells were purged and sampled using the installed pump. No special procedures were used to store and treat water pumped from domestic wells.

Samples were collected, processed, and preserved in the field within a sample collection chamber designed to protect the sample from ambient contamination (fig. E.1). Containers for each sample were filled in a consistent order from each well, generally summarized as field parameters, unfiltered constituents, filtered constituents including samples for Cr(VI) and Cr(t), followed by samples for isotopic analyses with dissolved gases collected from copper tubes, with samples for dissolved helium and neon gas analyses filled last. Field parameters were resampled periodically during sample collection and after the last sample container was filled. These data were used to verify that field parameters remained within 5 percent of initial values and that the chemistry of water yielded by the well did not change during sample collection. If field parameters changed during sample collection, changes were noted on field forms for later data interpretation. Containers for dissolved-atmospheric and industrial gas samples were filled according to USGS protocols that minimize exposure to atmosphere and loss of dissolved gases (U.S. Geological Survey, 2017). To ensure collection of representative dissolved-gas data, pump rates were adjusted (where possible) to ensure the water level was not drawn down into the screened interval of the well during purging and sample collection. After collection, samples were preserved and stored on ice (if required) and shipped by courier or overnight express (if required) to meet method-specific holding times.

Project-specific field and laboratory methods for Cr(VI) and Cr(t), including quality-assurance data, are discussed in the following sections. Project-specific field and laboratory methods for selected isotopes and environmental tracers, including age-dating parameters, are discussed in chapter F within this professional paper. Water chemistry and isotopic data collected as part of this study are available in U.S. Geological Survey (2021) and in appendix E.1 (table E.1.1).

E.2.1. Field and Laboratory Methods for Hexavalent Chromium

Samples for Cr(VI) and Cr(t) were field filtered, using a 0.45-micrometer (µm) pore-sized filter, into a 1-liter (L) plastic bottle. Water in the bottle was gently swirled to ensure complete mixing, and then subsampled into appropriate containers for analyses by various methods. About 20 milliliters (mL) of sample water was subsampled from the 1-L bottle and field speciated using cation exchange resins according to procedures described by Ball and McCleskey (2003). Field speciated and unspeciated samples were collected in duplicate in color-coded, 2-mL plastic vials, preserved with nitric acid using a micropipette, and shipped at the end of the sample collection period to the USGS Redox Chemistry Laboratory in Boulder, Colorado, for analyses within the Cr(t) holding time. When using this method, Cr(III) is removed by sorption onto an anion-exchange resin, and only Cr(VI) remains in the field-speciated sample for laboratory analyses, while both Cr(VI) and Cr(III) are present in the unspeciated sample vial. The remaining water in the 1-L bottle was subsampled into 500- and 250-mL bottles to be analyzed for Cr(VI) and Cr(t), respectively. Samples to be analyzed for Cr(VI) were adjusted to a pH of 9–9.5 with a concentrated buffer solution (U.S. Environmental Protection Agency, 1994a), stored on ice, and shipped from the field either by courier or overnight express to the same commercial laboratory used by PG&E for Cr(VI) regulatory data for analyses within 24 hours of collection. Samples for Cr(t) were acidified to a pH less than 2 with nitric acid, stored on ice, and shipped with Cr(VI) samples, although analyses for Cr(t) were not necessarily completed within 24 hours.

Hexavalent chromium within each duplicate field-speciated sample vial was analyzed as Cr(t) by Zeeman-corrected graphite furnace atomic absorption spectroscopy (GFAAS) using EPA Method 7010 (U.S. Environmental Protection Agency, 2007) at the USGS Redox Chemistry Laboratory. Total dissolved chromium within each duplicate unspeciated sample vial was analyzed using the same method. The laboratory reporting level (LRL) for Cr(t) analyses by GFAAS is 0.06 µg/L. Results of each duplicate field-speciated and unspeciated vial were averaged and reported; Cr(III) was calculated as the difference between reported Cr(t) and Cr(VI).

Hexavalent chromium was analyzed by ion chromatography using EPA Method 218.6 (U.S. Environmental Protection Agency, 1994a) at the commercial laboratory used for samples collected for regulatory purposes by PG&E. The EPA Method 218.6 (U.S. Environmental Protection Agency, 1994a) has a LRL for Cr(VI) of 0.2 µg/L; the method was modified by the commercial laboratory to provide an LRL of 0.06 µg/L. Total dissolved-chromium samples were analyzed at the commercial laboratory by inductively coupled plasma-mass spectrometry (ICP-MS) using EPA Method 200.8 (U.S. Environmental Protection Agency, 1994b) with a LRL of 0.20 µg/L.

Performance of laboratory analytical methods for Cr(VI) and Cr(t) was evaluated for more than 100 samples collected from wells outside the mapped Q4 2015 regulatory plume between March 2015 and November 2017 (fig. E.3). Hexavalent chromium concentrations ranged from less than the reporting level of 0.06 µg/L to about 11 µg/L. Comparison of Cr(VI) analyses by ion chromatography (EPA Method 218.6) with field speciation for Cr(VI) (Ball and McCleskey, 2003) and analyses by GFAAS (EPA Method 7010) yielded a least-squares regression line having a slope of 0.97, an intercept of 0, and a coefficient of determination (R^2) of 0.97 (fig. E.3*A*). The slope of the regression line was not statistically different from 1 on the basis of the t-test (Neter and Wasserman, 1974) with a significance criterion of α=0.05; Cr(VI) results from the two methods were statistically similar over the range of data tested. In contrast, comparison of more than 100 Cr(t) analyses by ICP-MS (EPA Method 200.8) with Cr(t) analyses by GFAAS yielded a least-squared regression line having a slope of 1.04, an intercept of 0, and an R^2 of 0.99. The slope of this line was significantly different from 1, indicating Cr(t) analyses by ICP-MS differed slightly from analyses by GFAAS (not shown on fig. E.3).

Comparison of Cr(VI) and Cr(t) data analyzed at the commercial laboratory by EPA Methods 218.6 and 200.8, respectively, yielded a least-squared regression line having a slope of 0.91, an intercept of 0, and an R^2 of 0.90 (fig. E.3*B*). Similar comparison of field-speciated Cr(VI) and unspeciated Cr(t) samples with subsequent analyses by GFAAS using EPA Method 7010 (fig. E.3*C*) yielded a slope of 0.87, an intercept of 0, and an R^2 of 0.97. Both results are consistent with data from previous studies of Cr(VI) in groundwater elsewhere in California that show about 90 percent of the Cr(t) present as Cr(VI) (Izbicki and others, 2008a, 2015). However, the slopes of these two regression lines are significantly different on the basis of the t-test (Neter and Wasserman, 1974) at a significance criterion of α=0.05; that difference, about 4 percent, corresponds to the difference between the analytical methods for Cr(t). The higher R^2 for Cr(VI) as a function of Cr(t) for the field-speciated data (fig. E.3*C*) compared to Cr(VI) as a function of Cr(t) for the commercial laboratory data (fig. E.3*B*) indicates more consistent performance and greater precision for the field speciation data.

Samples also were analyzed for Cr(t) by ICP-MS at the USGS National Water Quality Laboratory (NWQL) as part of the suite of trace elements analyzed as part of this study (table E.1). These samples were not subsampled from the same bottle as Cr(VI) samples but were from a different bottle used for other trace elements analyzed as part of the study by ICP-MS. Samples analyzed for Cr(t) and other trace elements at NWQL were filtered in the field, acidified with nitric acid, and shipped weekly to the NWQL. The LRL for Cr(t) from the NWQL was 0.3 µg/L in 2015 and 2016 but was raised to 0.5 µg/L in 2017.

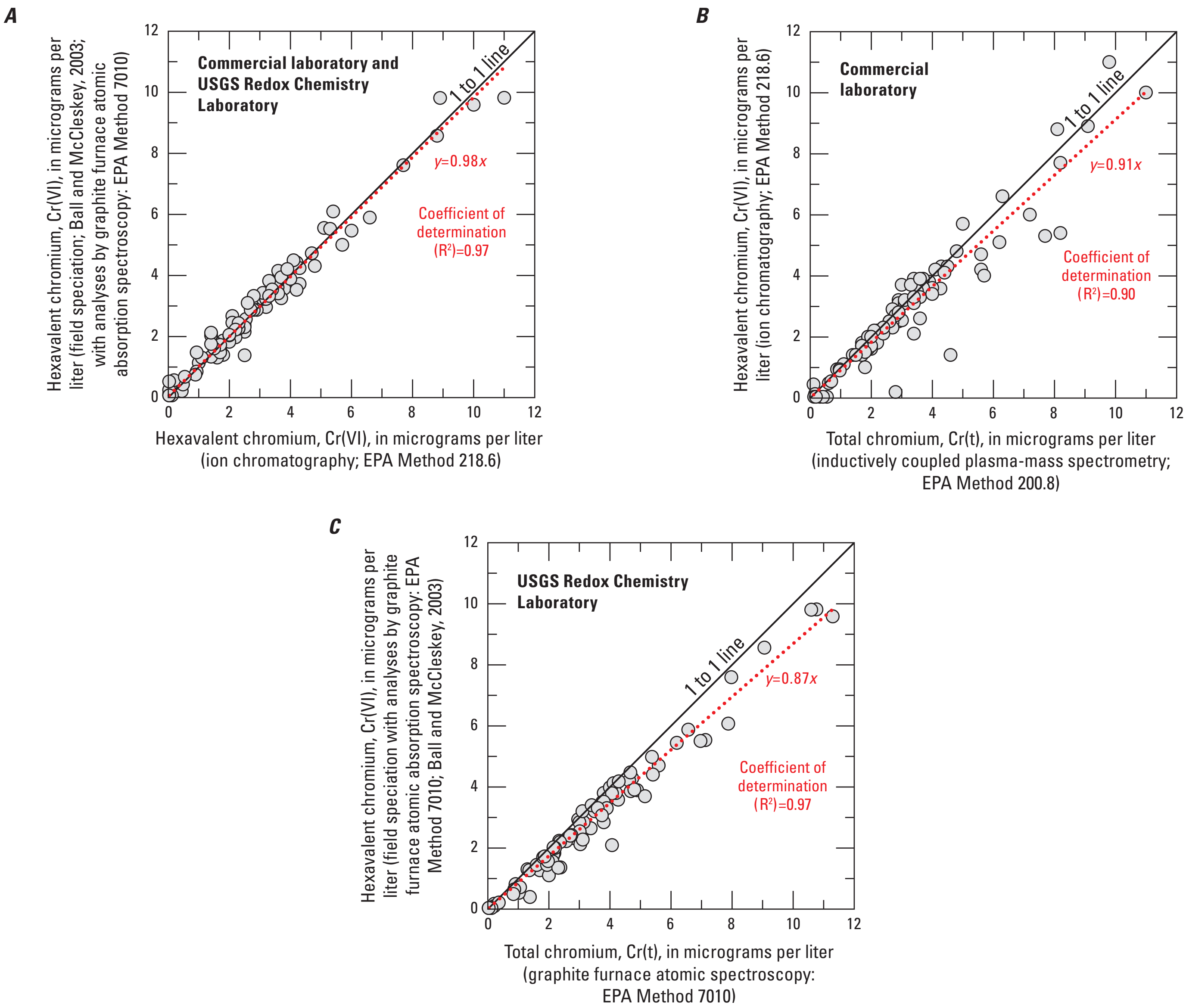


Figure E.3. Comparison of analytical methods for hexavalent chromium, Cr(VI), and total dissolved chromium, Cr(t). *A*, field speciation for Cr(VI) (Ball and McCleskey, 2003) with analyses at the U.S. Geological Survey (USGS) Redox Chemistry Laboratory by graphite furnace atomic absorption spectroscopy, GFAAS (U.S. Environmental Protection Agency, EPA, Method 70100), as a function of analysis at a commercial laboratory by ion chromatography for Cr(VI) (EPA Method 218.6); *B*, ion chromatography for Cr(VI) (EPA Method 218.6) as a function of inductively coupled plasma-mass spectrometry for Cr(t) (EPA Method 200.8); and *C*, field speciation for Cr(VI) (Ball and McCleskey, 2003) with subsequent analyses by GFAAS, as a function of Cr(t) analyses by GFAAS (EPA Method 7010), Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

E.2.2. Equipment and Field-Blank Data and Study Reporting Levels for Hexavalent Chromium

Equipment and field blanks for Cr(VI) and Cr(t) were prepared from freshly opened, reagent-grade, certified inorganic-free blank water having Cr(t) concentrations less than 0.02 µg/L. Equipment blanks were prepared in the USGS San Diego Office for equipment, other than sample pumps and dedicated tubing, in contact with sample water. Equipment blanks were analyzed prior to the March 2015, 2016, and 2017 field trips; Cr(VI) and Cr(t) were analyzed at the USGS Redox Chemistry Laboratory and other chemical constituents were analyzed at the NWQL. Field blanks were prepared in the field at randomly selected wells by each sample-collection team at approximately weekly intervals. Field blanks were prepared by pumping certified inorganic-free blank water through sample pumps, a short length of clean plastic tubing, and equipment in contact with sample water; plastic tubing dedicated to wells for purging and sample collection was not used in the preparation of field blanks. Field blanks were processed in the field in the same manner as environmental samples, and they were preserved and shipped blind to respective laboratories in the same manner as environmental samples. Field blanks were analyzed for Cr(VI) and Cr(t) at the USGS Redox Chemistry Laboratory in Boulder, Colo., and at the commercial laboratory. Field blanks were analyzed for other chemical constituents at the NWQL. Field-blank data are provided in appendix E.1 (table E.1.2).

Concentrations in equipment blanks were generally less than the Redox Chemistry Laboratory reporting levels for Cr(VI) and Cr(t) of 0.06 and 0.2 µg/L, respectively, and did not show increases in Cr(VI) or Cr(t) concentrations associated with sampling equipment. An exception to that generalization is that prior to the March 2015 sample collection, equipment blanks pumped through fittings to be attached to the sample pump showed detectable Cr(VI) and Cr(t). The fittings were designed to split flow from the pump into plastic sample lines used to collect water for chemical analyses and into copper tubing used to collect water for dissolved gases. As a consequence, the fittings were not used during the March 2015 sample collection. The fittings were redesigned to eliminate welds identified as the source of Cr(VI) and Cr(t). After successful analyses of subsequent equipment blanks, the fittings were used for the March 2016 and 2017 sample collection—decreasing sample collection time and expediting sample collection. The fittings were not used in the November 2017 sample collection because dissolved-gas samples requiring copper tubing were not collected.

Eight of 17 field blanks collected between March 2015 and March 2017 and analyzed at the commercial laboratory using EPA Method 218.6 had detectable Cr(VI); most Cr(VI) concentrations were 0.10 µg/L or less, although one field blank had a concentration of 0.28 µg/L. Similar results were obtained for blank samples collected for regulatory purposes by PG&E between March 2015 and March 2017 (data available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/), with 116 of 266 blank samples collected during this period having detectable Cr(VI), with concentrations as high as 0.21 µg/L in a small number of blank samples. Frequency of Cr(VI) detection was greater and concentrations were higher in field-blank samples analyzed by the commercial laboratory during March 2016, when five of six samples had detectable Cr(VI). Five of 15 blank samples analyzed using the field-speciation technique had detectable Cr(VI) with a maximum concentration of 0.09 µg/L. The frequency of Cr(VI) detection from each laboratory differed during each sample round, and the differences did not appear to be systematic because Cr(VI) detections in field blanks analyzed by one laboratory were not generally associated with Cr(VI) detections in the paired field blank that was analyzed by the other laboratory.

Six of 17 field blanks collected between March 2015 and March 2017 and analyzed for Cr(t) by the commercial laboratory using Method 200.8 had detectable Cr(t) with concentrations as high as 0.25 µg/L. Seven of 15 field blanks analyzed by GFAAS using Method 7010 at the USGS Redox Chemistry Laboratory had detectable Cr(t) at concentrations as high as 0.16 µg/L. None of the 12 field blanks analyzed at the NWQL had detections greater than the NWQL LRL for Cr(t) of 0.3 µg/L (or 0.5 µg/L in 2017).

The study reporting level (SRL) was estimated as the upper 90 percent quantile of the field-blank data. A SRL of 0.1 µg/L was assigned for Cr(VI) data analyzed by the commercial laboratory using EPA Method 218.6, and an SRL of 0.08 µg/L was assigned for the field-speciation data analyzed by the USGS Redox Chemistry Laboratory. A SRL of 0.25 µg/L was assigned for Cr(t) data from the commercial lab and 0.11 µg/L for Cr(t) data from the USGS Redox Chemistry Laboratory. The SRL for 266 Cr(VI) blank samples collected by PG&E for regulatory purposes between March 2015 and March 2017 and analyzed by the contract laboratory using EPA Method 218.6, was 0.12 µg/L—which is similar to the SRL for Cr(VI) of 0.1 µg/L estimated from blank data collected as part of this study. The binomial distribution 90/90 (BD-90/90) approach (Davis and others, 2014) used to estimate the SRL for regulatory data collected by PG&E (chapter D) was not used for data collected as part of the background study because of the smaller number of field blanks.

Analyses of field-blank data indicate that although the SRLs for Cr(VI) and Cr(t) were higher than the respective LRLs at both laboratories, there were no systematic issues associated with sample collection, handling, and analytical procedures used in this study. Field-blank data showed that SRLs assigned for Cr(VI) and Cr(t) are sufficiently low for the purposes of this study.

E.2.3. Replicate Data for Hexavalent Chromium

Between March 2015 and March 2017, 30 pairs of sequential-replicate samples were collected for Cr(VI) and Cr(t) determinations. Pumps were pulled from wells, and water levels were allowed to recover between collection of the replicate sample suite. Replicate samples were then collected, processed, and shipped to respective laboratories for analysis in the same manner as environmental data. Replicate data are provided in appendix E.1 (table E.1.2).

Sequential replicates are a suite of samples collected as close in time as possible after a suite of environmental samples were collected (Wilde, 2006). Sequential-replicate data provide information on variability introduced during collection, field processing, and shipping of samples, in addition to variability introduced during laboratory handling and analyses of samples (Wilde, 2006; Geboy and Engle, 2011). In contrast, concurrent-replicate data are a suite of samples where multiple bottles for individual analyses are collected one after the other as part of a suite of environmental samples. Concurrent-replicate data provide information on variability introduced during field processing, laboratory handling, and analysis of samples (Wilde, 2006; Geboy and Engle, 2011). Hexavalent chromium samples analyzed by the commercial laboratory and by the USGS Redox Chemistry Laboratory (fig. E.4*A*) are examples of concurrent replicates used to evaluate differences in laboratory analytical methods. For the purposes of this study, Cr(VI) replicate data collected by PG&E for regulatory purposes (chapter D) are concurrent-replicate data.

Paired sequential-replicate values for Cr(VI) analyzed at the commercial laboratory by EPA Method 218.6 compared favorably, with an R^2 greater than 0.99 (fig. E.4*A*), and a mean square error (MSE) of 0.06 consistent with a precision of about 6 percent at the mean value of 4.2 µg/L. Paired sequential-replicate data for field-speciated Cr(VI) samples analyzed by Method 7010 had an R^2 greater than 0.99 and an MSE of 0.32—consistent with a precision of about 12 percent at the mean value. Both precision values estimated from sequential-replicate data are poorer than the precision of 3 percent estimated from paired Cr(VI) regulatory data (chapter D) and reflect increased variability introduced during sample collection, field processing, and shipment of samples. On the basis of the t-test with a significance criterion of α=0.05 (Neter and Wasserman, 1974), the slope of the regression line through the paired sequential data analyzed at the commercial laboratory was statistically different from one (fig. E.4), which indicated that although the results from EPA Method 218.6 were more precise, they were less accurate over the range of values analyzed than results from the field-speciated samples; this may result from differences in the analytical procedures or from changes in dissolved-chromium species during shipment to the laboratory prior to analyses.

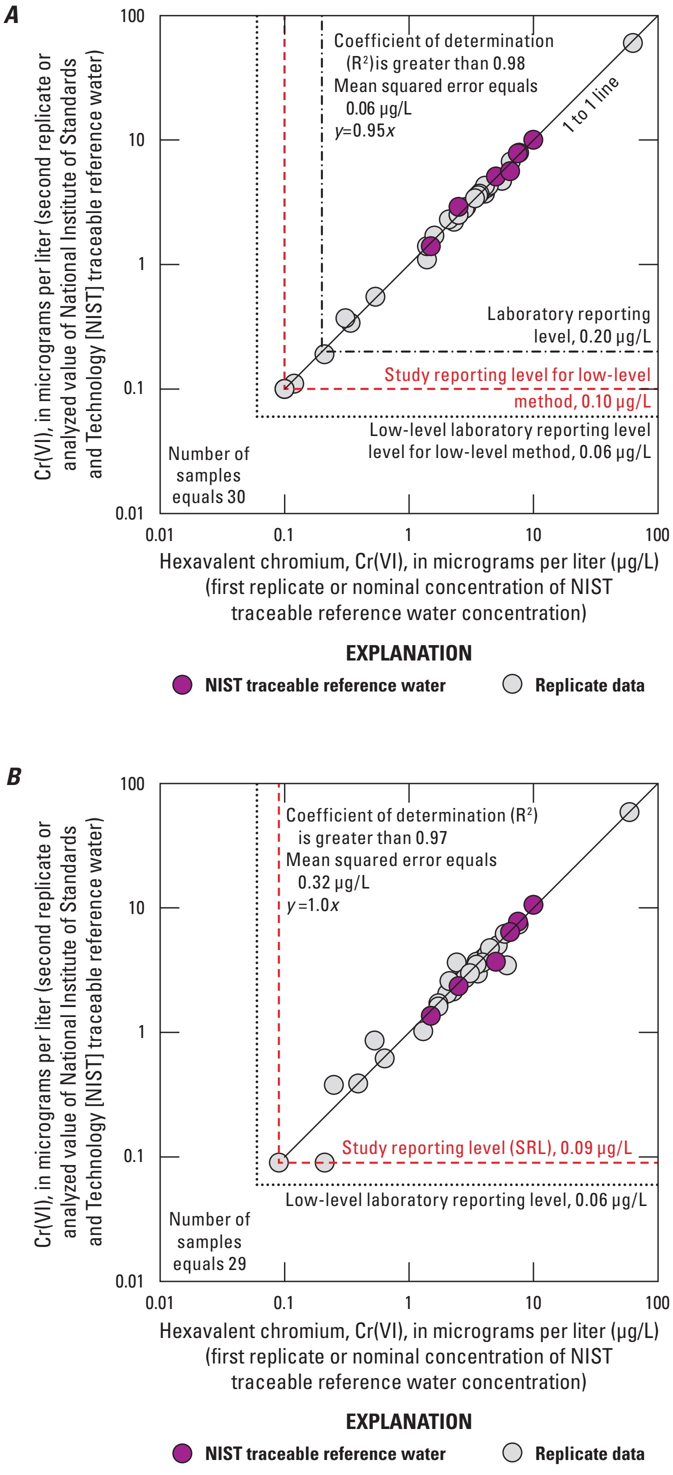


Figure E.4. Hexavalent chromium, Cr(VI), concentrations in replicate samples and in National Institute of Standards and Technology (NIST) traceable reference water samples that were analyzed by the *A*, commercial laboratory and *B*, U.S. Geological Survey Redox Chemistry Laboratory, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through March 2017. Data are available in appendix E.1 (table E.1.2) and U.S. Geological Survey (2021).

Samples of National Institute of Standards and Technology (NIST) traceable water, having known concentrations of Cr(VI) and Cr(t), were shipped to the field within 24 hours of preparation by a commercial vendor during the March 2015, 2016, and 2017 sample collections (table E.2). Because of the small sample volume, reference waters were not passed through sample pumps, but were otherwise processed in the field using the same techniques as field blanks. Samples were shipped blind to respective laboratories and analyzed with environmental samples. On the basis of least-squares regression analysis (Neter and Wasserman, 1974), measured Cr(VI) concentrations were similar to NIST-traceable concentrations analyzed by the contract laboratory (R^2 of 0.98, fig. E.4*A*) and by the U.S. Geological Survey Redox Chemistry Laboratory (R^2 of 0.97 fig. E.4*B*) despite the laboratories using different methods (R^2 values for NIST-traceable sample comparisons not shown on fig. E.4). Least-squares regression intercepts and slopes were not significantly different from zero and one, respectively, on the basis of the t-test (Neter and Wasserman, 1974) with a significance criterion of α=0.05. Regression statistics for reference waters are not shown on figures E.4*A*, *B*.

U.S. Geological Survey data were collected over a period of several years and, by design, were not a synoptic (single point in time) representation of Cr(VI) concentrations in Hinkley and Water Valleys. Hexavalent chromium concentrations in water from 14 wells collected in March 2015 were compared with concentrations in the same wells collected in March 2017 (appendix E.1, table E.1.1); there was a small, but statistically significant, decrease in Cr(VI) concentrations of 4 percent during the sample collection period (on the basis of the slope of 0.96 for the least-squares regression line fit through the data, evaluated using the t-test [Neter and Wasserman, 1974] at a significance criterion of α=0.05, not shown on figures). Only water from well MW-97S showed a statistically significant increase in Cr(VI) concentrations during this period. These data contrast with Cr(VI) concentration trend analyses of PG&E data that show generally increasing Cr(VI) concentration trends outside the mapped regulatory plume between July 2012 and June 2017 (chapter D).

Table E.2. Analytical results for National Institute of Standards and Technology (NIST) traceable samples analyzed as part of the U.S. Geological Survey hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through March 2017. Data are available in appendix E.1 (table E.1.2) and U.S. Geological Survey (2021).

[All concentrations in micrograms per liter. Commercial laboratory used by the Pacific Gas and Electric Company (PG&E) for regulatory data analyses. Commercial laboratory Cr(VI) analyzed by modified U.S. Environmental Protection Agency Method 218.6 (U.S. Environmental Protection Agency, 1994a), and Cr(t) analyzed by U.S. Environmental Protection Agency Method 200.8 (U.S. Environmental Protection Agency, 1994b). The USGS Redox Chemistry Laboratory Cr(VI) and Cr(t) field speciated (Ball and McCleskey, 2003) with subsequent analyses by U.S. Environmental Protection Agency Method 7010 (U.S. Environmental Protection Agency, 2007). **Abbreviations**: Cr(t), total chromium; USGS; U.S. Geological Survey; mm/dd/yyyy, month/day/year]

NIST traceable reference water	Date (mm/dd/yyyy)	Commercial laboratory		USGS Redox Chemistry Laboratory	
		Cr(VI)	Cr(t)	Cr(VI)	Cr(t)
1.5	03/09/2017	1.4	1.5	1.4	1.5
2.5	03/16/2016	2.9	2.8	2.4	2.7
5	03/06/2015	5.1	4.7	3.7	6.2
6.5	03/09/2017	5.6	5.8	6.4	6.5
7.5	03/16/2016	7.8	7.7	7.7	8.2
10	03/12/2015	10.0	9.7	10.6	10.6

E.2.4. Comparison of U.S. Geological Survey and Regulatory Sample Collection Protocols

To ensure comparable Cr(VI) data, the sample collection methods, equipment, and analytical procedures used in the USGS Cr(VI) background study were as similar as possible, given study constraints, to methods and equipment used by PG&E to collect data for regulatory purposes. However, a modified low-flow method was used for regulatory purposes in which only one casing volume was commonly removed from wells prior to sample collection (chapter D). Purging three casing volumes and the larger number of analyses done on samples collected by the USGS as part of the Cr(VI) background study required a greater volume of water to be pumped from monitoring wells than the volume of water pumped during regulatory sample collection. In addition, to ensure collection of representative data for dissolved gases and other constituents, water levels (where possible) were not drawn down into the screened interval of the well during purging and sample collection—this occasionally resulted in lower pumping rates and longer pumping times for USGS samples compared to samples collected by PG&E for regulatory purposes.

To address possible differences in data quality related to sample collection, USGS data for Cr(VI) were compared to PG&E regulatory data for Cr(VI) collected during the quarter prior to USGS sample collection. To provide a benchmark for this comparison, PG&E regulatory data for Cr(VI) collected the quarter prior to USGS sample collection were compared with PG&E regulatory data for Cr(VI) collected two quarters prior to USGS sample collection. It is assumed as part of this analyses that temporal trends in Cr(VI) concentrations were not large and that the quarterly samples were effectively sequential replicates collected 3 months apart. This assumption is supported by Cr(VI) concentration trend data (chapter D) and replicate data collection from wells sampled in March 2015 and March 2017 that show only small changes in Cr(VI) concentrations over time.

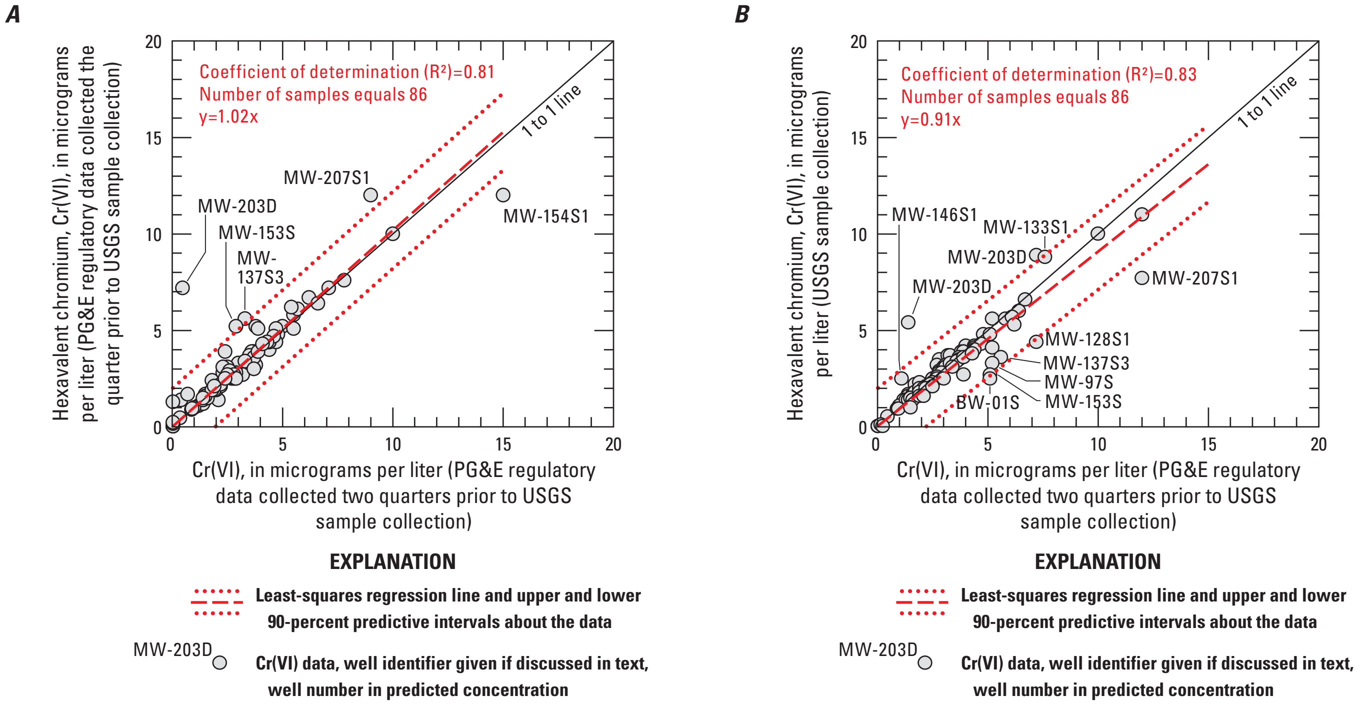


Figure E.5. Hexavalent chromium, Cr(VI), concentrations in water from wells sampled as part of the U.S. Geological Survey (USGS) Cr(VI) background study compared with *A*, regulatory data from Pacific Gas and Electric Company (PG&E) collected one quarter prior to USGS samples as a function of regulatory data collected two quarters prior to USGS samples and *B,* data from USGS samples as a function of regulatory data collected one quarter prior to USGS sample collection, Hinkley and Water Valleys, western Mojave Desert, California, October 2014 through November 2017. U.S. Geological Survey data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021). Pacific Gas and Electric Company regulatory data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/.

Hexavalent chromium concentrations in regulatory data collected from wells the quarter prior to USGS sample collection were similar to data collected from those same wells two quarters prior to USGS sample collection (fig. E.5*A*). The least-squares regression line fit between the two datasets had a slope of 1.02 and was not significantly different from 1, on the basis of the t-test (Neter and Wasserman, 1974) with a significance criterion of α=0.05. These results indicate that for the purpose of this discussion, Cr(VI) concentrations in water from most wells can be treated as sequential replicates collected 3 months apart. However, consistent with the greater timespan, samples collected 3 months apart showed greater variation than sequential-replicate samples collected immediately after collection of environmental samples (figs. E.4*A,B*)—as shown by the decrease in R^2 values from greater than 0.99 to 0.8 (figs. E.4*A*,E.5*A*). Increases in Cr(VI) concentrations in water from wells MW-203D, MW-153S, MW-137S3, and MW-207S1 and the decrease in Cr(VI) concentration in water from well MW-154S1, were significantly different over the 3-month sample period (falling outside the 90-percent predictive interval around the least-squares regression line shown on figure E.5*A*). Monotonic increasing and decreasing Cr(VI) concentration trends measured in these wells between July 2012 and June 2017 (chapter D, table D.1) were not large enough to explain changes in these wells over the 3-month sample period. Wells MW-203D, MW-153S, and MW-154S1 were difficult to sample because of low yields and measured differences likely reflect variability associated with sample collection issues in low-yielding wells.

In contrast, Cr(VI) concentrations in USGS samples differed from Cr(VI) concentrations in regulatory samples in water from the same wells sampled the quarter prior to USGS sample collection (fig. E.5*B*). The least-squares regression line between the two datasets had similar variability as sets of PG&E regulatory samples collected one quarter apart, with an R^2 of 0.83 and an MSE of 0.58; however, the slope of the line, 0.91, was significantly less than 1, on the basis of the t-test (Neter and Wasserman, 1974) with a significance criterion of α=0.05. These results indicate that the larger volume of water pumped from wells, coupled with slower pumping rates, may have resulted in Cr(VI) concentrations that were on average about 9 percent lower in USGS samples compared to PG&E samples collected for regulatory purposes. Significantly lower Cr(VI) concentrations were measured by the USGS in water from wells MW-207S1, MW-128S1 near the leading edge of the mapped Q4 2015 regulatory Cr(VI) plume, and BW-01S near the mapped plume margin by the Hinkley compressor station (falling outside the 90-percent predictive interval around the least-squares regression line shown on figure E.5*B*). Although not statistically significant, large decreases in Cr(VI) concentrations also were measured in USGS samples of water from wells MW-137S3, MW-97S, and MW-153S compared to PG&E regulatory data from the previous quarter (fig. E.5*B*). Only a few wells had increases in Cr(VI) concentrations in USGS data compared to PG&E regulatory data from the previous quarter. Significant increases were measured in water from well MW-203D between March 2015 and March 2017 (falling outside the 90-percent predictive interval around the least-squares regression line shown on figure E.5*B*), and although not statistically significant, large increases were measured in water from wells MW-133S1 and MW-146S (fig. E.5*B*). Sample collection in these wells was complicated by low well yields.

Overall Cr(VI) concentrations in USGS data were about 9 percent lower than in regulatory data from the same well collected in the previous quarter; however, in most wells the effects on Cr(VI) concentrations associated with pumping volume and rate were small. Maintaining water levels above the well screen interval during purging and sample collection necessitated lower pumping rates and longer pumping times, and may have resulted in lower Cr(VI) concentrations in samples collected by USGS compared to regulatory samples. Where present, effects on Cr(VI) concentrations associated with pumping volumes and rates varied on a well-by-well basis, and sample collection effects on Cr(VI) concentrations were more important in samples from low-yielding wells.

E.2.5. Laboratory Methods, Study Reporting Levels, and Precision Data for Other Constituents

Laboratory methods used by the USGS NWQL for chemical constituents other than Cr(VI) are available in Fishman (1993), Fishman and Friedman (1989), and Garbarino and others (2006), and laboratory reporting levels are provided in table E.1. Equipment blanks, field blanks, and sequential replicates were collected in a similar manner as quality control data for Cr(VI) discussed previously.

Low-level detections in field-blank samples measured at the NWQL resulted in slightly larger SRLs compared to LRLs for 11 of 31 constituents measured as part of this study (table E.3). Most detections in blank samples appeared random, although low-level detections were present in about two-thirds of blank samples analyzed for calcium, strontium, and manganese—indicating systematic low-level contamination for these constituents of 0.07 milligrams per liter (mg/L), 70 µg/L, and 2.2 µg/L, respectively (table E.3). The SRL was estimated as the highest concentration in the blank data; this differs from the approach discussed previously to estimate SRLs for Cr(VI) because of the fewer number of blanks analyzed at the NWQL. Differences between the NWQL's LRL and the SRL calculated for this study for other constituents were generally small and did not affect interpretation of the data. No constituents measured at the NWQL as part of this study were detected in equipment blanks.

Table E.3. Quality-assurance metrics calculated from blank and replicate data for constituents analyzed in the field or at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) as part of the USGS hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.2) and U.S. Geological Survey (2021).

[Values rounded according to U.S. Geological Survey conventions. Precision, in percent, calculated for mean of replicate concentrations as root mean squared error divided by average replicate concentration. **Abbreviations**: —, not applicable; <, less than; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; mg/L, milligram per liter; µS/cm, microsiemen per centimeter; °C, degrees Celsius]

Constituent	Metrics calculated from blank data					Metrics calculated from replicate data				
	Laboratory reporting level (LRL)	Number of blanks	Number of detections	Study reporting level (SRL)	Number of replicate pairs	Maximum	Average	Minimum	Root mean square error	Precision, in percent
Field parameters										
pH, standard units	—	—	—	—	12	9.4	7.7	6.9	0.03	<1
Alkalinity, mg/L as $CaCO_3$	—	—	—	4.6	12	500	230	140	11	4.6
Dissolved oxygen, in mg/L	—	—	—	0.2	12	7.9	4.5	0.2	0.2	4.5
Specific conductance, in µS/cm at 25 °C	—	—	—	—	12	2,000	970	460	7.2	<1
Major ions, in milligrams per liter										
Alkalinity, as $CaCO_3$	4.6	13	0	4.6	12	520	240	140	7.1	3.0
Calcium	0.02	13	11	0.07	12	180	75	1.2	2.2	2.9
Chloride	0.02	13	1	0.03	12	180	84	25	2.8	3.4
Fluoride	0.01	13	0	0.01	12	2.0	0.78	0.17	0.04	5.1
Magnesium	0.01	13	0	0.01	12	31	13	0.072	0.36	2.8
Potassium	0.03	13	1	0.1	12	4.9	2.7	0.33	0.09	3.4
Silica	0.02	13	4	0.03	12	44	29	15	1.1	3.8
Sodium	0.06	13	1	0.08	12	280	130	70	7.5	5.8
Sulfate	0.02	13	1	0.03	12	330	136	33	3.3	2.4
Residue on evaporation	20	13	0	20	12	1,350	620	270	9.3	1.5
Minor ions, in micrograms per liter										
Bromide	30	13	0	30	12	380	157	47	30	—
Boron	2	13	1	3	12	1,550	590	120	19	3.2
Iodide	1	13	0	1	12	57	13	<1	5	—
Strontium	20	13	9	70	12	1,870	880	31	23	2.6
Nutrients, in milligrams per liter										
Ammonia, as nitrogen	0.01	10	1	0.01	10	0.03	0.011	0.01	<0.01	—
Nitrite, as nitrogen	0.001	10	0	0.001	10	0.04	0.007	<0.001	0.002	—
Nitrite plus nitrate, as nitrogen	0.04	10	0	0.04	10	18	3.60	4.7	0.13	3.6
Total nitrogen, as nitrogen	0.05	10	0	0.05	10	19	5.0	0.18	0.22	4.3

Table E.3. Quality-assurance metrics calculated from blank and replicate data for constituents analyzed in the field or at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) as part of the USGS hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.2) and U.S. Geological Survey (2021).—Continued

[Values rounded according to U.S. Geological Survey conventions. Precision, in percent, calculated for mean of replicate concentrations as root mean squared error divided by average replicate concentration. **Abbreviations**: —, not applicable; <, less than; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; mg/L, milligram per liter; µS/cm, microsiemen per centimeter; °C, degrees Celsius]

Constituent	Metrics calculated from blank data					Metrics calculated from replicate data				
	Laboratory reporting level (LRL)	Number of blanks	Number of detections	Study reporting level (SRL)	Number of replicate pairs	Maximum	Average	Minimum	Root mean square error	Precision, in percent
Nutrients, in milligrams per liter—Continued										
Orthophosphorous, as phosphorous	0.004	10	0	0.004	10	0.097	0.041	0.015	0.001	2.3
Trace elements, in micrograms per liter										
Antimony	0.03	13	0	0.03	12	0.62	0.14	<0.03	0.05	—
Aluminum	3	13	0	3	12	66	26	<3	68	260
Arsenic	0.1	13	2	0.3	12	49	14	0.65	0.66	4.6
Barium	0.6	13	0	0.6	12	120	38	1.3	1.3	3.4
Cadmium	0.03	13	0	0.03	12	0.04	<0.03	<0.03	<0.03	—
Chromium	0.5	13	0	0.5	12	68	8.3	10.8	0.24	2.9
Iron	5	13	0	5	12	180	22	<5	47	220
Lead	0.04	13	0	0.04	12	0.06	<0.04	<0.04	<0.04	—
Lithium	0.2	13	0	0.2	12	54	20	5.6	0.82	4.0
Manganese	0.2	13	8	2.2	12	500	45	<0.2	1.0	2.2
Uranium	0.1	13	0	0.1	12	110	27	3.6	1.7	6.4
Vanadium	0.1	13	3	0.7	12	110	22	3.7	0.47	2.1

Analyses of replicate data showed most constituents measured either in the field or at the NWQL had a precision, calculated as the root mean squared difference (RMSD) divided by the mean concentration expressed as a percent (Hyslop and White, 2009), at the overall mean replicate concentration of plus or minus 5 percent or less. In contrast, aluminum and iron had precision values of plus or minus 260 and 220 percent, respectively. Aluminum and iron can form colloids that are not filtered using 0.45-µm pore-sized filters; when present, these colloids can cause poor precision in analytical data. Recalculation of the RMSD after removing the two sets of paired replicate samples that had the greatest difference and were potentially affected by colloids within the water, resulted in a precision of plus or minus 3.8 and 9.1 percent for these constituents, respectively. Aluminum and iron concentrations in water from wells should be interpreted with the understanding that values for these constituents can have higher variability than other constituents measured. Precision was not calculated for constituents such as bromide, iodide, ammonia, nitrite, antimony, lead, and cadmium, which either had few concentrations greater than the LRL or replicate concentrations near the SRL.

E.2.6. Field and Laboratory Methods for Porewater

Porewater from fresh core material, collected using an auger rig, was pressure extracted using a hydraulic device designed by Manheim and others (1994). Drilling fluids were not used, and contamination of porewater by drilling fluids was not an issue. In general, porewater was extracted in the field as soon as possible after collection under a pressure of about 5,000 pounds per square inch (psi) using techniques described by Izbicki and others (2008a). Each extraction produced between 2 and 10 mL of sample water depending on the material. An individual extraction required from 1 hour to as long as 24 hours to complete, with clay-textured materials requiring more time and yielding less water than silt-textured material. To avoid damage to the equipment, porewater was not pressure extracted from coarse-textured sand and gravel material. Most porewater samples were extracted from saturated material, although two samples were extracted from unsaturated material above the water table. Sample water from individual extractions collected at the same site and approximate depth were consolidated into a single sample to obtain about 30 mL of water required for sample processing and analyses. Although porewater samples were extracted and processed in the field at the time of core-material collection between September and December 2015, some porewater samples collected between March and May 2018 were extracted and processed off-site after extractions from clay-textured materials lagged behind drilling and core-material collection.

Porewater samples were analyzed in the field for pH and specific conductance using meters equipped with probes designed for low-volume samples. Samples for dissolved Cr(VI) and Cr(t) were filtered, field speciated, and preserved at the time of collection, using techniques described by Ball and McCleskey (2003), for analysis by GFAAS using EPA Method 7010 (U.S. Environmental Protection Agency, 2007) at the USGS Redox Chemistry Laboratory. Field speciation for Cr(VI) and Cr(t) with subsequent analyses by GFAAS requires less water than Cr(VI) analyses by ion chromatography and Cr(t) analyses by ICP-MS. Porewater samples were filtered in the field and analyzed for selected trace elements including iron, manganese, arsenic, chromium as Cr(t), vanadium, and uranium by ICP-MS at the NWQL. These samples were identified for special handling because of their low volume. Samples for the stable isotopes of oxygen and hydrogen in the water molecule (discussed in chapter F within this professional paper) were analyzed by mass spectroscopy at the Reston Stable Isotope Laboratory (RSIL) in Reston, Virginia, using methods described by Révész and Coplen (2008a, b).

Replicate porewater samples extracted from splits of core material had concentrations that agreed to within 0.06 µg/L for Cr(VI), and within 0.4 µg/L for manganese, arsenic, vanadium, and uranium. Replicate samples for iron agreed to within 6 µg/L.

The sample container and hydraulically driven piston used to pressure-extract porewater were made of stainless steel, which contains chromium. Blank samples for porewater extractions, intended to determine if equipment contributed chromium to sample water, were prepared by saturating fine-textured (60-mesh) silica sand with trace-metal grade inorganic-free blank water, certified to be chromium free. Prior to use as a blank, the silica sand was cleaned with acidified reagent-grade blank water and rinsed repeatedly with reagent-grade, inorganic-free blank water. Hexavalent chromium concentrations in porewater extracted from two silica sand blanks in the same manner as environmental samples ranged from 0.1 to 0.2 µg/L. In contrast, Cr(VI) concentrations in water extracted from silica-sand blanks using a centrifuge were less than the LRL of 0.06 µg/L. Although blank data show higher Cr(VI) concentrations associated with the pressure-extraction procedure compared to the centrifuge-extraction procedure, the differences were small relative to environmental concentrations and do not affect interpretation of porewater data. In contrast to Cr(VI), Cr(t) concentrations in the two silica blanks were 1.3 µg/L. This concentration is greater than Cr(t) concentrations in about 60 percent of sampled porewater. Manganese, arsenic, vanadium, and uranium concentrations in pressure-extracted blanks and centrifuged blank water were less than their respective reporting levels. Iron concentrations in pressure-extracted blank water ranged from 17 to 20 µg/L; iron in centrifuged blank water was less than the reporting level of 5 µg/L.

E.2.7. Field and Laboratory Methods for Domestic Wells

During January 27–31, 2016, more than 70 domestic and agricultural wells were sampled and analyzed for field parameters (including pH, specific conductance, and dissolved oxygen), selected anions (including chloride, sulphate, fluoride, and nitrate), selected trace elements (including arsenic, Cr(VI), Cr(t), iron, manganese, uranium, and vanadium), and the stable isotopes of oxygen and hydrogen in the water molecule (discussed in chapter F within this professional paper). Domestic wells were purged and sampled using the installed pump. Water chemistry and isotope data (including field-replicate and field-blank data) for sampled domestic wells are provided in appendix E.1 (table E.1.3).

Hexavalent chromium was analyzed by ion chromatography using EPA Method 218.6 (U.S. Environmental Protection Agency, 1994a) by the USGS in a mobile field laboratory shortly after the time of collection. Analysis of Cr(VI) in the mobile field laboratory enabled interested residents to follow water collected from their wells to the mobile lab, where it was analyzed in their presence—minimizing residents' concerns associated with delays in laboratory analyses and tracking analytical data. In addition, Cr(VI) and Cr(t) were speciated in the field by anion exchange (Ball and McCleskey, 2003) with subsequent analyses done at the USGS Redox Chemistry Laboratory in Boulder, Colo., using EPA Method 7010 (U.S. Environmental Protection Agency, 2007). Field-blank and replicate samples were collected using techniques reported previously.

To expedite collection of a large number of samples in a short period of time, sample collection chambers used to process other samples collected as part of this study were not deployed to process and preserve samples from these domestic wells. Field-blank and replicate data for Cr(VI) and Cr(t) for field-speciated samples collected during windy conditions on January 30–31, 2016, showed increased Cr(VI) concentrations and variability compared to other blank and replicate samples collected as part of this study. Field speciated samples collected in 2-mL plastic vials appear vulnerable to contamination by wind-blown particles. The larger volume field blanks and replicate samples collected for analyses using EPA Method 218.6 in the mobile laboratory were not similarly affected.

E.2.8. Results of Quality-Assurance Data Collection and Analyses

An SRL of 0.1 µg/L was assigned for Cr(VI) data analyzed by ion chromatography using EPA Method 218.6 at the commercial laboratory used by PG&E for regulatory data collection; an SRL of 0.08 µg/L was assigned for Cr(VI) data prepared using field speciation with analyses by GFAAS at the USGS Redox Chemistry Laboratory. Hexavalent chromium results analyzed by ion chromatography and by field speciation with analyses by GFAAS were statistically similar throughout the range of data tested. Hexavalent chromium SRLs for data collected as part of this study were similar to the Cr(VI) SRL of 0.12 µg/L for regulatory data collected between 2011 and 2017 (chapter D, fig. D.4). No systematic quality concerns were identified with sample collection, handling, or analytical procedures used in this study, and Cr(VI) and Cr(t) data were suitable for the purposes of this study.

For consistency with regulatory data, Cr(VI) data analyzed by ion chromatography at the commercial laboratory are most commonly reported and discussed in this chapter. However, field-speciation data for Cr(VI) and Cr(t) were used to calculate redox potential because of the lower SRLs for Cr(VI) and Cr(t). Field-speciation data with analyses by GFAAS were reported for Cr(VI) in porewater analyses because sample volume was insufficient for analyses of porewater by ion chromatography. Hexavalent chromium data analyzed by ion chromatography using EPA Method 218.6, on site in a mobile USGS field laboratory, are reported for samples from domestic wells collected in January 2016 because samples for analyses of Cr(VI) at the commercial laboratory were not collected from those wells.

Analyses of replicate data showed most constituents measured at the NWQL had a precision of plus or minus 5 percent or less. Although, aluminum and iron had poorer precision and should be interpreted with the understanding that concentrations of these constituents can have greater variability than other constituents measured.

To ensure comparable Cr(VI) data, sample collection methods, equipment, and analytical procedures used in the USGS Cr(VI) background study were similar to methods and equipment used by PG&E to collect data for regulatory purposes. However, a modified low-flow method in which one casing volume was purged from monitoring wells prior to sample collection was used for regulatory data collection. In contrast, three casing volumes were purged from wells prior to sample collection, and a larger volume of water was withdrawn for sample collection as part of this study than was collected for regulatory purposes. In addition, water levels were monitored during purging and USGS sample collection and pumping rates adjusted to ensure (where possible) water levels remained above the screened interval of the sampled well—resulting in lower pumping rates and longer pumping time in some wells. Differences in well purging and sample collection protocols, including adjusting pumping rates to maintain water levels above the well screen interval during purging and sample collection, may have resulted in lower Cr(VI) concentrations in samples collected by the USGS compared to PG&E regulatory samples; overall, this difference was less than 9 percent. Differences in Cr(VI) concentrations associated with well purging and sample collection protocols likely vary on a well-by-well basis but were commonly greater in samples from low-yielding wells and most wells showed little difference in Cr(VI) concentrations resulting from sample collection methods. Additionally, samples of water from 14 selected wells collected in 2015 and 2017 showed a small, but statistically significant, decrease in Cr(VI) concentrations of about 2 percent per year.

By design, Cr(VI) data collected as part of the USGS Cr(VI) background study between March 2015 and November 2017 were used within a SSA to define the Cr(VI) plume extent. Hexavalent chromium data collected quarterly between April 2017 and March 2018 (discussed in chapter G within this professional paper) using PG&E sample collection protocols were used to calculate Cr(VI) background concentrations. Data used to calculate Cr(VI) background provide a 1-year snapshot in time, and the data were not impacted by pumping of larger volumes of water for purging and sample collection in the same manner as samples collected between March 2015 and November 2017.

E.2.9. Statistical Methods

Most statistics in this chapter were calculated using the computer program Statistical Analysis System (SAS; SAS Institute, Cary, North Carolina). Regression analysis including slope, intercept, R^2, and MSE was done using the method of least-squares (Neter and Wasserman. 1974). The significance of slope and intercept values relative to expected values of 1 and 0, respectively, was evaluated on the basis of the t-test (Neter and Wasserman, 1974) at a significance criterion (significance level) of $\alpha=0.05$ unless otherwise stated. The 90-percent and 95-percent prediction intervals around regression lines were calculated according to methods described by Neter and Wasserman (1974) using Microsoft Excel (Microsoft, Redmond, Washington). Correlation coefficients were evaluated using Kendall's Tau β correlation coefficient (Kendall, 1938; Helsel and Hirsch, 2002; Helsel and others, 2020). Comparison of median values were done on the basis of the median test (Neter and Wasserman, 1974). Results of statistical tests presented within the chapter were considered statistically significant at a significance criterion of $\alpha=0.05$, unless otherwise stated. Probability values (p-values) for individual tests are not provided.

Principal component analysis is a multivariate technique that uses matrix algebra to transform potentially correlated and potentially non-linear data (in this case, concentrations of arsenic, Cr(VI), uranium, vanadium, iron, and manganese in groundwater) into new variables, which are uncorrelated linear combinations of the original data (Hotelling, 1933; Wold and others, 1987). The new variables are called principal components, and there is one principal component for each variable in the original dataset. The magnitude of the principal components for each measurement within the dataset is called a score; scores are calculated from eigenvectors, ranging from -1 to 1, that describe the contribution of each measured concentration to the principal component score. Principal component scores were used in this chapter to identify the source of Cr(VI) in water from wells. Principal component analysis was done using the computer program SAS (SAS Institute, Cary, North Carolina) and is discussed in greater detail in chapter B within this professional paper.

E.3. Groundwater Chemistry

Groundwater-chemistry data (including isotopic and groundwater-age data discussed in chapter F within this professional paper) were collected between March 2015 and November 2017 from wells in Hinkley and Water Valleys. Sampled wells included (1) 83 monitoring wells installed for regulatory purposes, (2) 12 monitoring wells installed by PG&E as part of the USGS Cr(VI) background study at 6 locations upgradient from the Hinkley compressor station (identified with the prefix "BG"), and (3) 7 domestic wells sampled in areas where monitoring wells were not available (fig. E.2). Depth-dependent water-quality data from five production wells sampled in Hinkley and Water Valleys (chapter H) are not discussed in this chapter, although data from the surface discharge of those wells are presented on map figures in this chapter. Sampled wells were selected by the USGS in collaboration with a TWG and represent a mutually agreed upon, spatially distributed set of wells covering a range of geologic, hydrologic, and geochemical settings within and near the PG&E Cr(VI) plume.

U.S. Geological Survey data were compared to data from more than 600 PG&E monitoring wells sampled for regulatory purposes during Q4 2015 (ARCADIS, 2016). The PG&E regulatory data provide a more complete visualization of the distribution of selected physical and chemical constituents in water from wells within Hinkley and Water Valleys. Examination of PG&E data during well selection helped ensure that important areas were not overlooked.

The spatial distribution of specific conductance, nitrate, and major-ion chemistry data are presented. The spatial distribution of Cr(VI) concentrations is presented with a process-oriented discussion of redox, pH, and selected trace-element data. The chemistry of porewater samples extracted from core material and of water samples from domestic wells collected in January 2016, outside the area covered by monitoring wells, also are discussed within this chapter.

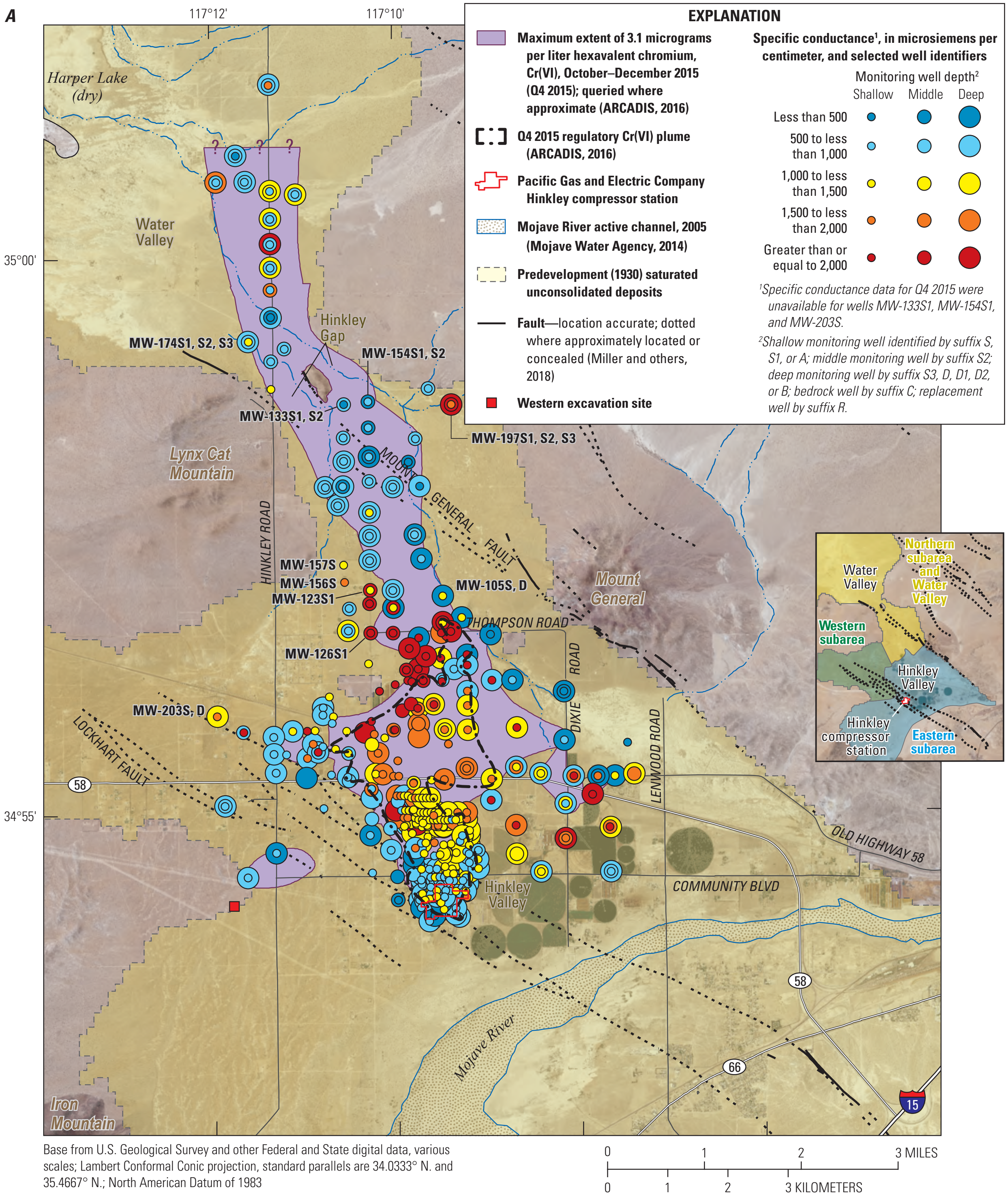
E.3.1. Specific Conductance and Nitrate

Specific conductance, a measure of the ability of water to conduct electricity that is related to its dissolved-solids concentration (McCleskey and others, 2011U.S. Geological Survey, 2019), ranged from 385 to 4,790 microsiemens per centimeter (µS/cm). Specific conductance was generally less than 600 µS/cm in wells near recharge areas along the Mojave River and increased as water flowed downgradient through agricultural areas in Hinkley Valley, with the highest specific conductance in water from shallower monitoring wells underlying agricultural land use. Specific conductance less than 500 µS/cm was measured in water from deeper wells in the eastern and northern subareas within Hinkley Valley and from domestic wells in locally derived alluvial-fan deposits along the flanks of Mount General (fig. E.6*B*). Specific conductance exceeded 1,000 µS/cm in water from some deeper monitoring wells and domestic wells in Water Valley and exceeded 1,500 µS/cm in water from wells MW-197S1, S2, and S3 in the northern subarea of Hinkley Valley (fig. E.6). Specific-conductance data collected by the USGS between March 2015 and November 2017 compare favorably with specific-conductance data collected by PG&E during Q4 2015 (fig. E.7), with an R^2 of 0.91, and values were spatially distributed in a similar manner.

Agricultural land use and irrigation return to groundwater in Hinkley Valley increased in the early 1950s (Stamos and others, 2001; Jacobs Engineering Group, Inc., 2019), about the same time as Cr(VI) releases began from the Hinkley compressor station. Specific conductance (along with delta oxygen-18 and delta deuterium isotope data, $\delta^{18}O$ and δD, respectively; chapter F) provide a measure of irrigation return in water from wells. High specific-conductance values, greater than 1,000 µS/cm, consistent with irrigation return were present in water from wells downgradient from the mapped Q4 2015 regulatory Cr(VI) plume as far as wells MW-105S and MW-123S1 (fig. E.6*B*), but these high values were not widely present within the northern subarea. The data are consistent with water-level data (Stone, 1957; California Department of Water Resources, 1967) that show groundwater pumping reversed the water-level gradient between the eastern and northern subarea within Hinkley Valley between 1953 and 1982, thereby limiting the movement of water containing irrigation return to the north. This reversal of the water-level gradients also likely limited movement of Cr(VI) released from the Hinkley compressor station into the northern subarea during this period.

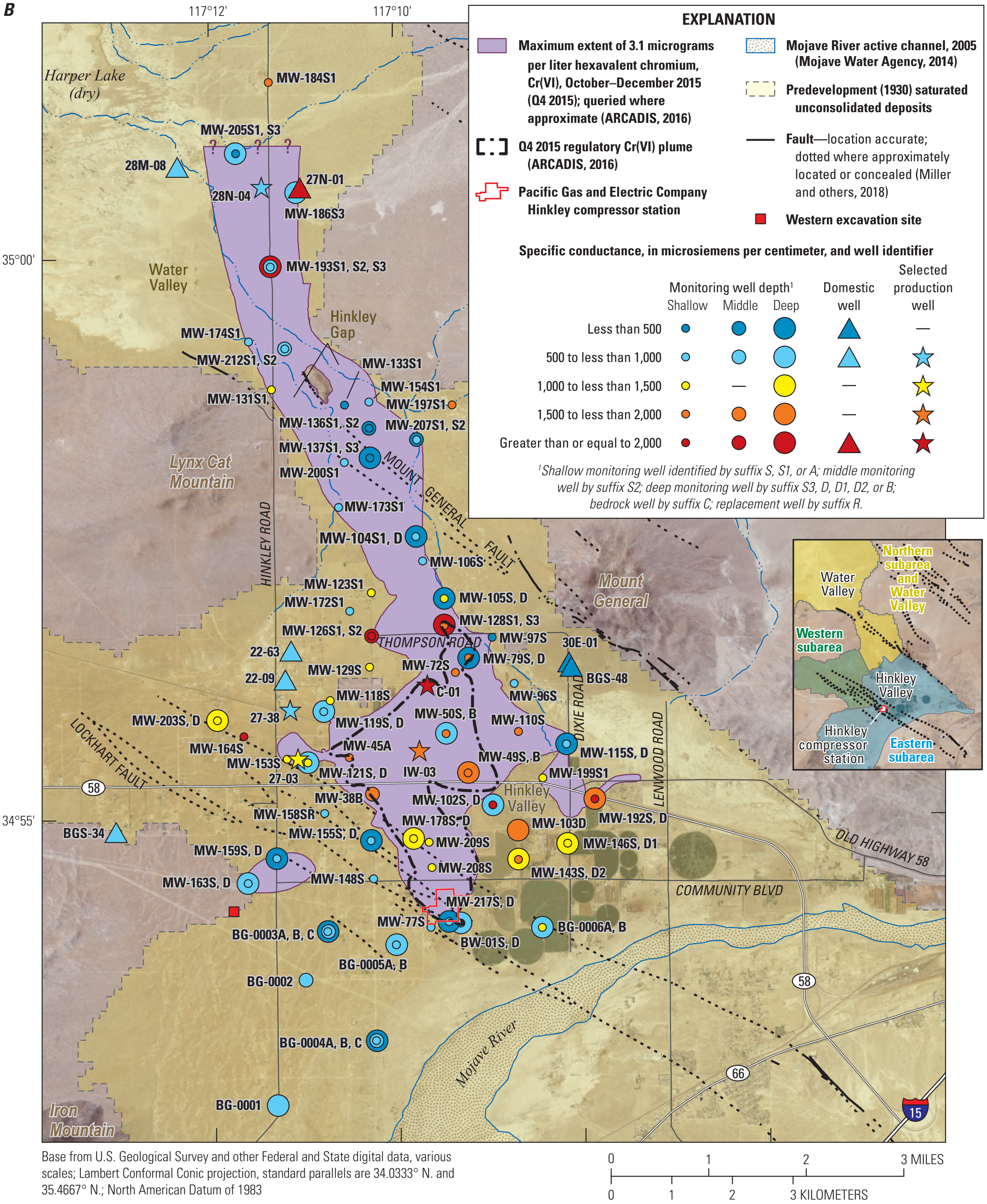
Specific conductance was not correlated with Cr(VI). Irrigation return water commonly has low Cr(VI) concentrations, likely as a result of Cr(VI) reduction to Cr(III) by biological activity within the crop root zone (Salt and others, 1995; Guertin and others, 2004). Land application of Cr(VI)-containing groundwater is used by PG&E to remove Cr(VI) at agricultural land treatment units (LTUs) operated by PG&E in Hinkley Valley (chapter A; Guertin and others, 2004; ARCADIS, 2017; Bell and others, 2019). Given the scale of agricultural pumping in Hinkley Valley and the widespread presence of irrigation return water within the mapped Q4 2015 regulatory Cr(VI) plume, it is likely that at least some anthropogenic Cr(VI) released from the Hinkley compressor station was inadvertently reduced to Cr(III) by irrigation of agricultural fields.

Nitrate in groundwater is commonly associated with irrigation return, other agricultural land uses, and septic return. Although not related to anthropogenic Cr(VI) from the Hinkley compressor station, nitrate concentrations in water from wells in Hinkley and Water Valleys are a public health concern (Lahontan Regional Water Quality Control Board, 2015). Nitrate concentrations were greater than the MCL of 10 mg/L as nitrogen (nitrate as N) in water from 20 percent of wells sampled as part of the USGS Cr(VI) background study, with the highest concentration of 36 mg/L nitrate as N in water from MW-126S2. Specific conductance in water from wells was significantly correlated with nitrate concentrations, with a Kendall's correlation coefficient (r) of 0.71; if high specific conductance in water from deep wells in Water Valley (which are associated with geologic conditions rather than with irrigation return water) are omitted, the correlation coefficient increases to 0.77.



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.6. Specific conductance in water from selected wells: *A*, Pacific Gas and Electric Company (PG&E), October–December 2015 (Q4 2015); and *B*, U.S. Geological Survey (USGS), Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Pacific Gas and Electric Company regulatory data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological Survey data are available in appendix E.1 (table.E.1.1) and U.S. Geological Survey (2021).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.6.—Continued

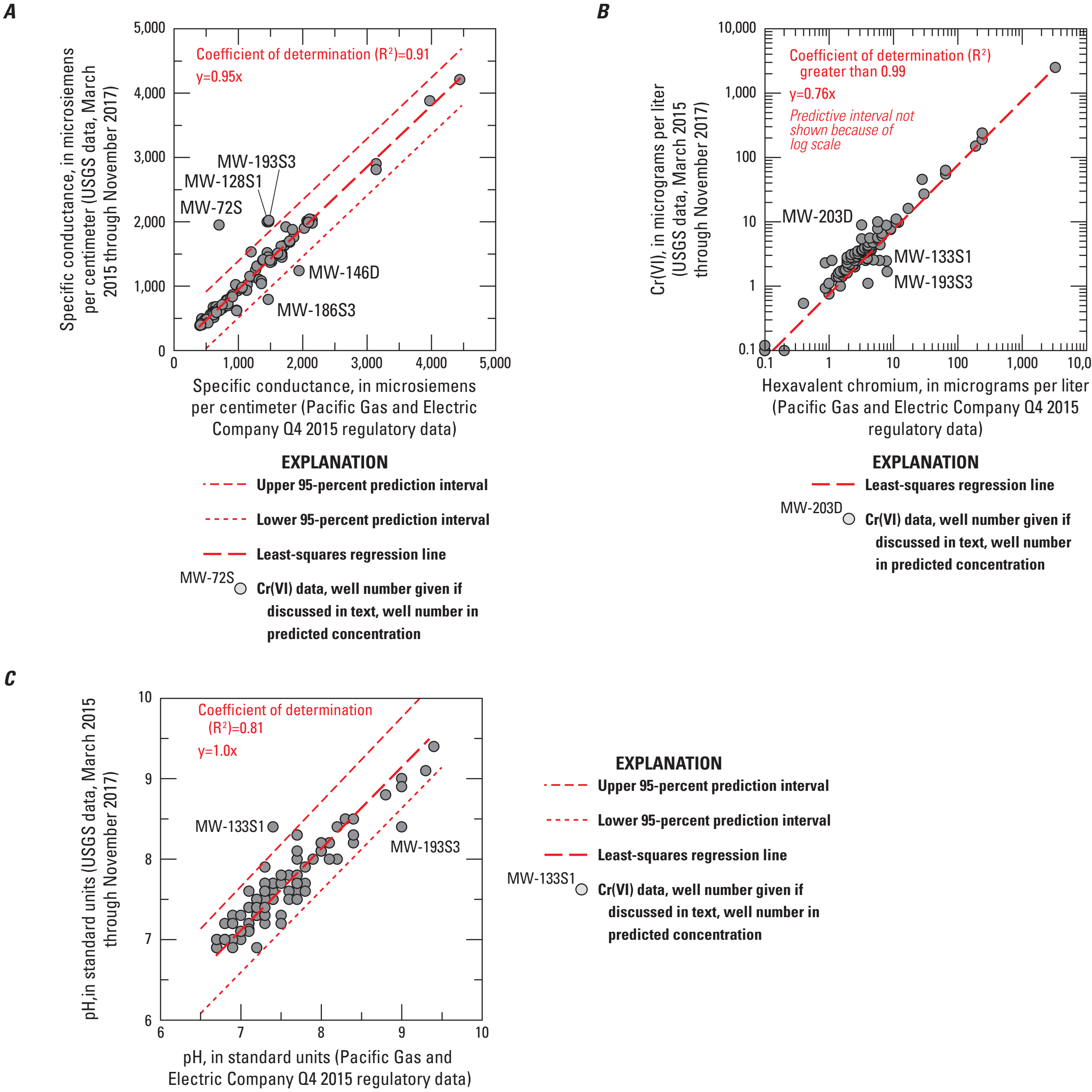


Figure E.7. Comparison between Pacific Gas and Electric Company Q4 2015 (October–December 2015) regulatory data and U.S. Geological Survey (USGS) data collected March 2015 through November 2017; *A*, specific conductance; *B*, hexavalent chromium, Cr(VI); and *C*, pH in Hinkley and Water Valleys, western Mojave Desert, California. Pacific Gas and Electric Company regulatory data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological Survey data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

E.3.2. Major-Ion Composition

Major ions in water from wells include the cations calcium, magnesium, sodium, and potassium, and the anions bicarbonate (including carbonate in water having pH greater than 8.3), sulfate, and chloride. The major-ion composition of water from wells sampled as part of this study was evaluated using a trilinear diagram (Piper, 1944). The diagram shows the proportions of major cations and major anions on a charge-equivalent basis in which the total positive charge of the cations and the total negative charge of the anions theoretically sums to zero. Cations are plotted on the lower left triangle, anions (including nitrate, which has a high enough concentration to contribute to the charge balance) are plotted on the lower right triangle, and the data are integrated in the central diamond within the trilinear diagram (fig. E.8). Trilinear diagrams are useful for understanding hydrologic, geologic, geochemical, and anthropogenic processes (including irrigated agriculture) that affect groundwater chemistry. On the basis of the relative proportions of major cations and anions, water from sampled wells was divided into four groups (fig. E.8):

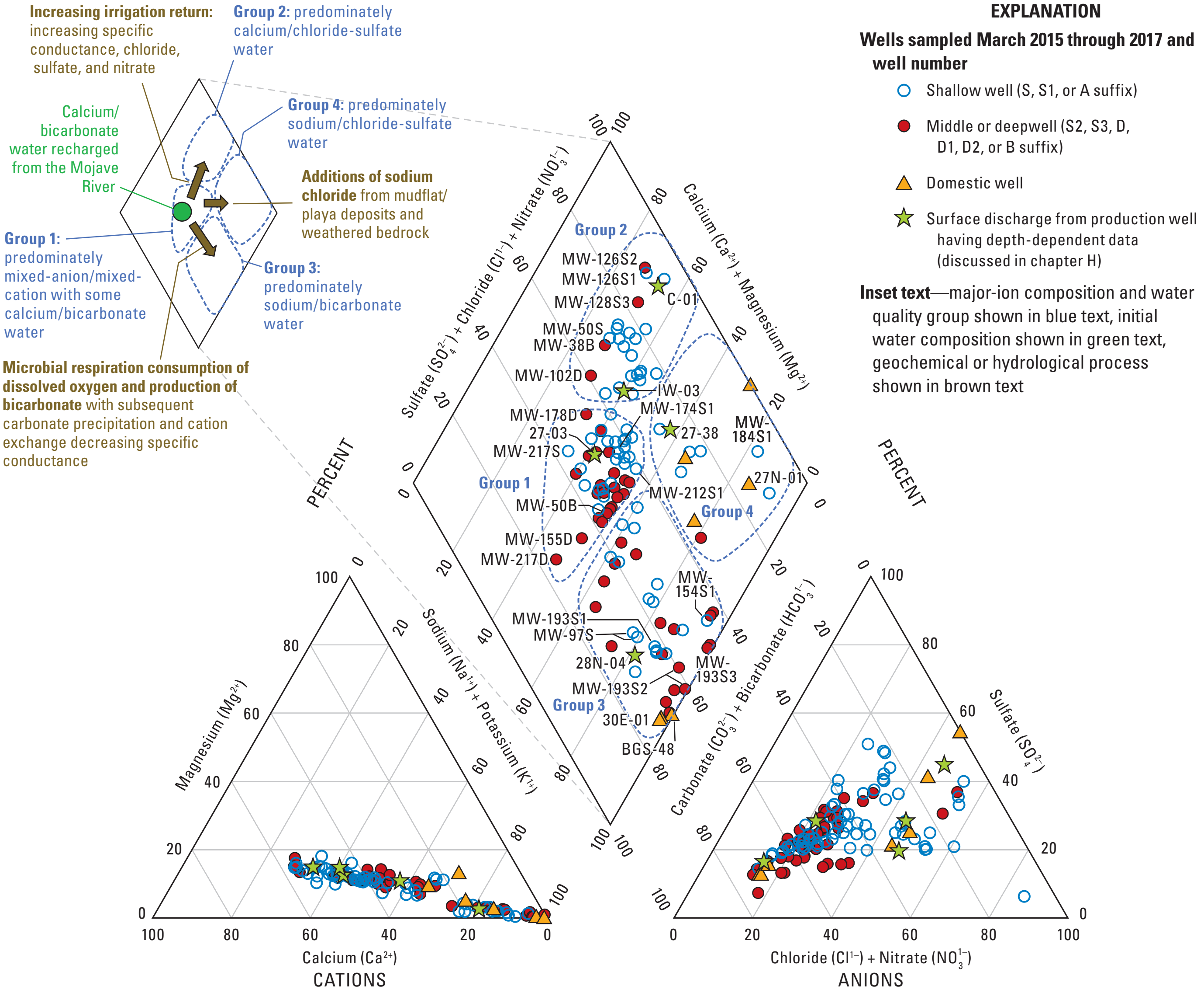


Figure E.8. Major-ion composition and geochemical and hydrologic processes for water from wells sampled as part of the U.S. Geological Survey hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

Group 1 was composed predominately of calcium/bicarbonate water from wells near recharge areas along the Mojave River and also includes mixed-cation/mixed-anion water.

Group 2 was composed predominately of calcium/chloride-sulfate water.

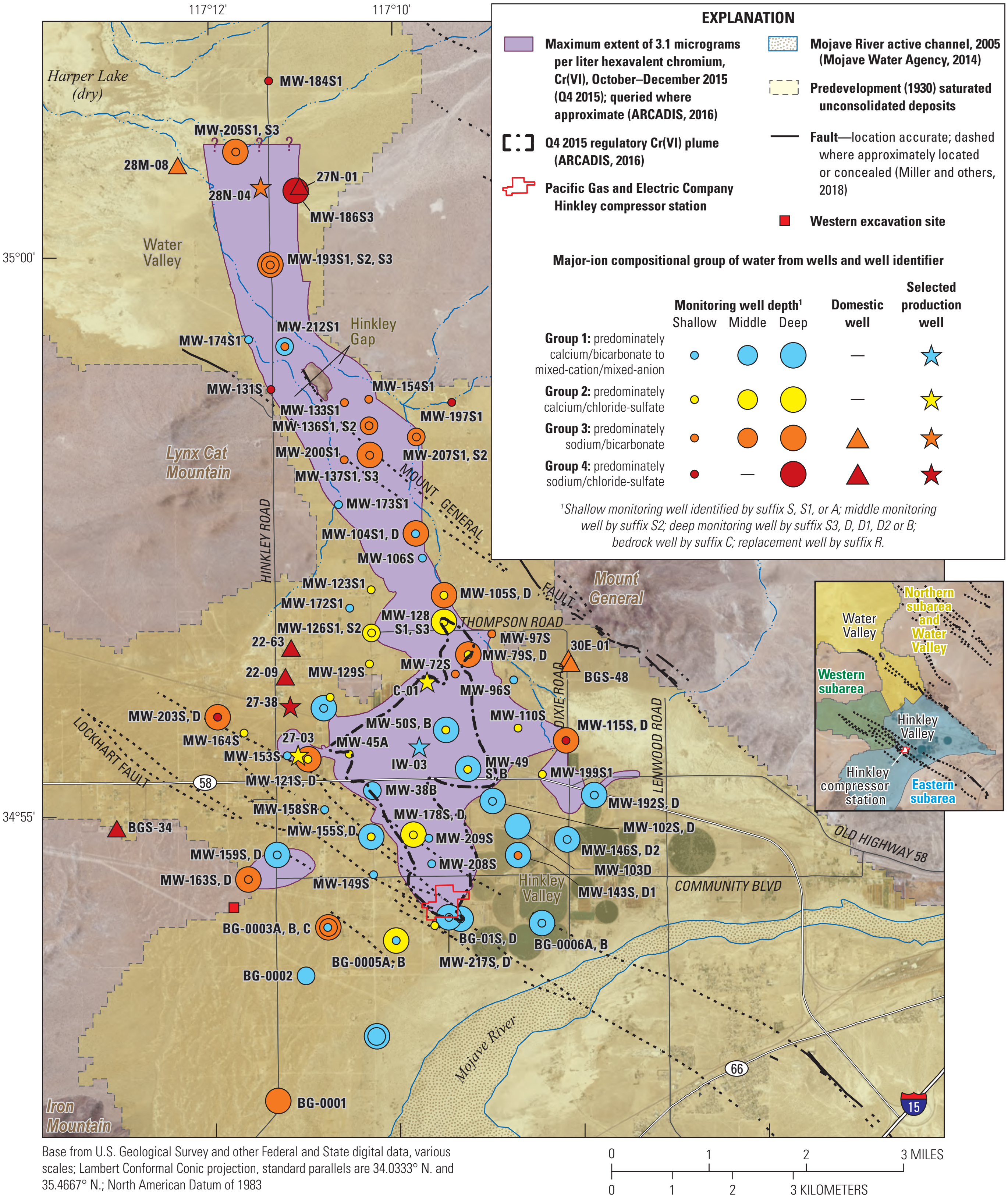
Group 3 was composed predominately of sodium/bicarbonate water.

Group 4 was composed predominately of sodium/chloride water.

Major-ion composition varies within each group, and water samples from some wells have major-ion compositions that appear to represent transitions between different groups. Major-ion data are not routinely collected by PG&E from monitoring wells for regulatory purposes. The characteristics of each group are discussed in the following paragraphs.

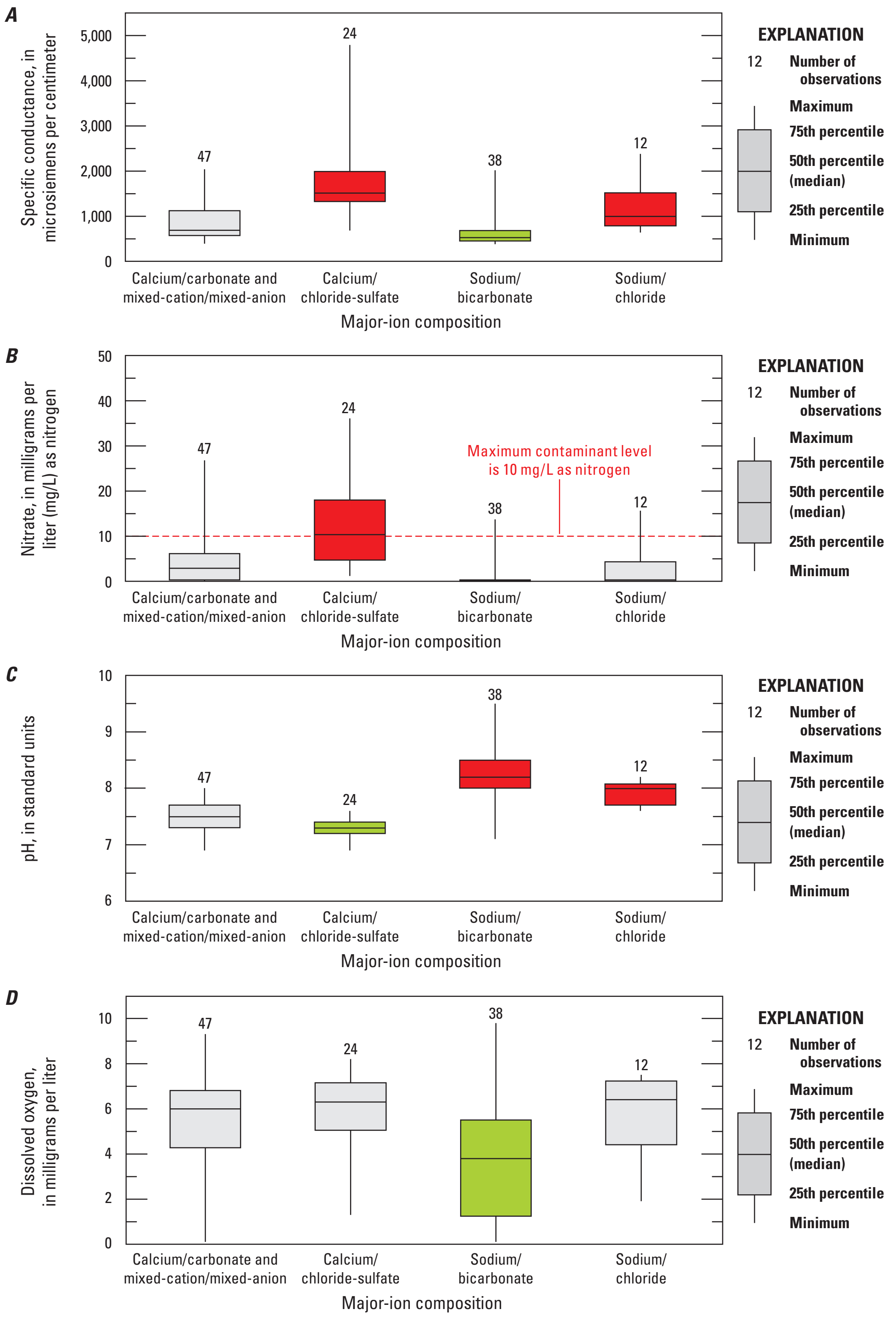
Group 1 water, having a calcium/bicarbonate or mixed-cation/mixed-anion composition, was present in almost 40 percent of wells and was the most common composition of water from sampled wells in Hinkley and Water Valleys (fig. E.8). Calcium/bicarbonate water predominated near sources of recharge along the Mojave River, whereas mixed-cation/mixed-anion water predominated in shallow wells within the eastern and western subareas (fig. E.9). The Hinkley compressor station is located near the Mojave River, and Cr(VI) from the Hinkley compressor station would have been released into groundwater having a major-ion composition predominately within group 1. Water having a mixed-anion/mixed-cation composition was present in wells completed in Mojave River alluvium as far north as well MW-174S1 in Water Valley (fig. E.9). Water from this well is downgradient from high specific-conductance irrigation return water and may have been recharged prior to the onset of large-scale irrigated agriculture in Hinkley Valley beginning in the early 1950s (Stamos and others, 2001)—potentially predating Cr(VI) releases from the Hinkley compressor station. Water from wells in group 1 had specific-conductance values ranging from less than 600 µS/cm near recharge areas along the Mojave River to more than 2,000 µS/cm (fig. E.10*A*). Specific conductance increased as calcium, sulfate, and chloride proportions increased in downgradient areas underlying agricultural land use. Nitrate concentrations ranged from less than the reporting limit of 0.04 to 27 mg/L nitrate as N, with more than 20 percent of wells exceeding the MCL for nitrate (fig. E.10*B*). Specific conductance and nitrate concentrations were highly correlated within group 1, with a correlation coefficient of r=0.90. Water from wells within group 1 upgradient (southwest) of the Lockhart fault or within mapped strands of the fault had higher proportions of bicarbonate than water from wells on the downgradient side of the fault. Changes in major-ion composition across the Lockhart fault are consistent with water-level data (Stone, 1957; California Department of Water Resources, 1967; Stamos and others, 2001) that indicate the Lockhart fault is an impediment to groundwater flow.

Group 2 water, having a calcium/chloride-sulfate composition, was present in almost 20 percent of sampled wells in Hinkley and Water Valleys (fig. E.8). Calcium/chloride-sulfate water is associated with irrigation return to groundwater in areas underlying agricultural land use (fig. E.8) and was present in shallow wells and some deep wells in the eastern subarea and in wells MW-126S1, MW-126S2, and MW-123S1 in the northern subarea downgradient from the mapped Q4 2015 regulatory Cr(VI) plume (fig. E.9). Large-scale irrigated agriculture in Hinkley and Water Valleys began in the early 1950s (Stamos and others, 2001), near the time of Cr(VI) releases from the Hinkley compressor station. Water from wells in group 2 had specific-conductance values ranging from 680 to 4,790 µS/cm. Nitrate concentrations in group 2 water ranged from 1.1 to 36 mg/L as nitrogen (fig. E.10*B*). Nitrate concentrations exceeded the MCL of 10 mg/L nitrate as N in water from 50 percent of wells within group 2. Median specific-conductance values and nitrate concentrations within group 2 are significantly higher than median specific-conductance values and nitrate concentrations within group 1 (figs. E.10*A*, *B*).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.9. Major-ion compositional groups of water from wells sampled as part of the U.S. Geological Survey hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).



Data shown in red if median value is statistically different and higher than median mixed-cation/mixed anion value, and data shown in green if median value is significantly different and lower than median mixed-cation/mixed anion value, on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

Data shown in red if median value is statistically different and higher than median mixed-cation/mixed anion value on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

Data shown in red if median value is statistically different and higher than median mixed-cation/mixed anion value, and data shown in green if median value is significantly different and lower than median mixed-cation/mixed anion value, on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

Data shown in green if median value is significantly different and lower than median mixed-cation/mixed anion value, on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman,1974).

Figure E.10. Water quality from wells grouped according to their major-ion composition, sampled as part of the U.S. Geological Survey hexavalent chromium, Cr(VI), background study: *A*, specific conductance, *B*, nitrate, *C*, pH, and *D*, dissolved-oxygen concentrations in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Groups assigned from data available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

Group 3 water, having a sodium/bicarbonate composition, was present in slightly more than 30 percent of sampled wells and was the second most common major-ion composition in water from sampled wells in Hinkley and Water Valleys (fig. E.8). Sodium/bicarbonate water in aquifers within the Mojave Desert (Izbicki and others, 1995; Izbicki and Michel, 2004) and elsewhere in California (Izbicki and Martin, 1997; Izbicki and others, 1995) indicates chemical changes in groundwater commonly driven by microbial respiration, consumption of oxygen, and production of bicarbonate, coupled with subsequent calcite precipitation and cation exchange within aquifers (fig. E.8). These chemical changes commonly require time to occur, and sodium/bicarbonate groundwaters tend to be isolated from surface sources of recharge by depth or by distance along long flow paths within an aquifer (fig. E.9). Water from wells in group 3 had specific-conductance values ranging from 385 to 2,020 µS/cm (fig. E.10). Low specific conductance in water is consistent with removal of calcium and bicarbonate through calcite precipitation, and the specific conductance of sodium/bicarbonate water from some wells in the northern subarea was lower than that of water near recharge sources along the Mojave River. Higher specific conductance in sodium/bicarbonate water from some wells in Water Valley results from differences in geologic material composing aquifers in that area. Although less common in the eastern subarea, strongly sodium/bicarbonate groundwater potentially isolated from surface sources of recharge was present in water from domestic wells 30E-01 and BGS-48 along the flanks of Mount General and in water from well MW-115D near mudflat/playa deposits near Mount General (fig. E.9). Nitrate concentrations in group 3 water ranged from less than the reporting limit of 0.04 to 14 mg/L nitrate as N (fig. E.10). Ninety-five percent of wells within group 3 had nitrate concentrations less than 1.2 mg/L as N, consistent with their depth within the aquifer and isolation from surface sources of recharge, including irrigation return water containing nitrate. The age (time since recharge) of sodium/bicarbonate water from sampled wells in Hinkley and Water Valleys likely predates large-scale irrigated agriculture and Cr(VI) releases from the Hinkley compressor station.

Group 4 water, having a sodium/chloride composition, was present in 10 percent of sampled wells in Hinkley and Water Valleys (fig. E.8). Sodium and chloride form salts with other major ions that are highly soluble, and sodium/chloride water may be present in low-permeability mudflat/playa deposits or other materials where water may have evaporated extensively during deposition. Water from well MW-197S1 in the northern subarea and wells MW-184S1 and 27N-01 in Water Valley, completed entirely or partly in lake margin and mudflat/playa deposits (Groover and Izbicki, 2018), have a sodium-chloride composition. Water having a sodium/chloride composition also was present in well MW-115S, near playa lake deposits near Mount General in the eastern subarea. High concentrations of sodium and chloride also are commonly associated with fluid inclusions within granitic and metamorphic bedrock; water from domestic wells BGS-34, 22-09, 22-63, and production well 27-38 completed entirely or partly in weathered bedrock or bedrock underlying the western subarea have a sodium/chloride composition. Water from wells in group 4 had specific-conductance values ranging from 640 to 2,380 µS/cm and nitrate concentrations ranging from 0.07 to 16 mg/L as nitrogen (fig. E.10). Specific conductance was inversely correlated with nitrate, correlation coefficient r=0.33, and only well 22-63, in a formerly residential area served by onsite (septic) treatment systems, had a nitrate concentration in excess of the MCL for nitrate. Similar to sodium/bicarbonate water, wells yielding sodium/chloride water tend to be isolated from surface sources of recharge, and the age of sodium/chloride water from sampled wells likely predates Cr(VI) releases from the Hinkley compressor station.

Differences in the major-ion composition of water from wells within Hinkley and Water Valleys result from differences in hydrology, geology, natural processes, and anthropogenic changes in groundwater chemistry (including agricultural activity and irrigation return) that occur along groundwater-flow paths through aquifers. Although qualitative, the differences in the major-ion composition of groundwater can be used to identify areas that are well connected to surface sources of recharge and areas where groundwater is more isolated and may predate Cr(VI) releases from the Hinkley compressor station (fig. E.8).

Wells near recharge areas along the Mojave River have water with a calcium/bicarbonate composition (group 1); Cr(VI) from the Hinkley compressor station likely would have been released into groundwater having a major-ion composition within group 1. Water with a calcium/chloride-sulfate composition (group 2), commonly having high specific conductance and nitrate concentrations, is affected by irrigation return water within Hinkley Valley and within the southern part of the northern subarea as far downgradient as well MW-123S1. The spatial distribution of water samples with mixed-cation/mixed-anion composition (group 1) showed that areas within the southern part of Water Valley as far downgradient as well MW-174S1 were recharged from the Mojave River, but recharge likely predated the onset of irrigated agriculture in Hinkley Valley and presumably predated Cr(VI) releases from the Hinkley compressor station. Sodium/bicarbonate water from wells (group 3) near the margins of the eastern and western subareas and within the northern subarea and Water Valley have reacted more extensively with aquifer materials; this water likely predates large-scale irrigated agriculture and Cr(VI) releases from the Hinkley compressor station. Similarly, sodium/chloride water from wells in bedrock and mudflat/playa deposits also have reacted extensively with aquifer materials and likely predate Cr(VI) releases from the Hinkley compressor station. Groundwater sources and ages (time since recharge) are addressed more quantitatively using chemical and isotopic tracers in chapter F within this professional paper.

E.3.3. Hexavalent Chromium

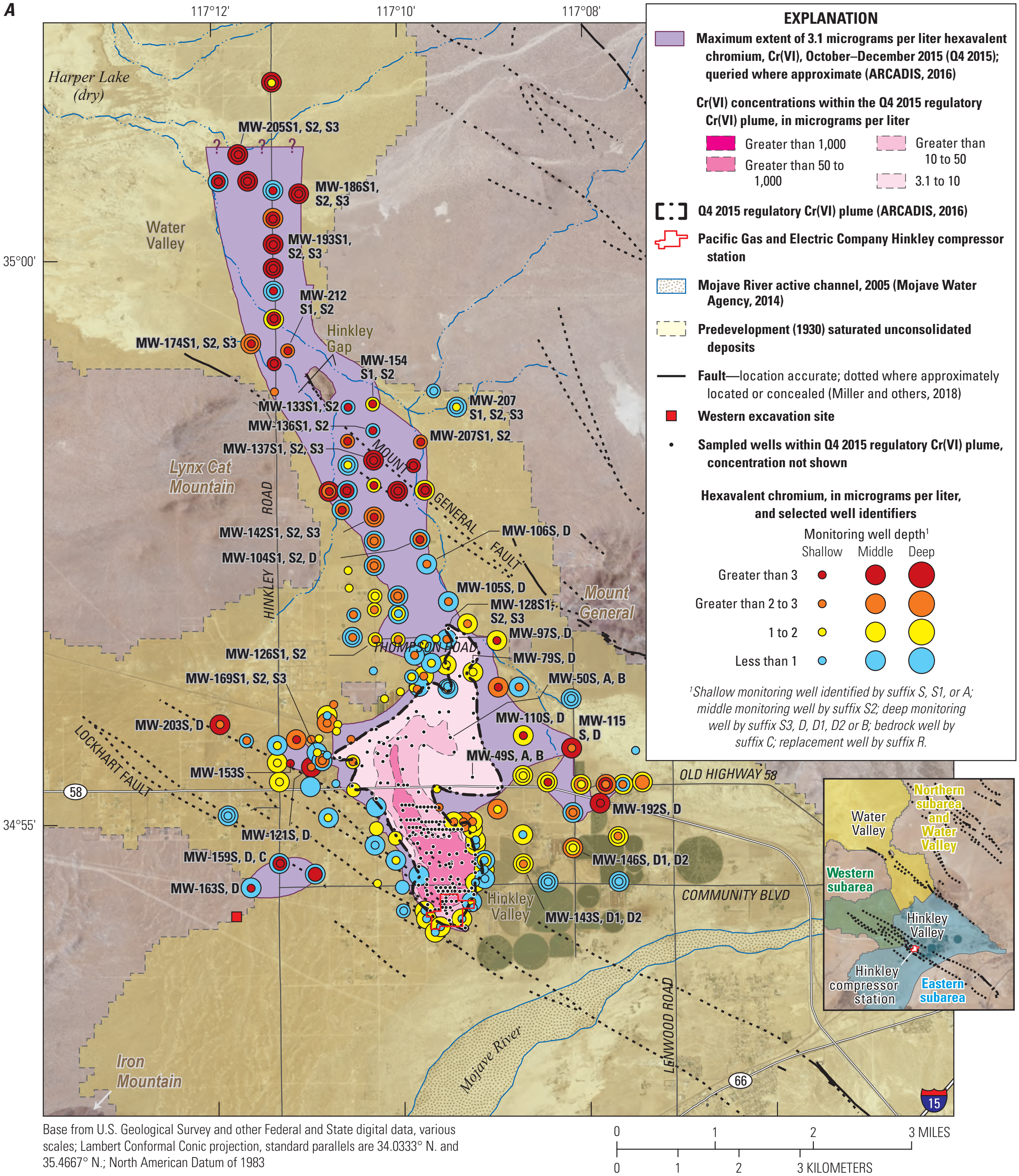
Hexavalent chromium concentrations in water from wells sampled between March 2015 and November 2017 ranged from less than the SRL of 0.10 to 2,500 µg/L. The highest Cr(VI) concentrations were in water from wells within the Q4 2015 regulatory Cr(VI) plume downgradient from the Hinkley compressor station that were sampled as end-members representative of anthropogenic Cr(VI) in groundwater. Consistent with Cr(t) and Cr(VI) occurrence in alkaline, oxic groundwater elsewhere in California (Izbicki and others, 2015), approximately 90 percent of the Cr(t) outside the mapped Q4 2015 regulatory plume, was present as Cr(VI) (fig. E.3*C*). In contrast, approximately 97 percent of the chromium in groundwater within the Q4 2015 regulatory Cr(VI) plume was in the form of Cr(VI).

Hexavalent chromium concentrations in samples, collected by the USGS between March 2015 and November 2017, were commonly lower than Q4 2015 regulatory Cr(VI) concentrations with a least-squares regression slope of 0.76 (fig. E.7*B*) but otherwise were strongly correlated with an R^2 greater than 0.99. Lower Cr(VI) concentrations in USGS data may result from a combination of differences in sample collection methodology (fig. E.5) and changes in Cr(VI) concentrations caused by management and remediation activities within the regulatory Cr(VI) plume. If the two highest Cr(VI) concentrations within the regulatory Cr(VI) plume are excluded, then the slope of the refitted regression line increases to 0.91 (not shown on fig. E.7*B*) and is consistent with the 9 percent difference in Cr(VI) concentrations attributable to differences in sample collection methodology.

Hexavalent chromium concentrations in water from wells outside the Q4 2015 regulatory Cr(VI) plume were as high as 11 µg/L in water from well MW-154S1, completed in fine-textured, mudflat/playa deposits in the northern subarea (fig. E.11*A*). Hexavalent chromium concentrations as high as 10 µg/L were measured in water from well MW-163S, downgradient from the “western excavation site” (Lahontan Regional Water Quality Control Board, 2014), and concentrations as high as 8.9 µg/L were measured in water from well MW-203D, completed in Miocene deposits (5.3 to 23 million years old) underlying the western subarea. In addition, Cr(VI) concentrations exceeded the interim 3.1 µg/L regulatory Cr(VI) background concentration in water from some wells completed near mudflat/playa deposits near Mount General in the eastern subarea and downgradient from the Lockhart fault in the western subarea (fig. E.11*B*). Hexavalent chromium concentrations also exceeded the interim 3.1 µg/L regulatory background in some wells in the northern subarea and Water Valley (fig. E.11*B*), with Cr(VI) concentrations as high as 4.2 µg/L in water from well MW-193S1 in Water Valley. Median Cr(VI) concentrations in water from wells outside the regulatory Cr(VI) plume were significantly higher in the northern subarea and Water Valley (fig. E.12*A*) compared to other areas, and the median Cr(VI) concentration was significantly higher in water from wells having a sodium/bicarbonate composition (that is presumably isolated from surface sources of groundwater recharge) than other wells outside the Q4 2015 regulatory Cr(VI) plume (fig. E.12*B*).

Hexavalent chromium concentrations in water from almost 40 percent of wells outside the Q4 2015 regulatory Cr(VI) plume sampled by the USGS between March 2015 and November 2017 exceeded the 3.1 µg/L interim regulatory Cr(VI) background concentration (fig. E.13). In contrast, Cr(VI) concentrations in water from about 20 percent of wells outside the Q4 2015 regulatory Cr(VI) plume sampled for regulatory purposes by PG&E during Q4 2015 exceeded the 3.1 µg/L interim regulatory Cr(VI) background concentration (fig. E.13). The data are consistent with selection of wells having higher Cr(VI) concentrations for sample collection by the USGS in collaboration with the TWG. The differences in PG&E and USGS Cr(VI) data are more pronounced in the western subarea and less pronounced in Water Valley. However, both datasets illustrate that reevaluation of natural Cr(VI) occurrence in water from wells and the 3.1 µg/L interim regulatory Cr(VI) background concentration in Hinkley and Water Valleys is appropriate.

Chromium concentrations in aquifer material adjacent to the screened interval of sampled wells outside the Q4 2015 regulatory Cr(VI) plume were higher in fine-textured materials than in coarser-textured materials (fig. E.14*A*). However, there was no statistically significant difference in median Cr(VI) concentrations in water from sampled wells grouped by the texture of aquifer materials (fig. E.14*B*). The data indicate there is poor correspondence between chromium concentrations in aquifer material and Cr(VI) concentrations in water from wells. It is likely that Cr(VI) concentrations in water from wells are controlled by factors other than geochemical abundance within aquifer materials. These factors include weathering of chromium from primary mineral grains and sorption of chromium to aquifer solids (discussed in chapter C within this professional paper), coupled with aqueous geochemical factors including the redox state and pH of groundwater.



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.11. Hexavalent chromium, Cr(VI), concentrations in water from selected wells: *A*, Pacific Gas and Electric Company (PG&E) data, October–December 2015 (Q4 2015) and *B*, U.S. Geological Survey data, March 2015 through November 2017, Hinkley and Water Valleys, western Mojave Desert, California. Pacific Gas and Electric Company data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological Survey data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

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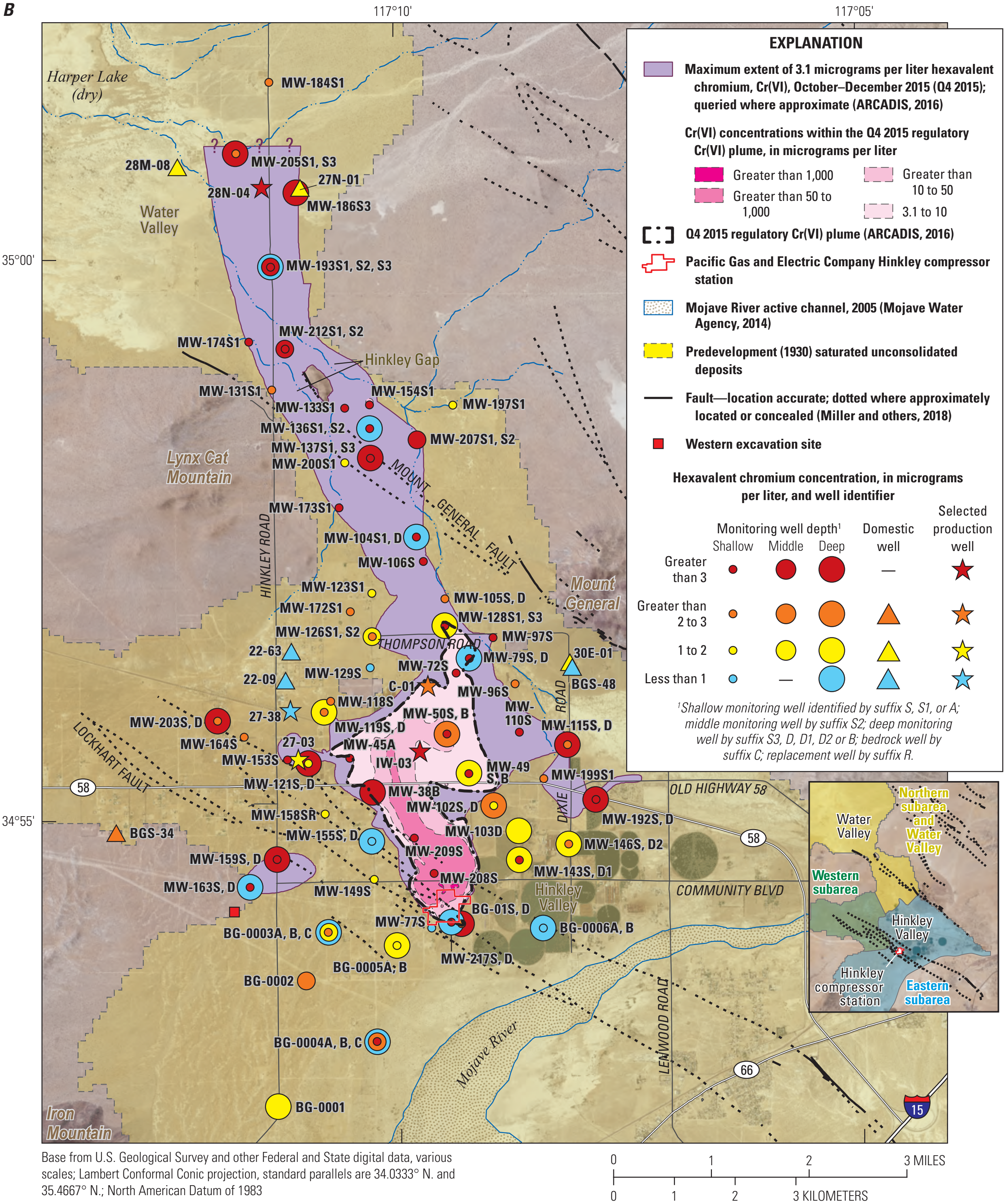
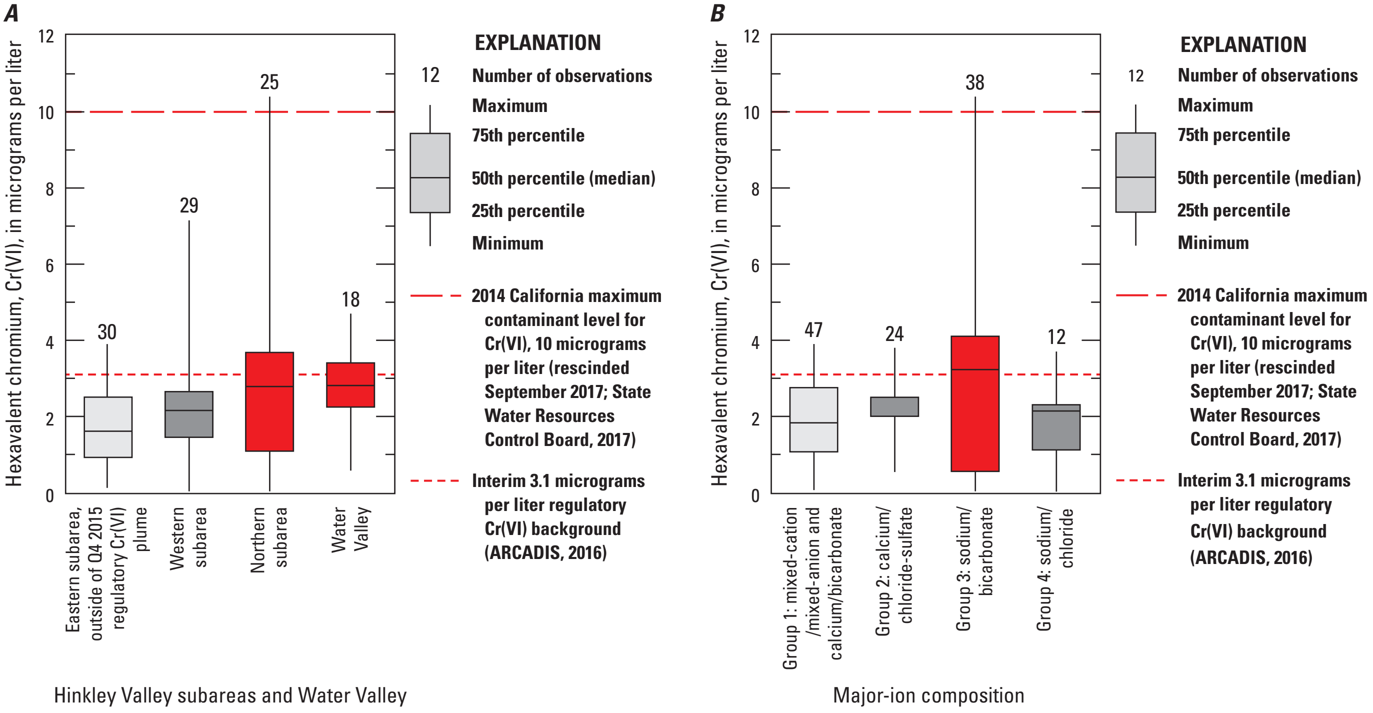


Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

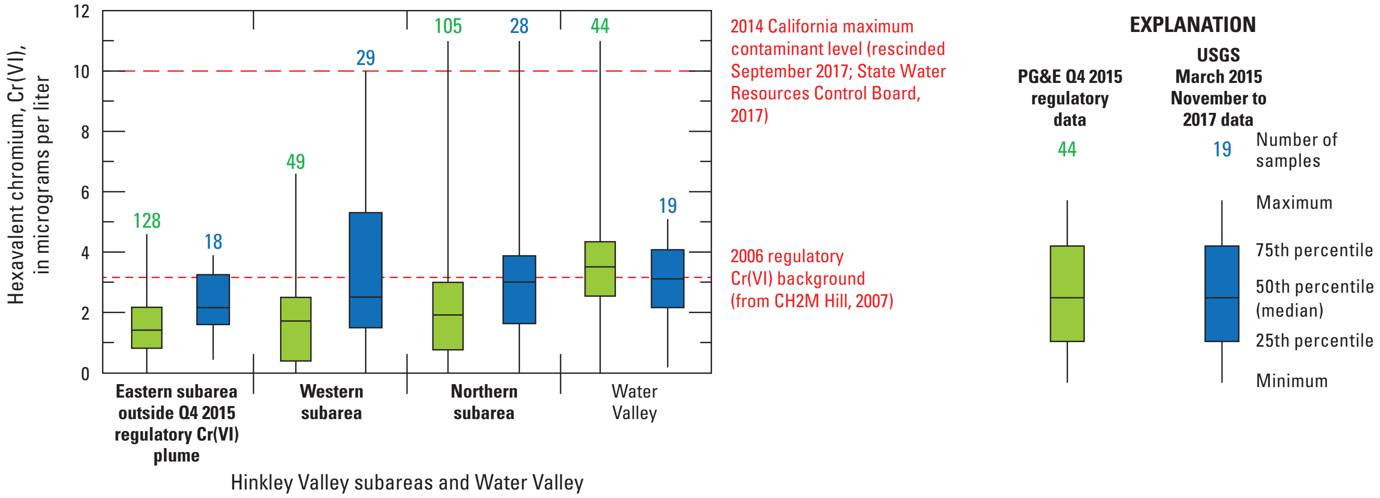
Figure E.11.—Continued



Data shown in red if median value is statistically different and higher than median eastern subarea or mixed-cation/mixed anion value, and dark grey if median value is not significantly different on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

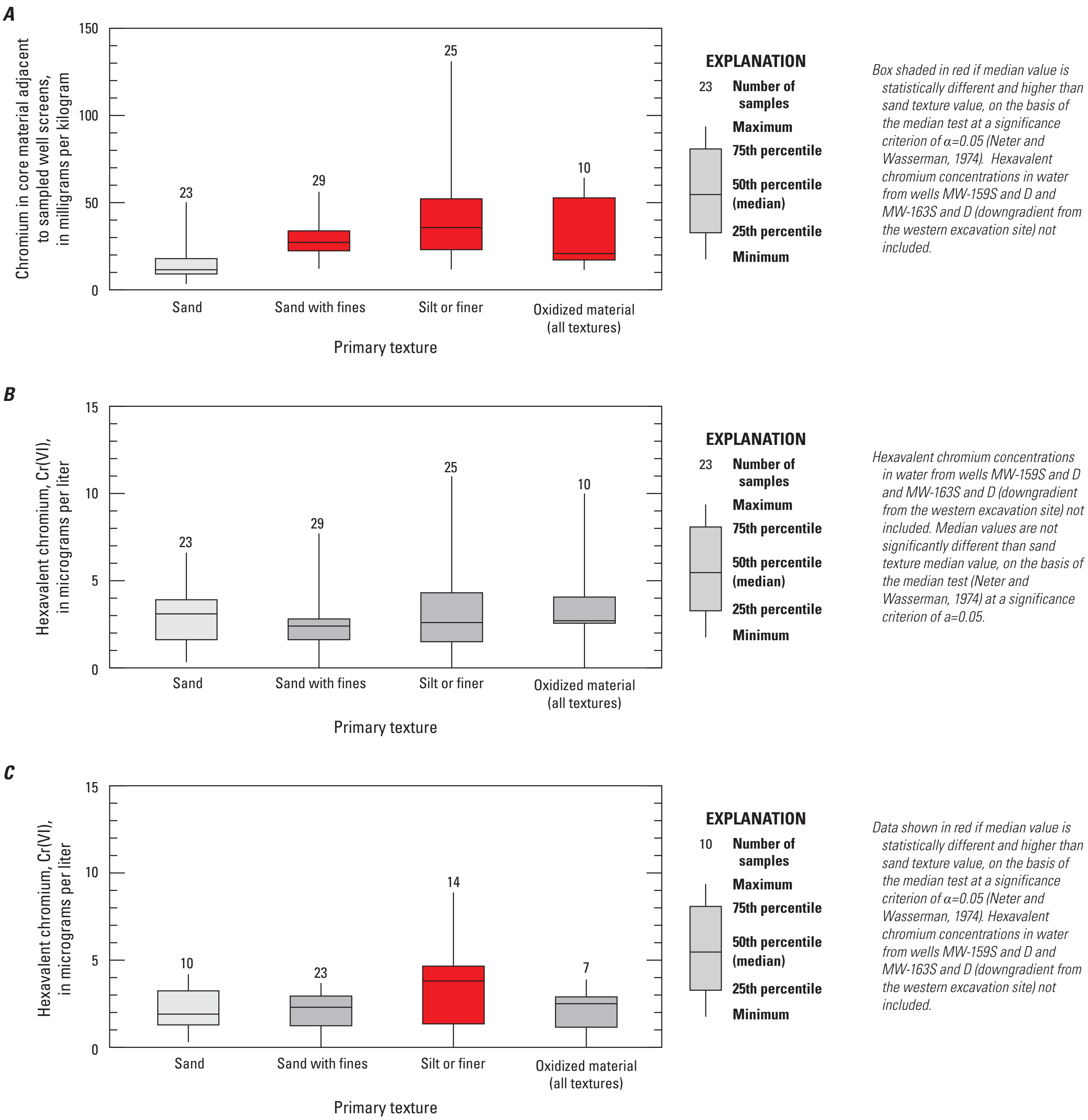
Data shown in red if median value is statistically different and higher than median eastern subarea or mixed-cation/mixed anion value, and dark grey if median value is not significantly different on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

Figure E.12. Hexavalent chromium, Cr(VI), concentrations in water from sampled wells outside the October–December 2015 (Q4 2015) regulatory Cr(VI) plume are grouped by *A*, subarea and *B*, major-ion composition, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).



Subarea in **bold** if median Cr(VI) concentration of PG&E and USGS data are significantly different on the basis of the Median Test at a significance criterion of α=0.05 (Neter and Wasserman, 1974).

Figure E.13. Hexavalent chromium, Cr(VI), concentrations in water from selected wells sampled by the Pacific Gas and Electric Company (PG&E), October–December 2015 (Q4 2015), and by U.S. Geological Survey (USGS), March 2015 through November 2017, Hinkley and Water Valleys, western Mojave Desert, California. Pacific Gas and Electric Company data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological Survey data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).



Box shaded in red if median value is statistically different and higher than sand texture value, on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974). Hexavalent chromium concentrations in water from wells MW-159S and D and MW-163S and D (downgradient from the western excavation site) not included.

Hexavalent chromium concentrations in water from wells MW-159S and D and MW-163S and D (downgradient from the western excavation site) not included. Median values are not significantly different than sand texture median value, on the basis of the median test (Neter and Wasserman, 1974) at a significance criterion of a=0.05.

Data shown in red if median value is statistically different and higher than sand texture value, on the basis of the median test at a significance criterion of α=0.05 (Neter and Wasserman, 1974). Hexavalent chromium concentrations in water from wells MW-159S and D and MW-163S and D (downgradient from the western excavation site) not included.

Figure E.14. Chromium or hexavalent chromium, Cr(VI), concentrations grouped by texture in core samples of aquifer material adjacent to the screened interval of sampled wells: *A*, median chromium concentrations in core material; *B*, Cr(VI) concentrations in water from sampled wells; and *C*, Cr(VI) concentrations in water from sampled wells having a greater than 30 percent natural Cr(VI) occurrence probability at the measured pH, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

E.3.3.1. Redox Processes

Redox, a measure of the net electron balance between coupled reduction and oxidation reactions within water (Stumm and Morgan, 1996), is often difficult to measure in the field. In equilibrium conditions, Cr(VI) may be present in oxic groundwater but is not present in reduced groundwater. Field measurements of dissolved oxygen provide a qualitative measure of the redox status of water, with concentrations greater than 0.5 mg/L classified as oxic, concentrations between 0.2 and 0.5 mg/L classified as suboxic, and concentrations less than 0.2 mg/L classified as reduced (McMahon and Chappelle, 2008). Water from most wells in Hinkley and Water Valleys contains dissolved oxygen greater than 0.5 mg/L and is oxic. Water from wells MW-79D, MW-105D, and MW-155D had dissolved-oxygen concentrations less than the SRL of 0.2 mg/L and Cr(VI) concentrations less than the SRL of 0.1 µg/L (fig. E.11*B*). Water from wells MW-104D, MW-136S2, and MW-193S3 had dissolved-oxygen concentrations less than 0.5 mg/L and Cr(VI) concentrations less than 0.12 µg/L. However, low dissolved-oxygen concentrations do not always mean Cr(VI) is absent, and water from well MW-137S3 in the northern subarea outside the Q4 2015 regulatory Cr(VI) plume had a dissolved-oxygen concentration of 0.2 mg/L and a Cr(VI) concentration of 3.6 µg/L (fig. E.11*B*).

The redox potentials, Eh, in water from sampled wells are shown as a function of pH (fig. E.15). The Eh was calculated, in volts, from the Cr(III)/Cr(VI) redox couple using the computer program PHREEQC (Parkhurst and Appelo, 2013), updated with thermodynamic data from Ball and Nordstrom (1998). Field speciated Cr(VI) and Cr(t) data from the USGS Redox Chemistry Laboratory were used for these calculations because of lower laboratory reporting limits for Cr(t) data and greater precision of Cr(VI) and Cr(t) data compared to data from the commercial laboratory (fig. E.3). We were unable to calculate Eh from the Cr(III)/Cr(VI) redox couple for reduced samples that have Cr(VI) concentrations less than the SRL, and field ORP measurements were used in place of Cr(III)/Cr(VI) data to calculate Eh for these samples using procedures described by Stumm and Morgan (1996).

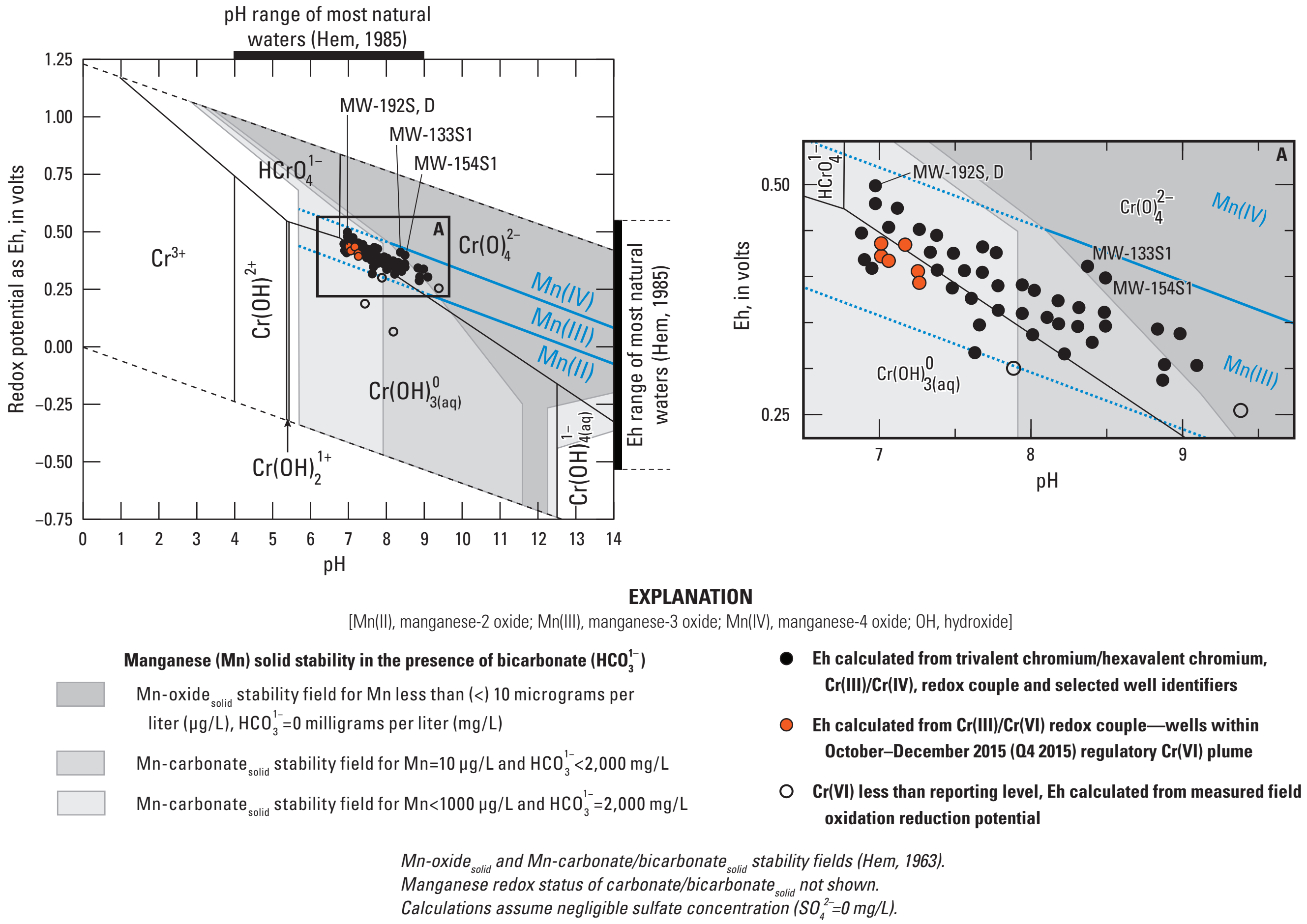


Figure E.15. Redox potential as a function of pH, for wells sampled as part of the U.S. Geological Survey hexavalent chromium, Cr(VI), background study, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

The stability fields for Mn oxides$_{(solid)}$ (Hem, 1963) also are shown as a function of pH and redox potential (fig. E.15). Manganese oxides, including Mn(III), Mn(III/IV), and Mn(IV) oxides, on the surfaces of mineral grains can oxidize Cr(III) to Cr(VI) given appropriate geochemical conditions (Nico and Zasoski, 2000; Oze and others, 2007; Kazakis and others, 2015). Manganese oxides are widely distributed on the surfaces of mineral grains and do not typically exist in pure form but rather are present in a range of oxidation states. Hem (1963) showed stability of Mn oxides increases as carbonate abundance increases (fig. E.15), and highly oxic Mn(IV)-oxide surface coatings on mineral grains may be present within fine-textured, carbonate-rich materials, similar to mudflat/playa deposits within the study area.

Calculated Eh values for samples containing measurable Cr(VI) were distributed in a narrow band within the overlapping chromate ion, $CrO_4^{2-}{}_{(aqueous)}$, and Mn(III)$_{(solid)}$ stability fields (fig. E.15). Most samples from wells with suboxic or reduced conditions plot below this band within the chromium hydroxide, $Cr(OH)_3^0$, stability field; chromium, as Cr(III), within this region would be sorbed to aquifer solids rather than dissolved.

Water from wells within the Q4 2015 regulatory Cr(VI) plume having Cr(VI) concentrations ranging from 16 to 2,500 µg/L plot within the overlapping $CrO_4^{2-}{}_{(aqueous)}$ and the Mn(III)$_{(solid)}$ stability fields. Water from these wells had redox potentials and pH values consistent with equilibrium with Mn(III) oxides on the surfaces of mineral grains similar to most other sampled wells (fig. E.15).

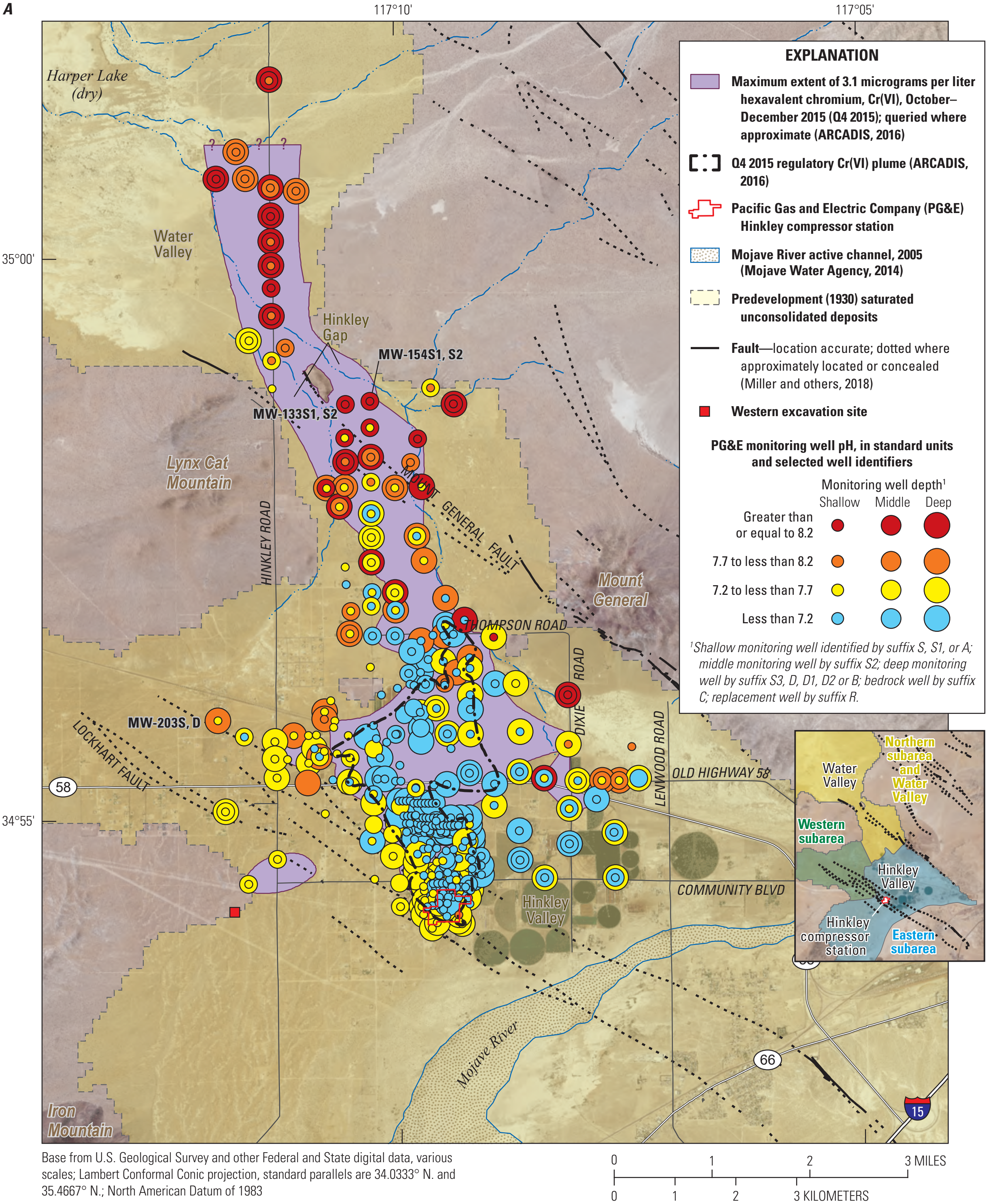
In contrast to wells within the Q4 2015 regulatory Cr(VI) plume, water from wells MW-192S, MW-192D, MW-133S1, and MW-154S1, completed within fine-grained, carbonate-rich mudflat/playa deposits, plotted above most other data near the Mn(IV) stability field. These data indicate equilibrium between $CrO_4^{2-}{}_{(aqueous)}$ and Mn(IV)-oxide surface coatings on aquifer solids that differs from most sampled groundwater. Visual examination of core material from these sites and similar materials from other sites within Hinkley Valley shows the presence of manganese nodules and dendritic manganese structures commonly known as “dragon’s breath” (chapter C). The presence of Mn(IV) oxides at these sites was confirmed using X-ray absorption near-edge structure (XANES) data collected using the Stanford Synchrotron Radiation Lightsource (SSRL; chapter C). These sites potentially represent highly favorable conditions where natural oxidation of Cr(III) to Cr(VI) may occur in the presence of Mn(IV) oxides. Porewater extracted from these materials was examined to determine if high concentrations of Cr(VI) are associated with these materials (see the “E.4 Porewater” section).

E.3.3.2. Probability of Natural Hexavalent Chromium Occurrence as a Function of pH

In addition to redox, Cr(VI) concentrations in groundwater also are controlled by pH-dependent sorption with aquifer solids. In general, Cr(VI) sorption is less and aqueous Cr(VI) concentrations are higher at higher pH values (Rai and Zachara, 1984; Xie and others, 2015). A probabilistic approach was used to examine Cr(VI) concentrations at the measured pH.

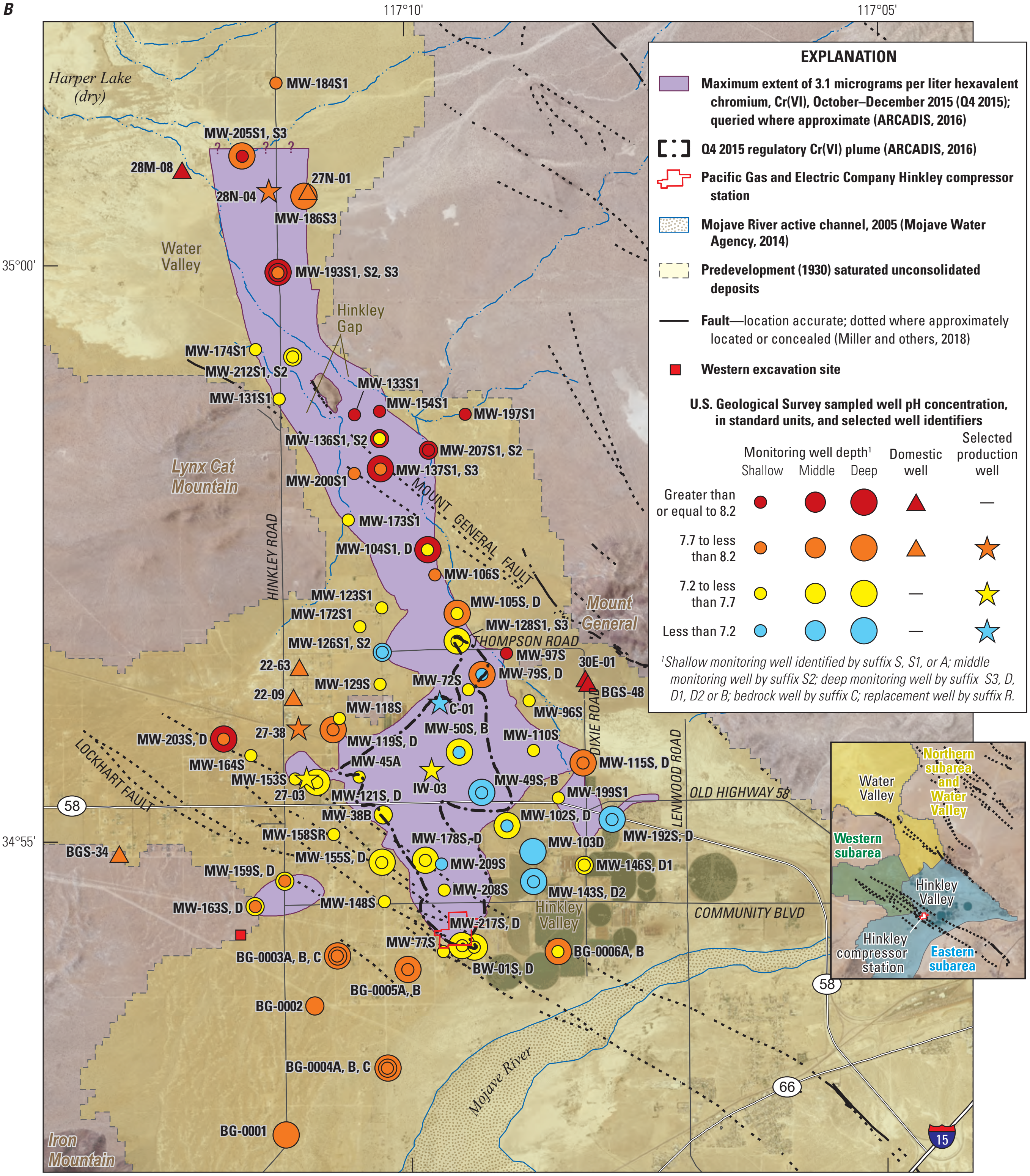
Values of pH in water from more than 600 monitoring wells sampled by PG&E in Q4 2015 ranged from 6.4 to 9.4 (fig. E.16*A*). Values of pH were less than 7.2 near the Mojave River and throughout much of the eastern subarea, and less than 7.2 in water from shallow wells as far north as the Mount General fault in the northern subarea (fig. E.16*A*). Higher pH values greater than 7.7 were present in water from wells completed near mudflat/playa deposits and within locally derived alluvium in the eastern subarea near Mount General and in deeper wells in the western subarea (fig. E.16*A*). Values of pH increased downgradient within the northern subarea but commonly remained less than 7.7 in water from shallow wells as far downgradient as the southern part of Water Valley. Values of pH were typically greater than 8.2 in water from deeper wells in the northern subarea and in water from deeper wells in much of Water Valley (fig. E.16*A*).

Similar to PG&E regulatory data, pH values ranged from 6.9 to 9.4 in water from wells sampled by the USGS between March 2015 and November 2017 (fig. E.16*B*). Values of pH of samples collected by the USGS compared favorably to PG&E Q4 2015 regulatory data, with a regression slope of 1 and an R^2 of 0.81 (fig. E.7). Values of pH in PG&E regulatory data and USGS data were similarly distributed across Hinkley and Water Valleys (fig. E.16).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.16. pH in water from selected wells: *A*, Pacific Gas and Electric Company (PG&E) data, October–December 2015 (Q4 2015), and *B*, U.S. Geological Survey (USGS) data, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Pacific Gas and Electric Company data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.16.—Continued

Izbicki and others (2015) evaluated Cr(VI) concentrations and pH in water from more than 900 public-supply wells across California that were sampled between 2004 and 2012 as part of the Groundwater Ambient Monitoring Assessment (GAMA) Priority Basin Project (U.S. Geological Survey, 2018). They developed a set of curves showing the probability of Cr(VI) concentrations occurring in oxic groundwater throughout a range of pH values. Each curve was significantly different for the broad pH ranges considered; lower Cr(VI) concentrations were measured in water from wells at slightly acidic to circumneutral pH, and higher Cr(VI) concentrations were measured at more alkaline pH. For the purposes of this study, these curves were updated using smaller increments of 0.3 pH units (fig. E.17). Although the individual curves were no longer significantly different from adjacent curves, on the basis of the F-test (Neter and Wasserman, 1974), the updated curves show a consistent monotonic increase in Cr(VI) concentrations with increases in pH. The updated curves quantify the statistical probability of a Cr(VI) concentration occurring in uncontaminated water from wells at a measured pH and provide a basis for comparing Cr(VI) concentrations in water from wells having different pH values. For example, at a pH of 7.0, the probability of the occurrence of Cr(VI) in uncontaminated groundwater at a concentration of 4 µg/L or greater in the GAMA dataset is 10 percent. Similarly, at a pH of 7.3, the probability of the occurrence of Cr(VI) in uncontaminated groundwater at a concentration of 5.0 µg/L or greater is 10 percent, and at a pH of 7.7, the probability of the occurrence of Cr(VI) in uncontaminated groundwater at a concentration of 8 µg/L or greater also is 10 percent (table E.4).

Applying the estimated probabilities from the updated curves (fig. E.17) to regulatory data collected by PG&E, the estimated probability of a Cr(VI) concentration occurring in water at the measured pH (hereafter referred to as the “Cr(VI) occurrence probability”) from most monitoring wells within the footprint of the mapped Q4 2015 regulatory Cr(VI) plume was 10 percent or less (fig. E.18*A*). This Cr(VI) occurrence probability is consistent with the presence of anthropogenic Cr(VI) released from the Hinkley compressor station in water from wells within the Q4 2015 regulatory Cr(VI) plume. Some deeper wells within the footprint of the mapped Q4 2015 regulatory Cr(VI) plume had Cr(VI) occurrence probabilities greater than 30 percent (fig. E.18*A*) and do not appear to be affected by Cr(VI) releases from the Hinkley compressor station. Similarly, water from wells affected by groundwater remediation within the Cr(VI) plume had low Cr(VI) concentrations and Cr(VI) occurrence probabilities greater than 30 percent. The mapped extent of Cr(VI) occurrence probabilities less than 10 percent corresponds favorably with the margin of the mapped Q4 2015 regulatory Cr(VI) plume along the Lockhart fault to the northwest of the Hinkley compressor station (fig. E.18*A*); elsewhere, the mapped extent of Cr(VI) occurrence probabilities less than 10 percent differs from the Q4 2015 regulatory Cr(VI) plume margins in the eastern and northern subareas (fig. E.18*A*).

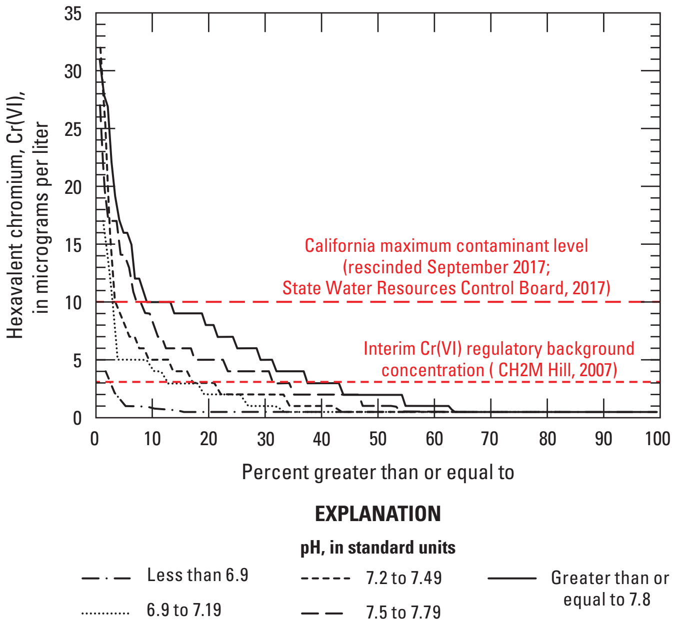


Figure E.17. Cumulative probability of hexavalent chromium, Cr(VI), concentration as a function of pH in water from public-supply wells in California. Modified from Groundwater Ambient Monitoring Assessment (GAMA) Program Priority Basin Project data, 2004–14 (Izbicki and others, 2015). Data are available in U.S. Geological Survey (2021).

Table E.4. Cumulative probability of a hexavalent chromium, Cr(VI), concentration at the measured pH in water from public-supply wells in California.

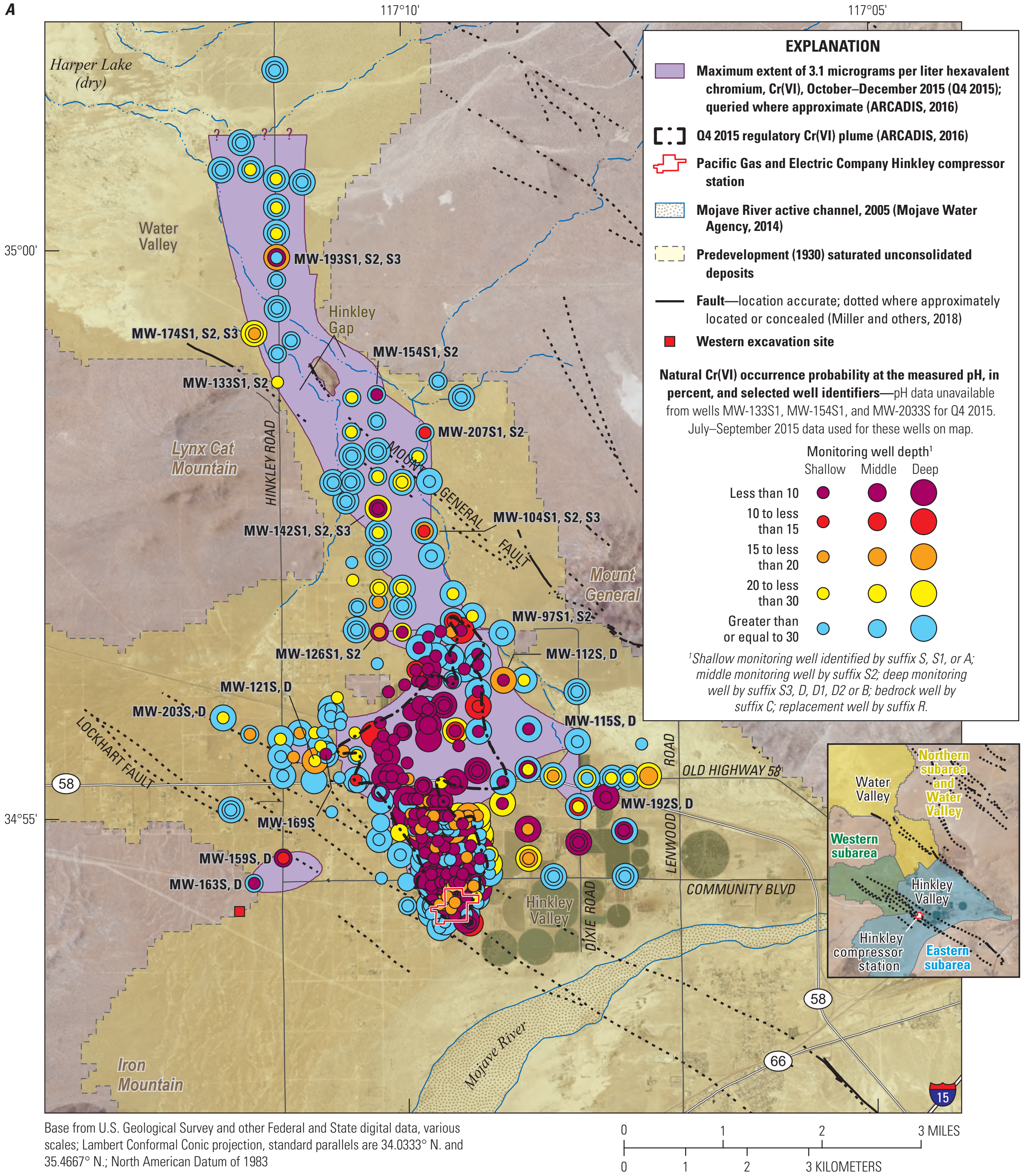
[Data from California Groundwater Ambient Monitoring Assessment (GAMA) Project, 2004–12, modified from Izbicki and others (2015). **Abbreviations**: µg/L, microgram per liter; <, less than; > greater than]

pH		Cr(VI) concentration, in µg/L, at selected probability of natural occurrence, in percent				
Minimum	**Maximum**	**30**	**20**	**15**	**10**	**5**
<6.6	6.8	<1	<1	<1	<1	1
6.9	7.1	<1	2	3	4	5
7.2	7.4	<2	3	4	5	8
7.5	7.7	<4	5	6	8	14
7.8	>8	<5	8	9	10	16

In the eastern subarea, nominally cross gradient from the Hinkley compressor station and upgradient from the Q4 2015 regulatory Cr(VI) plume (chapter H, fig. H.8), water from nine wells sampled by PG&E during Q4 2015 had Cr(VI) occurrence probabilities of 10 percent or less (fig. E.18*A*). Water from these wells was slightly acidic with pH values less than 6.9 (fig. E.16*A*) and Cr(VI) concentrations ranging from 1 to 3.2 µg/L (fig. E.11*A*). In contrast, within the California-wide GAMA database (Izbicki and others, 2015; U.S. Geological Survey, 2021), water from only two wells having a pH of 6.9 or less had Cr(VI) concentrations greater than 1 µg/L and a corresponding Cr(VI) occurrence probability of 10 percent or less. Both wells were located in urban areas within aquifers that were subsequently identified on the basis of other water-chemistry data as impacted by anthropogenic sources (Hausladen and others, 2018). Water from 22 wells crossgradient from the Hinkley compressor station had Cr(VI) occurrence probabilities of 30 percent or less. Water from these wells had circumneutral pH values ranging from 6.9 to less than 7.2 and Cr(VI) concentrations ranging from 1 to 4.6 µg/L. Within the California-wide GAMA database, almost three-quarters of the wells having circumneutral pH values within this range, with Cr(VI) concentrations greater than 1 µg/L and a corresponding Cr(VI) occurrence probability of 30 percent or less, were located along the west side of the Central Valley in alluvial aquifer materials eroded from chromium-containing mafic rock within the Coast Ranges (Izbicki and others, 2015). In contrast, most unconsolidated aquifer material in the eastern subarea of Hinkley Valley is composed of coarse-textured, felsic, low-chromium material deposited by the Mojave River. Regionally, in more than 60 samples from more than 40 wells collected and analyzed for Cr(VI) by the USGS in Mojave River alluvium upstream from Barstow to the east of Hinkley Valley (not shown) between 2000 and 2012 (Metzger and others, 2015), estimated Cr(VI) occurrence probabilities at the measured pH were greater than 30 percent. On the basis of both California-wide and regional data, the number of wells in the eastern subarea crossgradient from the Hinkley compressor station having Cr(VI) concentrations with a Cr(VI) occurrence probability of 30 percent or less at the measured pH was greater than expected.

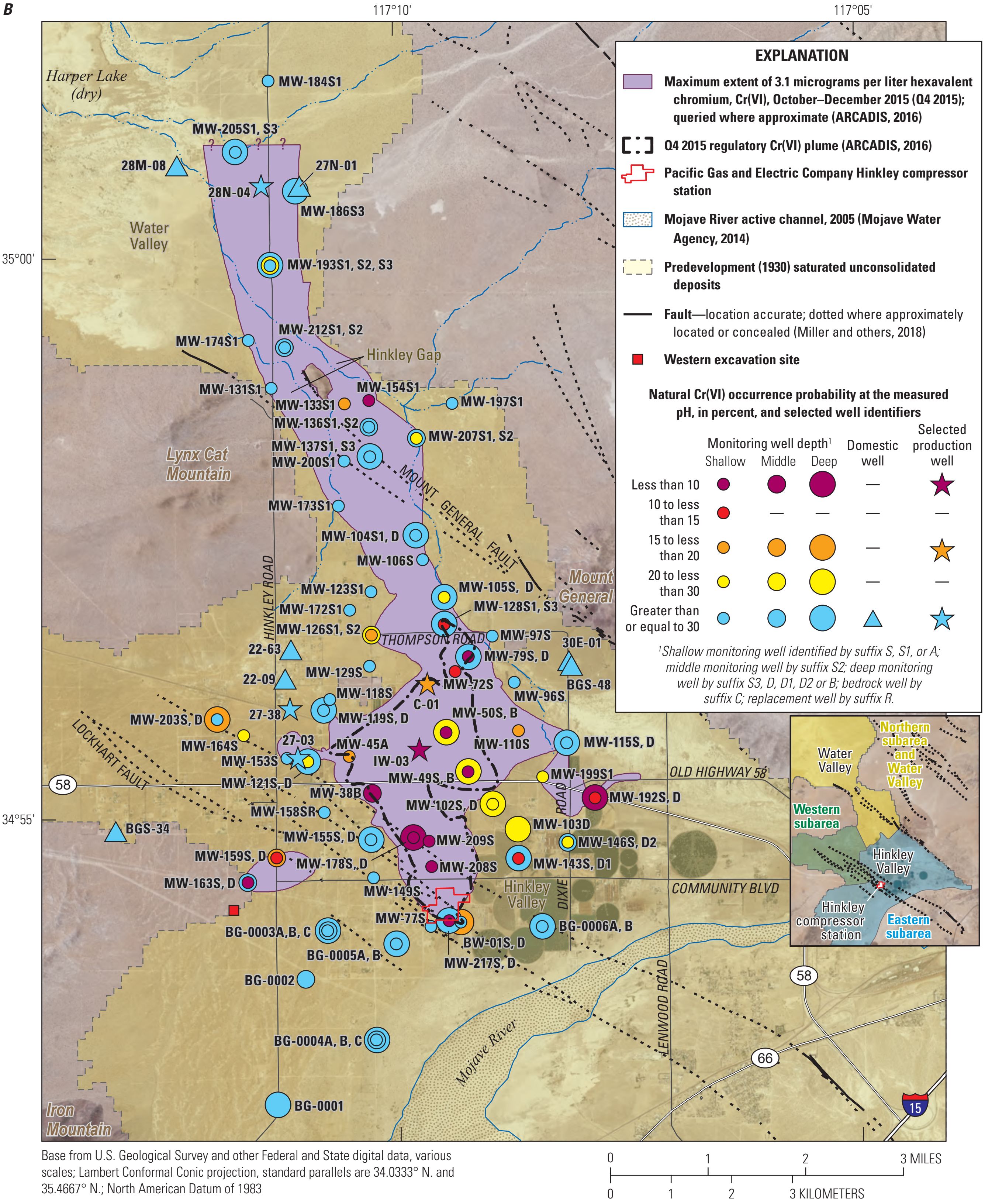
In the northern subarea and Water Valley, most wells had a Cr(VI) occurrence probability at the measured pH greater than 30 percent. Although Cr(VI) concentrations in the northern subarea and Water Valley are generally higher than in the eastern subarea, pH values also are higher (figs. E.16*A*, *B*) and pH dependent sorption from aquifer solids contributed to higher Cr(VI) concentrations in the northern subarea and Water Valley. However, shallow wells in the northern subarea downgradient from the leading edge of the Q4 2015 regulatory Cr(VI) plume had a 10 percent or less Cr(VI) occurrence probability (fig. E.18*A*). Shallow wells in this area had increasing water levels and increasing Cr(VI) concentrations between 2012 and 2017 (chapter D)—potentially indicative of groundwater movement to the north in response to infiltration of streamflow from the Mojave River during 2010, or in response to changing management practices used to control the Cr(VI) plume. Hexavalent chromium occurrence probabilities less than 10 percent were present in water from some wells in the northern subarea as far downgradient as wells MW-142S1 and MW-142S2 south of the Mount General fault and well MW-154S1 north of the Mount General fault (fig. E.18*A*).

Application of the probabilities from the updated curves (fig. E.17) to USGS data (fig. E.18*B*) collected between March 2015 and November 2017 (U.S. Geological Survey, 2021) produced results similar to the distribution of Cr(VI) occurrence probabilities in Q4 2015 regulatory data (fig. E.18*A*). On the basis of USGS data, Cr(VI) occurrence probabilities within the Q4 2015 regulatory Cr(VI) plume were commonly less than 10 percent, with some deeper wells within the footprint of the plume having higher Cr(VI) occurrence probabilities, consistent with less anthropogenic Cr(VI) at depth. However, outside the Q4 2015 regulatory Cr(VI) plume, Cr(VI) occurrence probabilities were not as low as probabilities estimated from PG&E Q4 2015 regulatory data, in part because of differences in sample collection protocols that resulted in lower Cr(VI) concentrations in USGS data (fig. E.5).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.18. Probability of hexavalent chromium, Cr(VI), occurrence at the measured pH in water from selected wells: A, Pacific Gas and Electric Company (PG&E) data, October–December 2015 (Q4 2015), and B, U.S. Geological Survey (USGS) data, March 2015 through 2017, Hinkley and Water Valleys, western Mojave Desert, California. Pacific Gas and Electric Company data are available at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/; U.S. Geological Survey data are available in U.S. Geological Survey (2021).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.18.—Continued

In the eastern subarea crossgradient from the Hinkley compressor station and upgradient from the mapped Q4 2015 regulatory Cr(VI) plume (chapter H, fig. H.8), water from 9 of 15 sampled wells had Cr(VI) occurrence probabilities less than 30 percent. In this area, wells MW-143S, MW-192S, and MW-192D had Cr(VI) occurrence probabilities less than 15 percent (fig. E.18*B*). Shallow wells in the northern subarea near the leading edge of the mapped plume, including MW-126S1, MW-126S2, MW-105S, and MW-128S1 had probabilities of Cr(VI) occurrence less than 30 percent. Most wells farther downgradient in the northern subarea and Water Valley had Cr(VI) occurrence probabilities greater than 30 percent, with the exception of water from wells MW-133S1 and MW-154S1, completed in mudflat/playa deposits in the northern subarea. Water from most deep wells in the western subarea downgradient from the Lockhart fault have Cr(VI) occurrence probabilities greater than 30 percent (fig. E.18*B*); this includes water from well MW-153S, completed in weathered hornblende diorite having chromium concentrations as high as 248 milligrams per kilogram (mg/kg), the highest measured as part of this study in core material adjacent to the screened interval of a sampled well (Groover and Izbicki, 2018). Water from well MW-203D, completed in partly consolidated Miocene deposits, had a Cr(VI) concentration of 8.9 at a pH of 8.3 with a Cr(VI) occurrence probability of less than 20 percent (fig. E.18*B*). Water from well MW-163S and wells MW-159S and MW-159D downgradient from the western excavation site had Cr(VI) occurrence probabilities of less than 10 percent and less than 20 percent, respectively (fig. E.18*B*). Unusual mineralogy or weathering in aquifer materials that may potentially explain high Cr(VI) concentrations in water from wells downgradient from the western excavation site were not identified (chapter C).

E.3.3.2.1. Sorption, Complexation, and Competition for Exchange Sites

The pH-dependent sorption and the Cr(VI) occurrence probability in water from wells in Hinkley and Water Valleys were evaluated on the basis of Cr(VI) and pH data from public-supply wells across California collected as part of the GAMA Priority Basin Project (fig. E.17; Izbicki and others, 2015). Water from some wells in Hinkley Valley affected by irrigation return and water from some deep wells in Water Valley affected by local geologic conditions, had high specific conductance (fig. E.6) with high concentrations of nitrate, sulfate, phosphate, and other ions. These ions may form aqueous complexes with CrO_4^{2-} that have different sorptive properties or may compete with CrO_4^{2-} for exchange sites on the surfaces of mineral grains; public-supply wells in California yielding water having high concentrations of these constituents would likely have been removed from service, and therefore would not have been included in the GAMA data used to evaluate pH-dependent sorption of Cr(VI) and the Cr(VI) occurrence probability. Complexation of CrO_4^{2-} and competition for exchange sites with other dissolved ions were evaluated to determine if they affect pH-dependent sorption of Cr(VI).

Calculations were done using the computer program PHREEQC (Parkhurst and Appelo, 2013), with thermodynamic data from Ball and Nordstrom (1998). Results showed that CrO_4^{2-} was the predominate aqueous form of Cr(VI) in water from wells in Hinkley and Water Valleys. The chromate ion, CrO_4^{2-}, composed 24 to 98 percent of Cr(VI) with a median of 84 percent, and the percentage was a function of pH, with the hydrogen chromate ion, $HCrO_4^{1-}$, composing slightly more than 20 percent of the Cr(VI) at slightly acidic to neutral pH values (fig. E.19*A*). Sodium chromate ions, $NaCrO_4^{1-}$, and associated aqueous complexes commonly composed less than 5 percent of the total Cr(VI), on a molar basis, in high specific-conductance calcium-chloride-sulfate water from wells impacted by irrigation return in Hinkley and Water Valleys (fig. E.19*B*). Hexavalent chromium complexation with sodium increased with increasing specific conductance to as much as 12 percent of the total Cr(VI) in sodium/bicarbonate water from wells MW-193S1, S2, S3 completed in local fan deposits in Water Valley and composed as much as 7 percent of the total Cr(VI) in sodium/bicarbonate water from wells MW-203D completed in Miocene deposits in the western subarea (fig. E.19*B*). Although Cr(VI) complexation with sodium ions (Na^{1+}) increased with specific conductance and changing major-ion composition in water from wells, laboratory data (Xie and others, 2015) shows Cr(VI) sorption is solely a function of pH and Cr(VI) concentration and is not influenced by complexation with Na^{1+}, even at very high ionic strengths. Consequently, $NaCrO_4^{1-}$ and aqueous complexation associated with irrigation return, sodium/bicarbonate groundwater, or subsurface geology in Hinkley and Water Valleys are unlikely to alter pH-dependent sorption of Cr(VI).

Hexavalent chromium complexation with calcium and magnesium was described by Lelli and others (2013); however, thermodynamic data to calculate aqueous complexation of CrO_4^{2-} with calcium and manganese were not available (Ball and Nordstrom, 1998) and were not evaluated as part of this study.

Consistent with the expected behavior of Cr(VI) in aqueous solutions (Rai and Zachara, 1984) and laboratory data (Xie and others, 2015), Cr(VI) speciation in water from wells in Hinkley and Water Valleys is a function of pH. Aqueous speciation of $HCrOH_4^{1-}$, $CrOH_4^{2-}$ and $NaCrOH_4^{1-}$ with pH did not covary with specific conductance, sulfate, nitrate, or phosphate concentrations in irrigation return affected water. Field data indicate that $HCrOH_4^{1-}$, CrO_4^{2-}, and $NaCrOH_4^{1-}$ speciation is explained almost entirely on the basis of pH, with an R^2 of 0.90 (fig. E.19*A*), not affected by increasing ionic strength or competing ions, and is not likely to influence pH-dependent sorption of Cr(VI) or the interpretation of Cr(VI) occurrence probability at the measured pH.

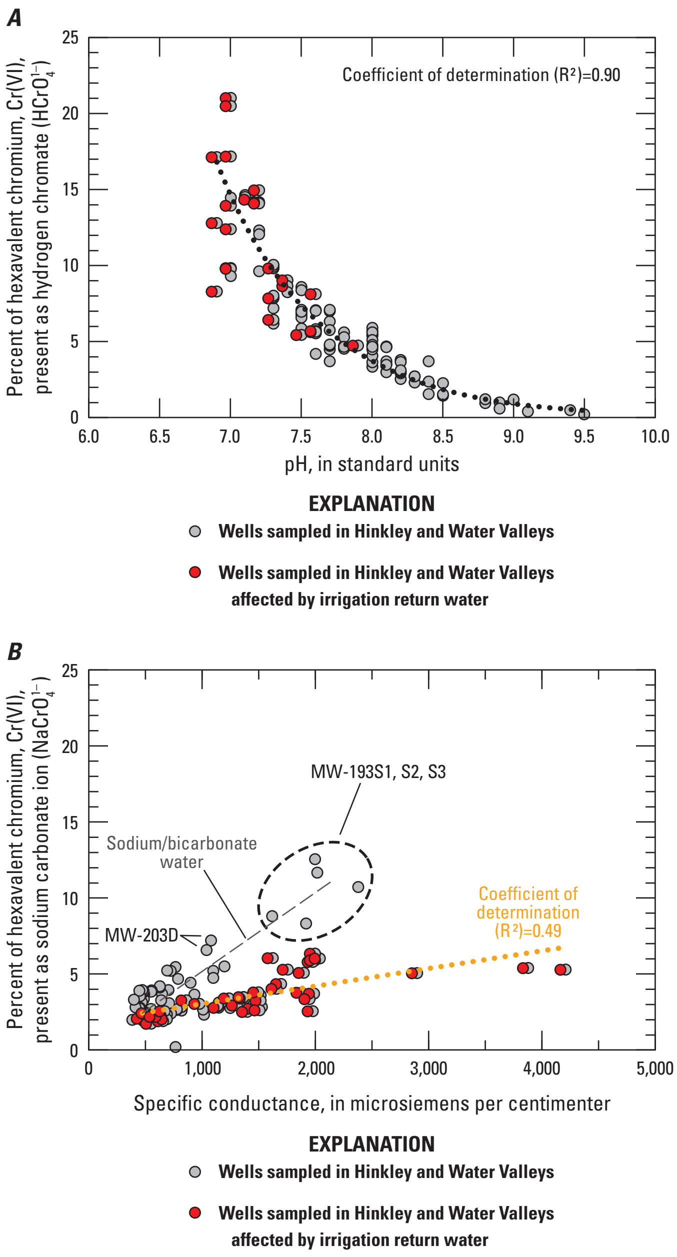


Figure E.19. Aqueous speciation of hexavalent chromium, Cr(VI), as a function of *A*, pH and *B*, specific conductance in water from wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

E.3.3.2.2. Limitations and Use of pH-Dependent Sorption Data

California is a large state with diverse geology. High concentrations of chromium are present in mafic and ultramafic rock across the state (Kruckeberg, 1984; Morrison and others, 2009; Mills and others, 2011; Smith and others, 2014), and groundwater in alluvial aquifers eroded from chromium-containing rock often has high Cr(VI) concentrations (Ball and Izbicki, 2004; Izbicki and others, 2008a, 2015; Manning and others, 2015; McClain and others, 2016). Although some rocks in Hinkley and Water Valleys locally contain high chromium concentrations (chapters B and C), chromium concentrations are low in most unconsolidated materials that compose aquifers within Hinkley and Water Valleys (Groover and Izbicki, 2018); geologic materials in only 4 percent of California have chromium concentrations as low as those in Hinkley and Water Valleys (Smith and others, 2014). California-wide GAMA data (U.S. Geological Survey, 2021) likely overestimate the probability of natural Cr(VI) occurrence in water from wells in Hinkley and Water Valleys. Consequently, potential limitations associated with evaluation of pH-dependent sorption estimated from data for public-supply wells are minor, and curves developed from California-wide GAMA data provide a conservative estimate of the extent of anthropogenic Cr(VI) in Hinkley and Water Valleys.

As discussed previously, no samples collected and analyzed for Cr(VI) by the USGS in Mojave River alluvium upstream from Barstow between 2000 and 2012 (Metzger and others, 2015) had a Cr(VI) occurrence probability at the measured pH of less than 30 percent. A Cr(VI) occurrence probability of 30 percent or less in water from wells in Hinkley and Water Valleys is unusual and not consistent with measured Cr(VI) occurrence in alluvial deposits along the Mojave River and represents an excess of Cr(VI) at the measured pH (fig. E.16) that is not consistent with natural conditions within Hinkley and Water Valleys. A Cr(VI) occurrence probability of 30 percent, estimated from Cr(VI) and pH data, was used for the SSA of the Cr(VI) plume extent in this professional paper (chapter G). The Cr(VI) occurrence probability was used with other metrics within the SSA that provide additional information on aquifer materials and groundwater.

Hexavalent chromium and pH are routinely measured as part of regulatory data collection (https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/) and independently provide information on the occurrence of Cr(VI), with Cr(VI) occurrence probabilities less than 10 percent commonly present within the Q4 2015 regulatory Cr(VI) plume. In the absence of other data, the 10 percent Cr(VI) occurrence probability may correctly identify anthropogenic Cr(VI) in most settings, with the notable exception of wells completed in mudflat/playa deposits.

E.3.3.3. Selected Oxyanions and Trace Elements

In addition to Cr(VI), concentrations of the trace elements arsenic, iron, manganese, uranium, and vanadium were measured in water from wells sampled by the USGS between March 2015 and November 2017 (U.S. Geological Survey, 2021). Arsenic, uranium, and vanadium form negatively charged oxyanions, in some ways similar to Cr(VI), that also are soluble in alkaline, oxic groundwater.

Arsenic concentrations in water from wells sampled between March 2015 and November 2017 in Hinkley and Water Valleys were as high as 1,030 µg/L, uranium concentrations were as high as 114 µg/L, and vanadium concentrations were as high as 530 µg/L (appendix E.1, table E.1.1; U.S. Geological Survey, 2021). Approximately 27 percent of sampled wells exceeded the MCLs for arsenic and uranium in drinking water of 10 and 30 µg/L, respectively (U.S. Environmental Protection Agency, 2019). There is no MCL for vanadium; however, 10 percent of sampled wells exceeded the State Water Resources Control Board (2018b) notification level (NL) for vanadium in drinking water of 50 µg/L. Cooling water released from the Hinkley compressor station contained almost exclusively Cr(VI), and arsenic, uranium, and vanadium concentrations in water from wells in Hinkley and Water Valley are not related to those releases. Oxyanions of arsenic, uranium, and vanadium have pH-dependent sorption properties with aquifer material similar to Cr(VI); however, their aqueous geochemistry differs with respect to redox, speciation, and complexation with other dissolved ions (especially uranium in the presence of bicarbonate). Throughout the pH range of sampled water, iron and manganese concentrations are largely controlled by the redox status of water from wells, and the reduced form of arsenic, arsenite, is soluble under reduced conditions (Rai and Zachara, 1984; Stumm and Morgan, 1996).

The concentrations of these trace elements in groundwater results from the (1) combined effects of geology, mineral weathering, and aqueous geochemistry—including redox and pH-dependent sorption in oxic groundwater; (2) anthropogenic effects, including irrigation return; and (3) in the case of chromium, additions of anthropogenic Cr(VI) associated with releases from the Hinkley compressor station. As groundwater containing Cr(VI) flowed downgradient from the Hinkley compressor station, anthropogenic Cr(VI) was sorbed to sites on the surfaces of mineral grains, increasing Cr(VI) concentrations on those sites (chapter C, figs. C.21, C.22). Desorption of Cr(VI) from affected aquifer materials may increase Cr(VI) concentrations in groundwater relative to other trace elements, long after aqueous Cr(VI) concentrations associated with the initial releases from the Hinkley compressor station moved downgradient.

Similarities and differences in selected trace-element concentrations (including arsenic, Cr(VI), uranium, vanadium, iron, and manganese; table E.5) in water from sampled wells were evaluated using principal component analysis (PCA). Although measured as part of this study, iron redox species [ferrous, Fe(II), and ferric, Fe(III)] and arsenic redox species [arsenite, As(III), and arsenate, As(V)] were not used in the PCA, to allow comparison with porewater and domestic well data discussed in the “Porewater” and “Water from Domestic Wells” sections (E.4 and E.5, respectively) within this chapter. Redox species for uranium and vanadium were not measured as part of this study. Principal component analysis was used previously in chapter B within this professional paper to describe elemental assemblages in alluvium, and more detailed information on the use of PCA is presented in the “B.3.2. Statistical Methods” section of that chapter.

First principal component scores were composed of positive eigenvectors for iron, manganese, arsenic, and vanadium, which are more soluble in reduced groundwater, and a negative eigenvector for uranium, which is more soluble in oxic groundwater (table E.5). Second principal component scores were composed of negative eigenvectors for iron and manganese and positive eigenvectors for arsenic, uranium, and vanadium, which form negatively charged oxyanions soluble in alkaline, oxic water. First and second principal component eigenvectors for Cr(VI) were smaller in magnitude than eigenvectors for the other trace elements measured, although the negative and positive signage of the Cr(VI) eigenvectors are consistent with the redox and oxyanion chemistry of Cr(VI) (table E.5). The first and second principal components account for 46 percent of the variability in the data.

Table E.5. First, second, and third principal component eigenvectors for selected trace elements in water from sampled wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Statistics calculated from data available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

[Eigenvectors range from −1 to 1]

Element	Symbol	Eigenvectors, unitless		
		First	Second	Third
Iron	Fe	0.485	−0.277	0.225
Manganese	Mn	0.273	−0.550	0.217
Arsenic	As	0.473	0.513	0.072
Vanadium	V	0.562	0.383	−0.004
Uranium	U	−0.348	0.447	0.112
Hexavalent chromium	Cr(VI)	−0.172	0.102	0.940

Third principal component scores were dominated by a large-magnitude positive eigenvector of 0.94 for Cr(VI) (table E.5). This was the largest magnitude eigenvector calculated for the six trace elements included within the PCA, and it approaches the maximum possible value of 1. The third principal component accounts for 16 percent of the variability in the data; almost all of that variability is explained by Cr(VI) concentrations. The third principal component was examined to determine its usefulness in identification of anthropogenic Cr(VI) released from the Hinkley compressor station.

First and second principal component scores for water from wells within the Q4 2015 regulatory Cr(VI) plume are distributed along a straight line, with most values occurring within the 95-percent predictive interval around the regression line through the data (fig. E.20). First and second principal component eigenvectors for Cr(VI) are small in magnitude (table E.5), and the distribution of scores for water from wells within the Q4 2015 regulatory Cr(VI) plume results from trace-element concentrations other than Cr(VI). Water from wells in Mojave-type deposits outside the Q4 2015 regulatory Cr(VI) plume as far north as well MW-174S1 in Water Valley also plot within the 95-percent predictive interval and are consistent with the trace-element assemblage in groundwater associated with the felsic geology of Mojave-type deposits. The distribution of data along the regression line is consistent with uranium concentrations within irrigation water, especially in water from wells MW-192S, D; MW-126S1, S2; and MW-102S, having uranium concentrations ranging from 54 to 114 µg/L.

Water from wells in non-Mojave-type deposits and water from deeper wells completed within Mojave-type deposits that have iron and manganese concentrations consistent with more reduced conditions plot outside the 95-percent confidence prediction interval about the regression line and have different trace-element assemblages consistent with their geologic and geochemical histories. Water from well MW-208S, having a Cr(VI) concentration of 2,500 µg/L (the highest sampled as part of this study), also plots outside the 95-percent predictive interval (fig. E.20). Well MW-208S was not used in the least-squares regression. Physical examination of core material and sequential-extraction data (chapter C) show alteration of aquifer materials and sorption sites in aquifer material adjacent to the screened interval of MW-208S that had been exposed to high Cr(VI) concentrations within the plume.

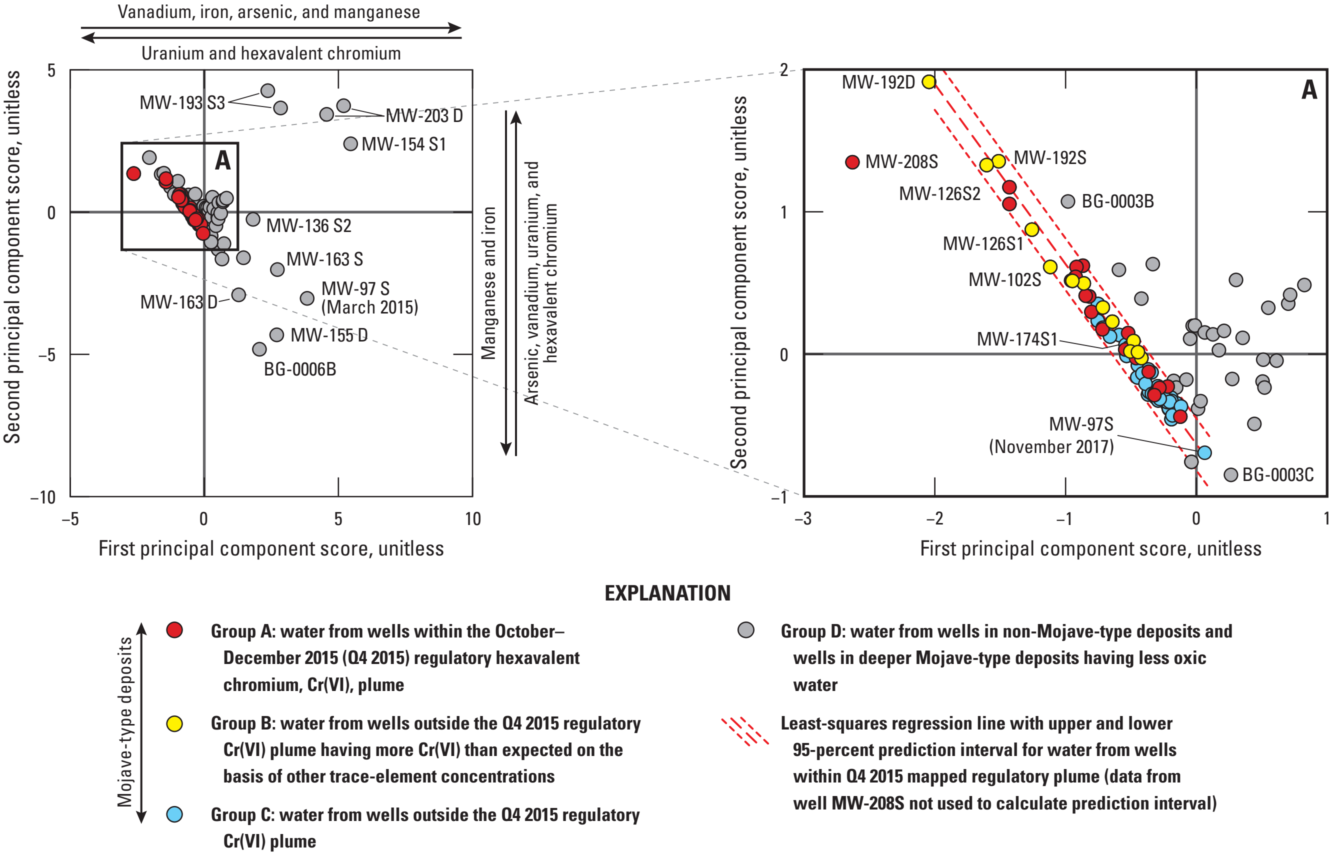


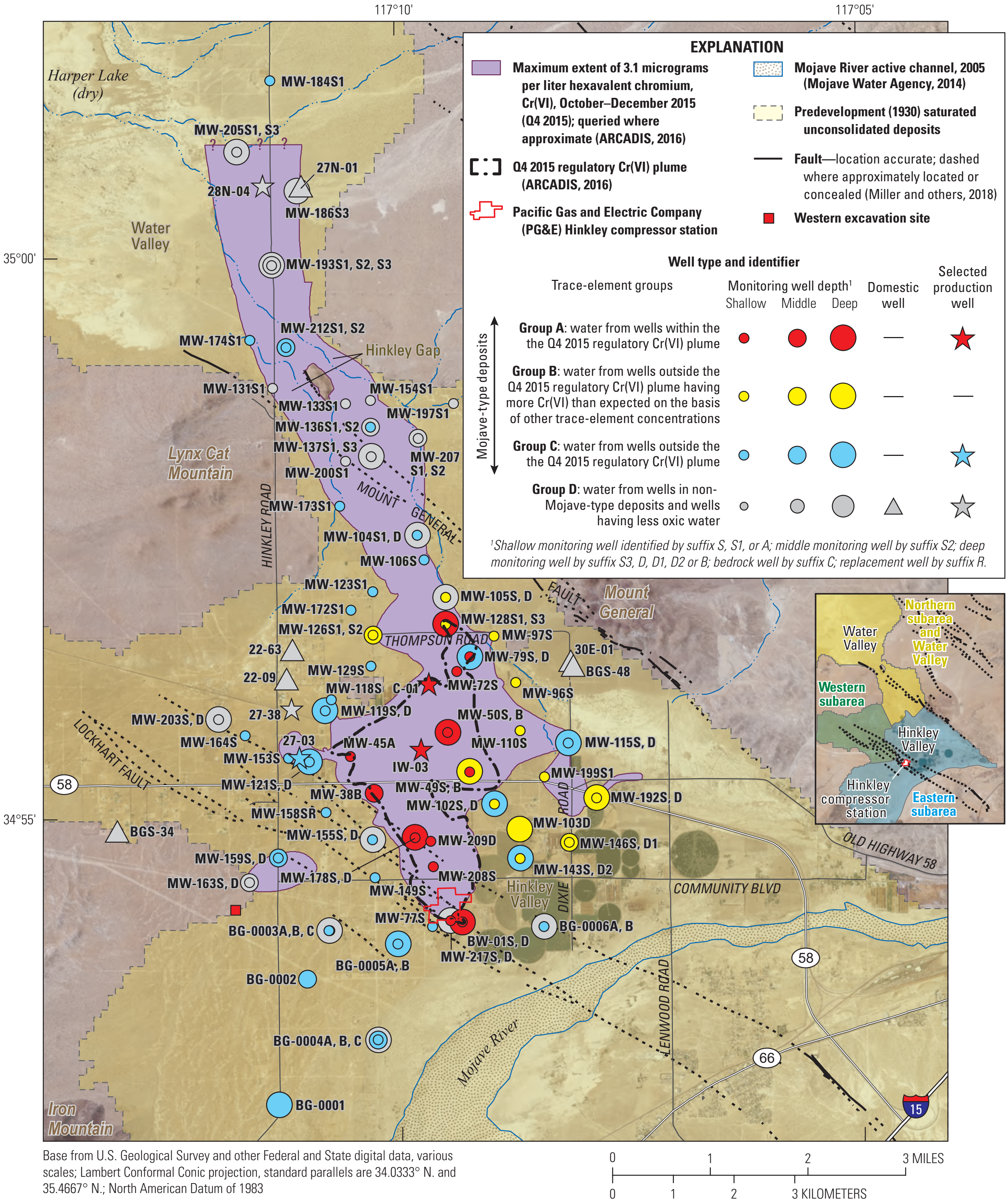
Figure E.20. First and second principal component scores calculated for *A*, selected trace-element data in water from sampled wells and *B*, data in the indicated subset of part *A* showing data grouped by geology and third principal component scores, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Statistics calculated from data available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

The third principal component scores for water from wells within the mapped Q4 2015 regulatory Cr(VI) plume ranged from −0.20 to 0.99 (unitless). The third principal component is composed primarily of the high-magnitude positive eigenvector for Cr(VI), which has a dominant influence on the third principal component scores (table E.5), and it identifies water from wells in Mojave-type deposits having higher concentrations of Cr(VI) than expected after accounting for the concentrations of the other selected trace elements included within the PCA. These higher Cr(VI) concentrations are associated with releases from the Hinkley compressor station. Consistent with this interpretation, water from deeper wells within the footprint of the Q4 2015 regulatory Cr(VI) plume, such as wells MW-50B and MW-79D that have Cr(VI) concentrations less than 3.1 µg/L, have third principal component scores more negative than −0.20 that are not indicative of anthropogenic Cr(VI).

Water from wells within the 95-percent confidence prediction interval having third principal component scores of −0.20 or greater are located (1) in the eastern subarea crossgradient from the Hinkley compressor station and upgradient of the mapped Q4 2015 regulatory Cr(VI) plume and (2) in water from wells in the northern subarea immediately downgradient from the mapped plume (fig. E.21). These areas also were identified as having natural Cr(VI) occurrence probabilities of less than 10 percent at the measured pH (figs. E.18*A,B*). Hexavalent chromium concentrations in water from wells screened in Mojave-type deposits in the western subarea and from wells farther downgradient in the northern subarea and Water Valley do not appear related to Cr(VI) from the Hinkley compressor station when compared with measured concentrations of other trace elements (fig. E.21).

Principal component analysis results divide data in Hinkley and Water Valleys into four groups on the basis of their trace-element composition (figs. E.20, E.21). Groups A, B, and C include water from wells within Mojave-type deposits. Wells within group A are located within the Q4 2015 regulatory Cr(VI) plume. First and second principal component scores within group A plot along a straight line, with third principal component scores greater than −0.2. Wells within groups B and C are outside the mapped Q4 2015 regulatory Cr(VI) plume extent. First and second principal component scores within group B plot along the same line as wells within the Q4 2015 regulatory Cr(VI) plume (group A), and they also have third principal component scores greater than −0.2 and are not distinguishable from group A wells within the Q4 2015 regulatory Cr(VI) plume on the basis of the PCA. First and second principal component scores within group C also plot along the same line with wells in groups A and B but have third principal component scores more negative than −0.2, which are less than values within the Q4 2015 regulatory Cr(VI) plume and not consistent with anthropogenic Cr(VI) from the Hinkley compressor station. On the basis of PCA results, the trace-element composition of water from wells in group B is similar to water from wells in group A, and PCA results show an excess of Cr(VI) after accounting for the concentrations of the other trace elements measured. On the basis of PCA results, Cr(VI) concentrations in water from wells within groups A and B are consistent with anthropogenic Cr(VI) released from the Hinkley compressor station, and Cr(VI) concentrations in water from wells within group C are consistent with natural Cr(VI). Group D includes water from wells in non-Mojave-type deposits or in Mojave-type deposits having higher iron and manganese concentrations, indicating a less oxic redox status and a different trace-element assemblage. Given their different hydrologic and geochemical history, the third principal component score for samples from group D wells was not evaluated with respect to Cr(VI) in the same manner as wells within groups A, B, and C.

Principal component analysis results and the processes described by those results are often difficult to visualize. For purposes of visualization, the four groups of data identified by PCA (fig. E.21) are shown as box plots (fig. E.22). Water from wells completed in Mojave-type deposits, groups A, B, and C, have a similar oxyanion chemistry with respect to arsenic, uranium, and vanadium concentrations (figs. E.22*A*, *B*, *C*); however, that similar chemistry differs from water from group D wells completed in non-Mojave-type deposits (fig. E.22*D*). The highest Cr(VI) concentrations are in water from group A wells located within the Q4 2015 regulatory Cr(VI) plume (fig. E.22*A*). Uranium concentrations are higher in water from wells completed in Mojave-type deposits underlying areas impacted by irrigated agriculture including wells within the Q4 2015 regulatory Cr(VI) plume (figs. E.22*A, B*). Water from wells within group B outside the Q4 2015 regulatory Cr(VI) plume are impacted by irrigation return (fig. E.22*B*). Hexavalent chromium concentrations in water from group B are only slightly higher than concentrations in group C wells (fig. E.22). Irrigation return water (sampled as porewater pressure extracted from core material and discussed in the "E.4. Porewater" section in this chapter) has low Cr(VI) concentrations, less than 0.5 µg/L (blue bars on fig. E.22*B*). Low Cr(VI) concentrations in irrigation return water are consistent with the land application of Cr(VI)-containing groundwater by PG&E to remediate the Cr(VI) plume (chapter A). The data show that Cr(VI) concentrations within group B are higher than expected on the basis of their trace-element assemblage concentrations and are affected by Cr(VI) from a source other than irrigation return, most likely the Hinkley compressor station.



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.21. Water-quality groups estimated from principal component analysis (PCA) scores calculated for selected trace-element data, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Statistics calculated from data available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

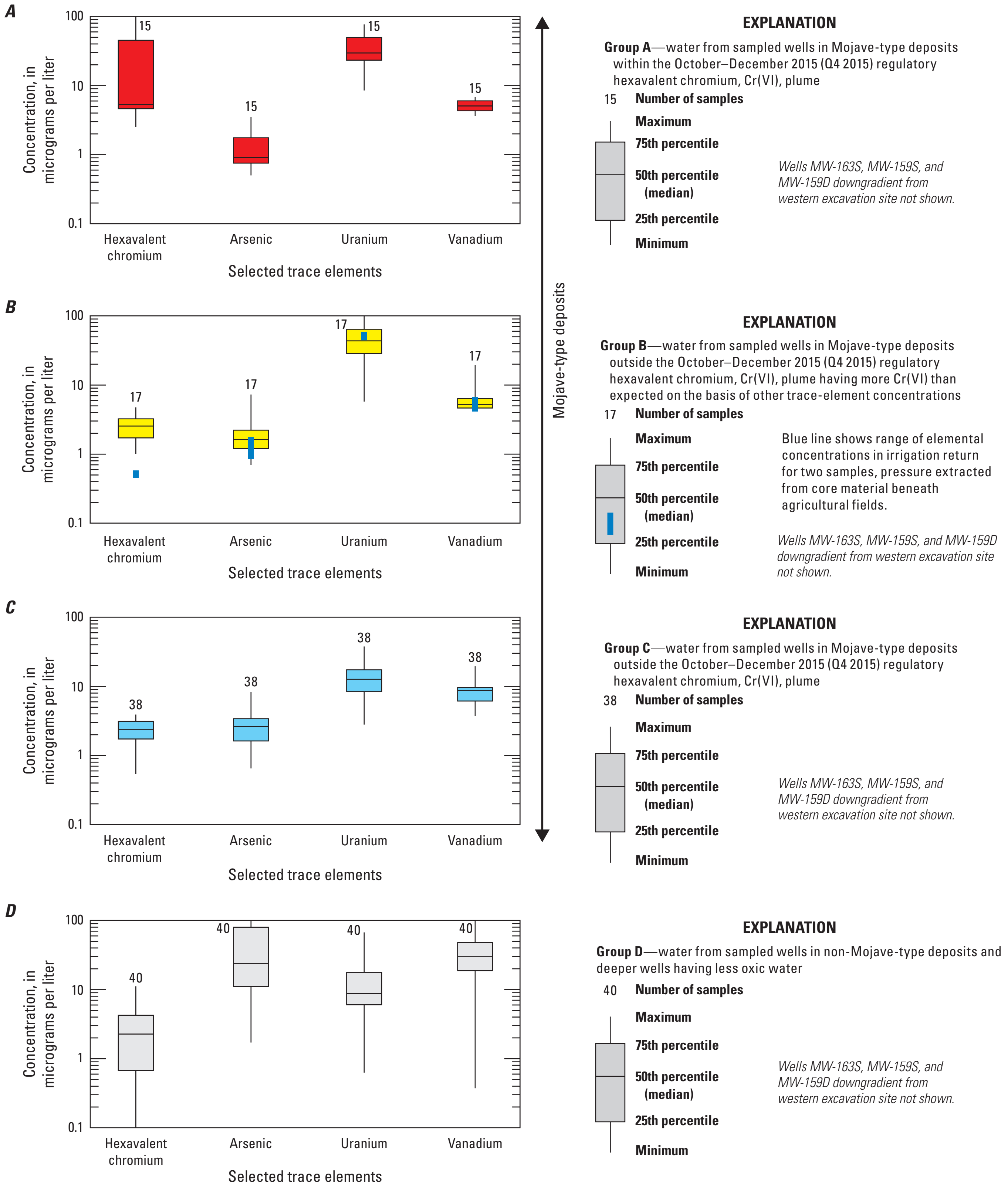


Figure E.22. Selected oxyanion concentrations in water from wells completed *A*, within the Q4 2015 (October–December 2015) regulatory hexavalent chromium, Cr(VI), plume; *B*, outside the plume in Mojave-type deposits impacted by irrigation return and having excess Cr(VI); *C*, outside the plume in other Mojave-type deposits; and *D*, in non-Mojave-type deposits or deposits yielding less oxic water, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix E.1 (table E.1.1) and U.S. Geological Survey (2021).

Principal component scores incorporate trace-element concentrations associated with geology and geochemistry including pH-dependent sorption of selected oxyanion-forming trace elements. The third principal component score is dominated by a high magnitude eigenvector for Cr(VI) and was used to identify wells in Mojave-type deposits near the Q4 2015 regulatory Cr(VI) plume having more Cr(VI) than expected on the basis of their trace-element composition. The third principal component score was used as a metric to identify natural and anthropogenic Cr(VI) within the SSA in chapter G within this professional paper. Principal component analysis results also were used to evaluate the trace-element composition of porewater and water from sampled domestic wells discussed (in the "E.4 Porewater" and "E.5 Water from Domestic Wells" sections, respectively) later in this chapter.

E.4. Porewater

Within Hinkley and Water Valleys, fine-textured (silt and clay) aquifer materials have more chromium than coarse-textured (sand and gravel) aquifer materials (fig. E.14*A*). Porewater within fine-textured materials is a possible natural source of Cr(VI) to water from wells—especially in mudflat/playa deposits containing Mn(IV) oxides that may facilitate oxidation of Cr(III) to Cr(VI) (fig. E.15). Although porewater data are difficult and expensive to collect, requiring drilling to collect fresh cores and specialized sample collection and handling techniques, porewater data collected as part of this study provide a direct measure of specific conductance, pH, Cr(VI), and other trace-element concentrations within fine-textured material within the study area.

Hexavalent chromium concentrations in porewater pressure extracted from 38 samples of core material (table E.6) collected at 11 sites in Hinkley Valley that were selected with input from the TWG (fig. E.23) ranged from less than 0.30 to 3.3 µg/L. Hexavalent chromium concentrations were highest in porewater extracted from MW-192 between 86.5 and 87 ft bls. Hexavalent chromium concentrations in porewater within Hinkley Valley were lower than porewater from mafic alluvium in the Sheep Creek fan eroded from the San Gabriel Mountains (fig. E.2) southwest of the study area, having Cr(VI) concentrations as high as 13 µg/L (Izbicki and others, 2008a).

The pH of sampled porewater ranged from 6.9 to 9.5, with a median value of 7.7 (table E.6). Most Cr(VI) concentrations in porewater had a Cr(VI) occurrence probability at the measured pH greater than 30 percent and were within the range expected for uncontaminated groundwater. However, porewater extracted from locally derived alluvium at BG-0004 between 158 and 159 ft bls had a Cr(VI) concentration of 2.3 µg/L at a measured pH of 7.2, with a Cr(VI) occurrence probability between 20 and 30 percent. Well BG-0004 is upgradient from the Hinkley compressor station and not affected by anthropogenic releases of Cr(VI). Chromium concentrations in core material from this depth were as high as 60 mg/kg with manganese concentrations as high as 1,470 mg/kg (Groover and Izbicki, 2018). Locally derived alluvium at this depth predates the arrival of the Mojave River in Hinkley Valley (chapter A), and this was the geologically oldest material from which porewater was extracted. Porewater was not extracted from similar age or older deposits elsewhere in the study area, including Miocene material underlying the western subarea or alluvium eroded in part from Miocene material in Water Valley.

Fine-textured mudflat/playa deposits contain Mn(IV) oxides (chapter C) that may facilitate oxidation of Cr(III) to Cr(VI). Redox potentials calculated from Cr(VI) and Cr(III) concentrations in water from wells MW-192S and MW-192D in the eastern subarea approach equilibrium with Mn(IV) oxides in mudflat/playa deposits penetrated by these wells (fig. E.15). Mineralogic analyses showed aquifer material collected at this site was deposited by the Mojave River. Material at this site is felsic (chapter C, fig. C.10), and chromium concentrations in core material adjacent to the screened interval of wells MW-192S and MW-192D do not exceed 25 mg/kg, with a median concentration of 9.6 mg/kg (Groover and Izbicki, 2018). More detailed mineralogic analyses show that most chromium within aquifer materials at this site is substituted for iron within magnetite mineral grains (chapter C, fig. C.11), which are resistant to weathering. Consistent with these data, Cr(VI) concentrations in porewater extracted from core material at site MW-192 did not exceed 3.3 µg/L (table E.6), and porewater does not appear to be a source of natural Cr(VI) concentrations greater than this value in water from wells in the eastern subarea.

Table E.6. Selected chemical and isotopic data for porewater samples pressure extracted from core material at selected monitoring-well sites, Hinkley Valley, western Mojave Desert, California. Data are available in U.S. Geological Survey (2021).

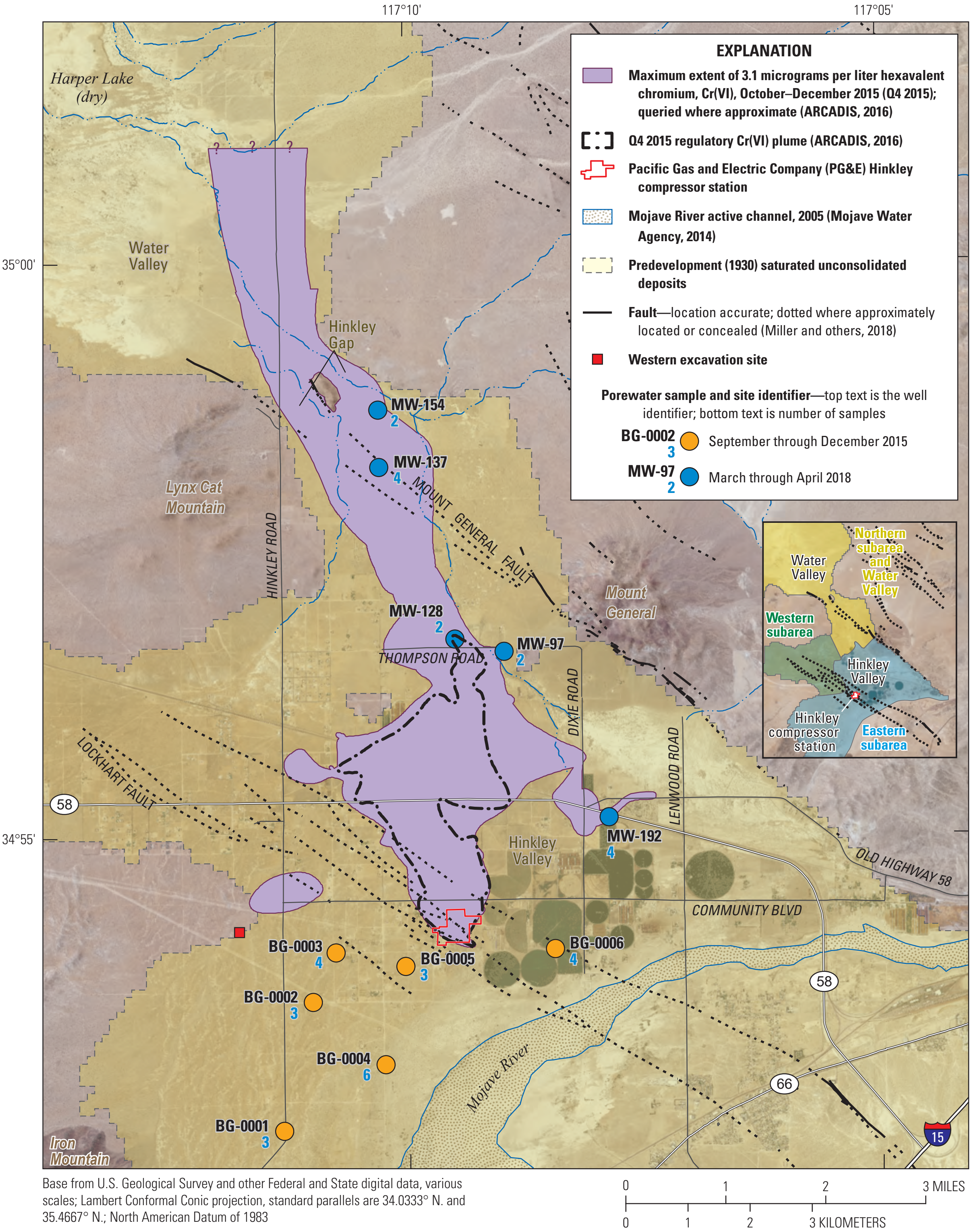
[It was not possible to extract sufficient water to analyze for all constituents from every sample. Numbers are rounded for presentation. Samples for trace-element analyses were filtered in the field through a 0.45-micrometer pore-sized filter. Hexavalent chromium, Cr(VI); total dissolved chromium, Cr(t); and iron values are from the U.S. Geological Survey Trace Element Laboratory, Boulder, Colorado. Other trace-element data from U.S. Geological Survey National Water Quality Laboratory (NWQL). **Abbreviations**: mm/dd/yyyy, month/day/year; bls, below land surface; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; per mil, parts per thousand; δD, delta deuterium; $\delta^{18}O$, delta oxygen-18; <, less than; —, no data]

Site name	Date (mm/dd/yyyy)	Sample interval, in feet bls		pH, in standard units	Specific conductance, in µS/cm at 25 °C	Selected trace elements, in µg/L							Stable isotopes of water, in per mil	
		Top of interval	Bottom of interval			Cr(VI)	Cr(t)	Arsenic	Iron	Manganese	Uranium	Vanadium	δD	$\delta^{18}O$
BG-0001	11/03/2015	162	164	7.6	480	1.8	2.2	2.6	27	45	12	7.1	−61	−8.2
BG-0001	11/04/2015	182	184	7.8	510	1.3	1.7	2.2	14	32	12	6.4	−60	−8.3
BG-0001	11/04/2015	192	194	7.9	520	0.60	0.70	1.8	5.0	23	9.8	5.1	−61	−8.4
BG-0002	11/19/2015	97	99	6.9	1,080	0.35	0.59	0.81	6.8	24	35	9.4	−61	−8.2
BG-0002	11/19/2015	135	138.5	7.1	940	0.35	0.59	0.30	6.6	16	47	3.9	−61	−8.5
BG-0002	11/20/2015	150	155	8.9	380	0.48	0.62	31	75	7.7	30	9.5	−60	−8.2
BG-0003	11/09/2015	103	105	7.7	390	1.0	1.5	1.2	16	9.1	5.5	6.6	−59	−8.3
BG-0003	11/10/2015	127	132	7.4	600	0.90	1.3	0.87	28	30	11	34	−58	−8.0
BG-0003	11/11/2015	153	155	8.8	520	1.2	1.2	89	17	6.9	31	19	−59	−8.2
BG-0003	11/11/2015	187	189	7.7	430	1.2	1.2	7.9	6.5	7.1	8.1	21	−59	−8.2
BG-0004	12/02/2015	62	63.5	7.4	630	0.76	0.76	0.90	14	64	8.9	4.2	−60	−8.1
BG-0004	09/01/2015	64	65	7.2	510	1.2	1.6	1.4	7.8	20	3.8	7.4	−58	−7.7
BG-0004	12/02/2015	70	71	7.6	580	1.0	1.2	0.99	4.8	13	8.3	4.1	−60	−8.5
BG-0004	09/01/2015	74	75	7.8	470	1.2	1.6	2.3	<40	74	2.9	8.4	—	—
BG-0004	09/01/2015	140	141	7.5	380	1.7	2.1	7.9	10	13	5.8	19	−60	−8.2
BG-0004	09/01/2015	158	159	7.2	480	2.3	3.1	—	—	—	—	—	—	—
BG-0005	12/09/2015	101	102	7.2	490	0.50	0.59	1.5	11	22	5.0	4.0	−61	−8.4
BG-0005	12/10/2015	158.2	158.2	7.2	400	0.62	0.94	1.8	150	42	7.5	2.3	−60	−8.4
BG-0005	12/10/2015	168	169	8.8	320	0.60	0.71	23	5.3	12	13	8.8	−60	−8.1
BG-0006	12/15/2015	46.5	47.5	7.2	1,380	0.49	0.58	1.5	11	26	50	5.7	−62	−8.2
BG-0006	12/15/2015	60	61	7.0	1090	0.48	0.60	0.9	14	10	47	4.4	−59	−7.7
BG-0006	12/16/2015	108	110	7.6	600	0.62	0.90	2.2	11	18	3.1	5.7	−59	−8.2
BG-0006	12/16/2015	148	150	8.0	390	0.52	0.56	4.9	13	5.2	6.9	11	−60	−8.5
MW-128	03/07/2018	79	80	7.6	1740	0.70	2.3	0.93	3.5	13	8.7	3.6	−56	−7.6

Table E.6. Selected chemical and isotopic data for porewater samples pressure extracted from core material at selected monitoring-well sites, Hinkley Valley, western Mojave Desert, California. Data are available in U.S. Geological Survey (2021).—Continued

[It was not possible to extract sufficient water to analyze for all constituents from every sample. Numbers are rounded for presentation. Samples for trace-element analyses were filtered in the field through a 0.45-micrometer pore-sized filter. Hexavalent chromium, Cr(VI); total dissolved chromium, Cr(t); and iron values are from the U.S. Geological Survey Trace Element Laboratory, Boulder, Colorado. Other trace-element data from U.S. Geological Survey National Water Quality Laboratory (NWQL). **Abbreviations**: mm/dd/yyyy, month/day/year; bls, below land surface; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; per mil, parts per thousand; δD, delta deuterium; $\delta^{18}O$, delta oxygen-18; <, less than; —, no data]

Site name	Date (mm/dd/yyyy)	Sample interval, in feet bls		pH, in standard units	Specific conductance, in µS/cm at 25 °C	Selected trace elements, in µg/L							Stable isotopes of water, in per mil	
		Top of interval	Bottom of interval			Cr(VI)	Cr(t)	Arsenic	Iron	Manganese	Uranium	Vanadium	δD	$\delta^{18}O$
MW-128	03/07/2018	89	89.5	7.7	1540	0.30	0.50	0.74	6.5	17	9.9	4.2	−56	−7.3
MW-137	04/26/2018	80	80.5	9.2	220	1.9	2	—	9.0	—	—	—	—	—
MW-137	03/13/2018	82	82.5	8.3	300	—	—	58	36	1.3	3.2	66	−59	−8.5
MW-137	04/30/2018	99	99.5	8.8	420	0.70	0.90	4.8	<20	1.9	3.8	11	−59	−8.3
MW-137	04/11/2018	131	135	9.1	340	1	1.3	24	3,460	36	4.1	97	−59	−8.3
MW-154	05/15/2018	41.5	41	7.8	300	—	5.4	—	—	—	—	—	—	—
MW-154	05/15/2018	72.5	73.5	9.2	340	0.90	1.5	—	—	—	—	—	—	—
MW-154	05/15/2018	73.5	75.2	9.5	310	1.3	1.6	270	110	2.0	2.2	190	−59	−8.4
MW-192	04/18/2018	61	71	8.1	800	0.90	<50.0	11	<3	<40.0	9.8	14	−58	−8.0
MW-192	03/01/2018	80.5	85.5	8.1	300	2.4	3.8	12	230	9.6	8.2	23	−60	−8.8
MW-192	03/01/2018	86.5	87	7.9	630	3.3	4	5.0	<3	2.7	5.4	16	−60	−8.5
MW-192	04/16/2018	86.5	91	7.8	390	0.40	0.60	—	230	—	—	—	—	—
MW-97	03/05/2018	82.5	83	8.1	410	2.7	2	4.2	15	21	4.5	11	−53	−7.4
MW-97	03/05/2018	97	97.5	8.2	510	0.90	1.1	2.9	3.2	13	4.9	6.7	−60	−8.3



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.23. Location of cores used for porewater extractions, Hinkley Valley, western Mojave Desert, California, September 2015 to May 2018. Data are available in U.S. Geological Survey (2021).

Redox potentials calculated from Cr(VI) and Cr(III) concentrations in water from wells MW-133S1 and MW-154S1 in the northern subarea also approach equilibrium with Mn(IV) oxides in mudflat/playa deposits (fig. E.15). In contrast to material in the eastern subarea, core material collected from mudflat/playa deposits penetrated by wells MW-133S1 and MW-154S1 were not exclusively sourced from the Mojave River, and core material contains some Miocene material as well as minerals eroded from basaltic chromium-containing rock (chapter C). Chromium concentrations adjacent to the screened intervals of wells MW-133S1 and MW-154S1 were as high as 85 and 77 mg/kg, and manganese concentrations were as high as 838 and 1,340 mg/kg, respectively (Groover and Izbicki, 2018). Core material from MW-133S1 equaled the summative-scale threshold for chromium of 85 mg/kg (chapter B, fig. B.11*A*), and MW-154S1 exceeded the summative-scale threshold for manganese of 970 mg/kg (chapter B, fig. B.11*B*). Chromium-containing magnetite was not present at MW-154S1 and, on the basis of optical examination, may have weathered to hematite, which was widely disseminated throughout the core material (chapter C, fig. C.9*C*). Consistent with redox data (fig. E.15), manganese substituted for iron within magnetite would likely form Mn(IV) oxides with mineral weathering (Dixon and Weed, 1989).

The Cr(VI) concentration in porewater from core material collected within the saturated zone at MW-154 between 73.5 and 75 ft bls was 1.1 µg/L. The core material was visibly gleyed (gray in color), and low Cr(VI) concentrations in porewater at this site may have resulted from reduced (low oxygen) conditions within the core. Porewater extracted from core material collected from 41 ft bls within the overlying unsaturated zone at MW-154 had a Cr(t) concentration of 5.4 µg/L—the highest porewater Cr(t) concentration collected as part of this study. It was not possible to extract enough porewater from this material to analyze for Cr(VI). Although not as high as Cr(VI) concentrations of 8.8 and 11 µg/L in water from wells MW-133S1 and MW-154S1, respectively, on the basis of mineralogic data collected at these sites, it is possible that porewater may be a source of naturally occurring Cr(VI) to water from wells in this part of the northern subarea.

Arsenic concentrations in porewater were as high as 270 µg/L, with 24 percent of porewater samples exceeding the MCL of 10 µg/L; uranium concentrations were as high as 50 µg/L, with 15 percent exceeding the MCL of 30 µg/L; and vanadium concentrations were as high as 190 µg/L, with 9 percent exceeding the NL of 50 µg/L (table E.6). Porewater was not extracted from calcite-rich groundwater discharge deposits that had high uranium concentrations in aquifer solids. Unlike Cr(VI), porewater may be a potential source of arsenic, uranium, and vanadium in water from wells.

Most porewater did not show an excess of Cr(VI) with respect to concentrations of other trace elements measured. Only porewater from well BG-0006 at 46.5 to 47.5 ft bls, having a Cr(VI) concentration of 0.49 µg/L, had a higher Cr(VI) concentration than expected on the basis of principal component scores calculated from its trace-element composition (not shown on fig. E.20).

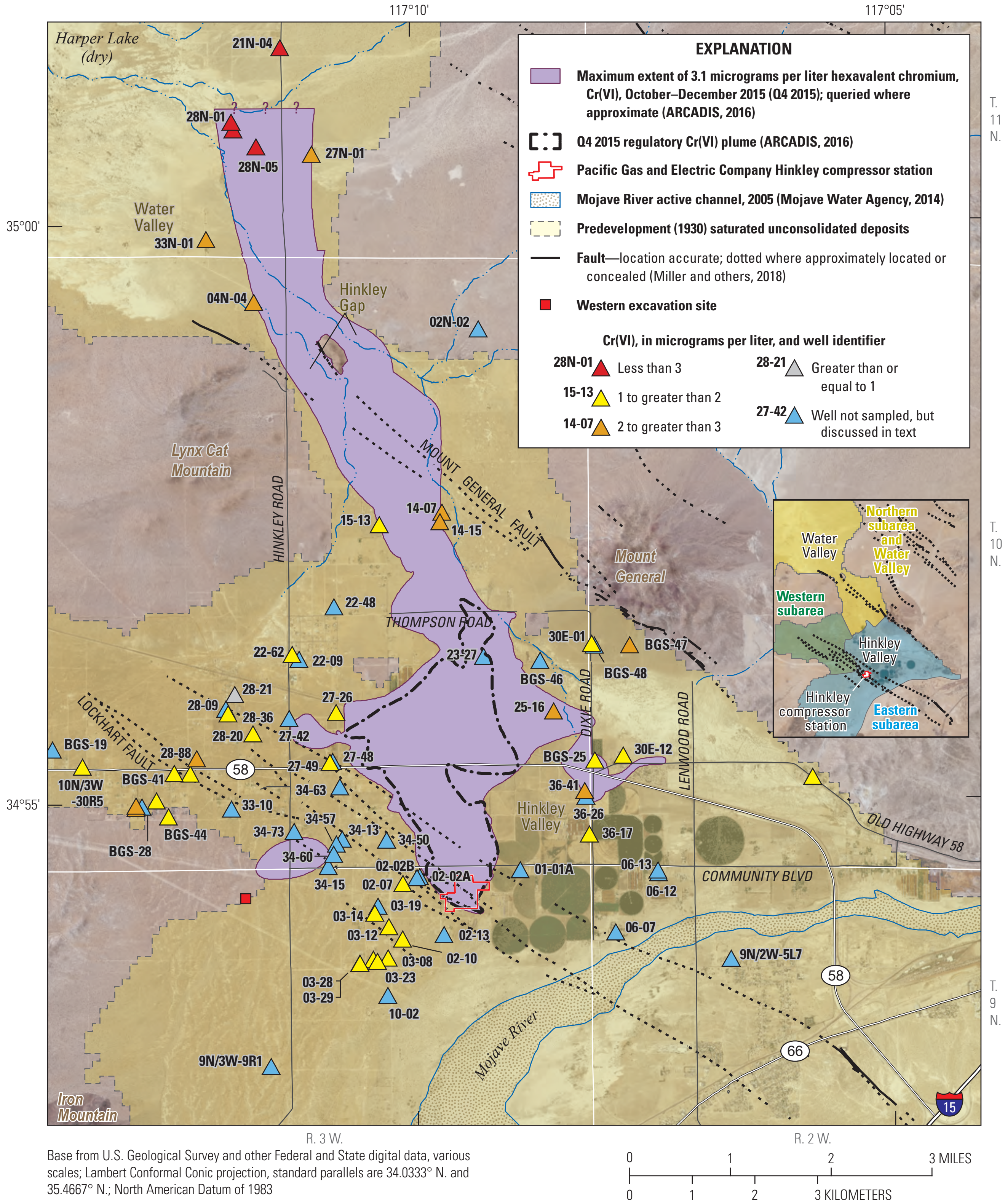
E.5. Water from Domestic Wells

Between January 27 and 31, 2016, more than 70 domestic wells were sampled and analyzed for field parameters (including pH, specific conductance, and dissolved oxygen), selected trace elements [including arsenic, Cr(VI), Cr(t), iron, manganese, uranium, and vanadium], and the stable isotopes of oxygen and hydrogen (oxygen-18 and deuterium, respectively, discussed in chapter F within this professional paper). Data are available in appendix E.1 (table E.1.3).

Hexavalent chromium concentrations in sampled domestic wells ranged from less than the reporting limit of 0.06 to 4 µg/L (fig. E.24), with the highest Cr(VI) concentration in water from well 21N-04, the northernmost well sampled in Water Valley. The median Cr(VI) concentrations in water from sampled domestic wells in the eastern, western, and northern subareas (including Water Valley) were 1.1, 0.8, and 2.7 µg/L, respectively. The median Cr(VI) concentration in the northern subarea (including Water Valley) was significantly higher than the median concentrations in the eastern and western subareas on the basis of the median test (Neter and Wasserman, 1974), with a significance criteria of $\alpha=0.05$.

Dissolved oxygen and specific conductance in sampled domestic wells ranged from less than the reporting limit of 0.2 to 12.8 mg/L and 380 to 5,560 µS/cm, respectively. Only three domestic wells had dissolved-oxygen concentrations less than the reporting limit of 0.2 mg/L. There were no statistically significant differences between the three subareas in dissolved oxygen or specific conductance in water from domestic wells.

The pH in water from sampled domestic wells ranged from 7.0 to 9.1. The median pH values in the eastern, western, and northern subareas (including Water Valley) were 7.8, 7.9, and 8.0, respectively. Hexavalent chromium concentrations in domestic wells were evaluated with respect to pH using the same approach as water from wells sampled for more complete chemical analyses (fig. E.17). Only one domestic well, 36-41 in the eastern subarea (fig. E.24), having a Cr(VI) concentration of 2.1 µg/L and a pH of 7.2, had a Cr(VI) occurrence probability at the measured pH of less than 30 percent when compared with California-wide Cr(VI) occurrence; the well is in an area where PG&E monitoring wells also show low Cr(VI) occurrence probabilities (fig. E.18*A*).



Base from U.S. Geological Survey and other Federal and State digital data, various scales; Lambert Conformal Conic projection, standard parallels are 34.0333° N. and 35.4667° N.; North American Datum of 1983

Figure E.24. Hexavalent chromium, Cr(VI), concentrations in water from domestic wells in Hinkley and Water Valleys, western Mojave Desert, California, January 27–31, 2016. Data are available in appendix E.1 (table E.1.3) and U.S. Geological Survey (2021).

Arsenic concentrations in water from domestic wells were as high as 295 µg/L, with 39 percent of sampled wells exceeding the MCL of 10 µg/L. Uranium concentrations were as high as 62 µg/L, with 8 percent of sampled wells exceeding the MCL of 30 µg/L. Vanadium concentrations were as high as 90 µg/L, with 9 percent of sampled wells exceeding the NL of 50 µg/L. In addition, nitrate concentrations were as high as 18 mg/L nitrate as N, with 10 percent of sampled wells exceeding the MCL of 10 mg/L nitrate as N. Water from 47 percent of domestic wells sampled between January 21, and 31, 2016, had arsenic, uranium, or nitrate concentrations above their respective MCL (appendix E.1, table E.1.3).

Trace-element concentrations in domestic wells were evaluated on the basis of scores calculated from PCA eigenvectors using the same approach as water from wells sampled for more complete chemical analyses (table E.5). Most domestic wells have first and second principal component scores consistent with non-Mojave-type deposits. Sampled domestic wells within the 95-percent prediction interval about the Q4 2015 regulatory Cr(VI) plume data have third principal component scores more negative than −0.2 (unitless), indicative of natural Cr(VI) in water from domestic wells.

The Pacific Gas and Electric Company purchased most land overlying and near the mapped Q4 2015 regulatory Cr(VI) plume. After the land was purchased, unused domestic wells were routinely destroyed based on guidance from the Lahontan Regional Water Quality Control Board (2013b) and were unavailable for sample collection. Consequently, domestic wells such as 28-21, which had regulatory Cr(VI) concentrations as high as 8.6 µg/L (chapter D, fig. D.7), were not available for sample collection in January 2016.

E.6. Conclusions

The U.S. Geological Survey (USGS) was requested by the Lahontan Regional Water Quality Control Board to complete an updated background study of hexavalent chromium, Cr(VI), concentrations in Hinkley and Water Valleys. As part of the USGS Cr(VI) background study in Hinkley and Water Valleys, California, the chemical compositions and Cr(VI) concentrations in groundwater were evaluated. The scope of the work included evaluating the quality of USGS data; the chemistry of groundwater in Hinkley and Water Valleys, including the spatial distribution of Cr(VI); and the geochemical controls on Cr(VI) concentrations in water from wells, including redox, pH-dependent sorption processes, speciation, and cooccurrence of Cr(VI) with selected trace elements. In addition to evaluating Cr(VI) concentrations in water from monitoring wells, evaluations of Cr(VI) concentrations in porewater extracted from fine-textured material within the study area and in water from selected domestic wells were included within the scope of the study.

Hexavalent chromium concentrations in water from sampled wells were analyzed at a commercial laboratory using ion chromatography (U.S. Environmental Protection Agency, EPA Method 218.6; with selected samples analyzed using a low-level analytical technique modified from EPA Method 218.6) and at the USGS Redox Chemistry Laboratory using field speciation with subsequent analyses by graphite furnace atomic absorption spectroscopy (GFAAS; EPA Method 7010). The low-level ion chromatography and field speciation techniques have laboratory reporting levels (LRL) of 0.06 microgram per liter (µg/L). Replicate data and analysis of reference waters showed Cr(VI) results from the commercial laboratory and from the USGS Redox Chemistry Laboratory were statistically similar and suitable for the purposes of this study. To facilitate comparison with regulatory data collected by the Pacific Gas and Electric Company (PG&E), data from the commercial laboratory, having a study reporting level (SRL) of 0.10 µg/L with a precision of 6 percent (at the replicate mean value), were commonly presented in this chapter. However, field speciation Cr(VI) and total dissolved chromium, Cr(t), data analyzed at the USGS Redox Chemistry Laboratory were used to calculate redox, and field speciation Cr(VI) data were reported for porewater.

The larger number of analyses done on samples collected as part of the USGS Cr(VI) background study required that a greater volume of water was pumped from monitoring wells compared to samples collected for regulatory purposes by PG&E. In addition, USGS samples were often collected at lower pump-flow rates so that, when possible, water levels were not drawn down into the screened interval of wells during purging and sample collection. As a consequence of differences in sample collection methods, Cr(VI) concentrations in samples collected as part of this study were slightly lower (about 9 percent) than Cr(VI) concentrations in regulatory samples, with the largest differences in samples from low-yielding wells. In accordance with the study design in which earlier samples were used to guide collection of later samples, U.S. Geological Survey data collected between March 2015 and November 2017 were not synoptic (single point in time) representations of Cr(VI) concentrations in Hinkley and Water Valleys. Comparison of data from selected wells sampled in March 2015 with data from those same wells resampled in March 2017 showed a small decrease in Cr(VI) concentrations of about 4 percent during that time.

Water from most wells sampled as part of the USGS Cr(VI) background study in Hinkley and Water Valleys was generally alkaline and oxic. Calcium/bicarbonate to mixed-cation/mixed-anion composition water predominated in wells near recharge areas along the Mojave River, with mixed-cation/mixed-anion composition water present as far downgradient as well MW-174S1 in the southern part of Water Valley. Calcium/chloride-sulfate water predominated in areas affected by irrigation return. Mixed-cation/mixed-anion composition water in the southern part of Water Valley, recharged from the Mojave River, likely predates the onset of large-scale irrigated agriculture in Hinkley Valley beginning in the early 1950's and presumably predates Cr(VI) releases from the Hinkley compressor station. Sodium/bicarbonate and sodium/chloride waters, isolated from surface sources of recharge by depth or by distance along long groundwater-flow paths within aquifers, also may predate releases from the Hinkley compressor station. Groundwater sources and ages (time since recharge) were addressed more quantitatively using chemical and isotopic tracers in chapter F within this professional paper.

Hexavalent chromium concentrations in water from sampled wells ranged from less than the reporting limit of 0.06 to 2,500 µg/L. The highest Cr(VI) concentrations were in monitoring wells downgradient from the Hinkley compressor station, within the mapped October–December 2015 (Q4 2015) regulatory Cr(VI) plume. Chemical data within the Q4 2015 regulatory Cr(VI) plume were collected to obtain end-members representative of anthropogenic Cr(VI) within groundwater.

Hexavalent chromium concentrations outside the Q4 2015 regulatory Cr(VI) plume were lower in the eastern and western subarea and higher in the northern subarea (including Water Valley). Hexavalent chromium concentrations in water from almost 40 percent of USGS sampled wells outside the Q4 2015 regulatory Cr(VI) plume exceeded the interim 3.1 µg/L regulatory background Cr(VI) concentration developed on the basis of the 2006 PG&E background study. Water from about 20 percent of wells outside the Q4 2015 regulatory Cr(VI) plume sampled for regulatory purposes by PG&E during Q4 2015 exceeded the 3.1 µg/L interim regulatory Cr(VI) background concentration. These data show that reevaluation of (1) natural Cr(VI) concentrations in water from wells in Hinkley and Water Valleys, (2) the interim 3.1 µg/L regulatory Cr(VI) background concentration, and (3) the regulatory Cr(VI) plume extent as part of this study was appropriate.

Water from most wells containing measurable Cr(VI) was distributed in a narrow band within the overlapping chromate ion, $CrO_4^{2-}{}_{(aqueous)}$, and manganese, $Mn(III)_{(solid)}$, redox and pH stability fields. Water from some wells completed in fine-grained, carbonate-rich, mudflat/playa deposits had redox values approaching the $Mn(IV)_{(solid)}$ stability field. Manganese-(IV) oxides were identified on aquifer solids within carbonate-rich, mudflat/playa deposits and have a greater potential for oxidation of trivalent chromium, Cr(III), to Cr(VI) than Mn(III) or Mn(III/IV) oxides, which are more commonly present on the surfaces of mineral grains. However, Cr(VI) concentrations in porewaters pressure extracted from fine-textured mudflat/playa deposits in the eastern subarea did not exceed 3.3 µg/L because of the felsic, low-chromium nature of the deposits in this area. Fine-textured mudflat/playa deposits in the northern subarea contain more chromium than felsic deposits in the eastern subarea and porewater may be a source of Cr(VI) in water from wells in the northern subarea. Porewaters contain high concentrations of arsenic, uranium, and vanadium and may be a potential source of those elements in water from wells.

Values of pH in water from wells ranged from 6.4 to 9.4 in Q4 2015 regulatory data. Hexavalent chromium does not commonly occur in groundwater having slightly acidic to circumneutral pH, but does occur in alkaline, oxic groundwater. The occurrence of Cr(VI) with pH was expressed probabilistically on the basis of Cr(VI) occurrence at the measured pH in groundwater throughout California. Within the footprint of the Q4 2015 regulatory Cr(VI) plume, almost all water from shallow wells had a 10 percent or lower Cr(VI) occurrence probability at the measured pH. The margin of the mapped Q4 2015 regulatory Cr(VI) plume northwest of the Hinkley compressor station along the Lockhart fault corresponds with the mapped extent of Cr(VI) occurrence probabilities at the measured pH of 10 percent or less. The mapped Q4 2015 regulatory Cr(VI) plume margins agree less well with the Cr(VI) occurrence probability in water from wells in (1) the eastern subarea crossgradient from the Hinkley compressor station and upgradient from the Q4 2015 regulatory Cr(VI) plume and (2) shallow wells in the northern subarea downgradient from the leading edge of the Q4 2015 regulatory Cr(VI) plume. Higher Cr(VI) concentrations in the northern subarea and in Water Valley are consistent with higher pH values in these areas. Complexation and competition for exchange sites with other dissolved ions has little effect on pH-dependent sorption and the Cr(VI) occurrence probability at the measured pH.

Arsenic, uranium, and vanadium form negatively charged oxyanions, in many ways similar to Cr(VI), that are soluble in alkaline, oxic groundwater. Although there are differences in aqueous chemistry, concentrations of these trace elements in water are partly controlled by pH-dependent sorption similar to Cr(VI). Differences in selected trace-element assemblages in water from wells may result from differences in geology (including the geologic source of aquifer materials) and from the hydrologic history of the water with respect to anthropogenic Cr(VI) releases from the Hinkley compressor station. Water from wells in two areas showed excess Cr(VI) compared to other oxyanion-forming trace elements, consistent with a hydrologic history of anthropogenic Cr(VI) releases. These areas were similar to areas identified on the basis of Cr(VI) occurrence probability at the measured pH and included (1) the eastern subarea crossgradient from the Hinkley compressor station and upgradient from the mapped Q4 2015 regulatory Cr(VI) plume and (2) the northern subarea downgradient from the leading edge of the mapped Q4 2015 regulatory Cr(VI) plume.

Hexavalent chromium concentrations did not exceed 4.0 µg/L in sampled domestic wells in Hinkley and Water Valleys. Only one sampled domestic well, 36-41 in the eastern subarea, having a Cr(VI) concentration of 2.1 µg/L at a pH of 7.2, had a Cr(VI) occurrence probability of less than 30 percent. The presence of anthropogenic Cr(VI) was not indicated in any domestic wells on the basis of trace-element data. Water from 47 percent of domestic wells sampled in Hinkley and Water Valleys had arsenic, uranium, or nitrate concentrations above a maximum contaminant level (MCL).

Interpretations derived from Cr(VI) and pH data, and from Cr(VI) and selected trace-element data, were used within the summative-scale analysis (SSA) in chapter G within this professional paper to redefine the extent of the Cr(VI) plume. Hexavalent chromium concentration data expressed as the Cr(VI) occurrence probability at the measured pH support the inclusion of aquifer material texture within the SSA. However, Cr(VI) concentrations in porewater pressure extracted from fine-textured material in the eastern subarea did not exceed 3.3 µg/L, and porewater does not appear to be a source of Cr(VI) concentrations greater than this value in water from wells in the eastern subarea. Arsenic and uranium concentrations in some porewater exceeded their respective MCLs, while vanadium concentrations in some porewater exceeded the notification level (NL) for vanadium, and porewater may be a source of high concentrations of these constituents in water from some wells.

Hexavalent chromium concentrations presented in this chapter were collected during several years using procedures that were similar to procedures used for the collection of regulatory data. However, the volume and rates of water pumped from wells sampled as part of this study differed from the volume and rates pumped for regulatory data collection, resulting in small differences in Cr(VI) concentrations in water from some wells, especially low-yielding wells. Furthermore, data collected as part of this study between March 2015 and November 2017 were not a snapshot in time, and a statistically significant decrease in Cr(VI) concentrations of 4 percent was measured in 14 wells during the sample collection period. Although data collected as part of this study between March 2015 and November 2017 were used to define the summative scale Cr(VI) plume extent, they were not used to calculate Cr(VI) background concentrations in chapter G within this professional paper. Instead, Cr(VI) background concentrations were calculated from regulatory data collected from selected wells between April 2017 and January 2018. Water from selected wells sampled during this period was only analyzed for field parameters, Cr(VI), and Cr(t); consequently, Cr(VI) concentrations used to calculate background values were not affected by pumping large volumes of water, pumping rates, or other differences in sample collection and handling techniques.

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Appendix E.1. Water Chemistry and Isotope Data Collected by the U.S. Geological Survey in Hinkley and Water Valleys, Western Mojave Desert, California, March 2015 through November 2017

This appendix contains tables of (1) water chemistry and isotopic data collected from selected monitoring and domestic wells between March 2015 and November 2017 (table E.1.1, available for download at https://doi.org/10.3133/pp1885), (2) field replicate and field blank data collected from selected monitoring and domestic wells between March 2015 and November 2017 (table E.1.2, available for download at https://doi.org/10.3133/pp1885), and (3) water chemistry and isotopic data (including replicate and field blank data) collected from selected domestic wells between January 27 and 31, 2016 (table E.1.3, available for download at https://doi.org/10.3133/pp1885). Samples were collected using field protocols developed for this study that were consistent with procedures described in the U.S. Geological Survey (USGS) Field Manual (Wilde, 2006; U.S. Geological Survey, variously dated) by U.S. Geological Survey field crews with assistance for some wells provided by the Pacific Gas and Electric Company (PG&E). Most constituents were analyzed by the USGS National Water Quality Laboratory in Denver, Colorado, other USGS laboratories, or laboratories contracted through the National Water Quality Laboratory. Hexavalent chromium, Cr(VI), and total dissolved chromium, Cr(t), in samples collected from monitoring and domestic wells between March 2015 and November 2017 were analyzed at the same contract laboratory used by PG&E for regulatory analyses using U.S. Environmental Protection Agency (EPA) Method 218.6 (U.S. Environmental Protection Agency, 1994a) and EPA Method 200.8 (U.S. Environmental Protection Agency, 1994b), respectively; Cr(VI) and Cr(t) also were speciated in the field using procedures described by Ball and McCleskey (2003) and analyzed using EPA Method 7010 (U.S. Environmental Protection Agency, 2007) at the USGS Redox Chemistry Laboratory in Boulder, Colo. Hexavalent chromium, Cr(VI), in samples from domestic wells collected January 27–31, 2016, was analyzed in a mobile field laboratory using EPA Method 218.6 (U.S. Environmental Protection Agency, 1994a); Cr(VI) and Cr(t) in water from these wells also were speciated in the field using procedures described by Ball and McCleskey (2003) and analyzed using EPA Method 7010 (U.S. Environmental Protection Agency, 2007) at the USGS Redox Chemistry Laboratory. Data are available from U.S. Geological Survey (2021).

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