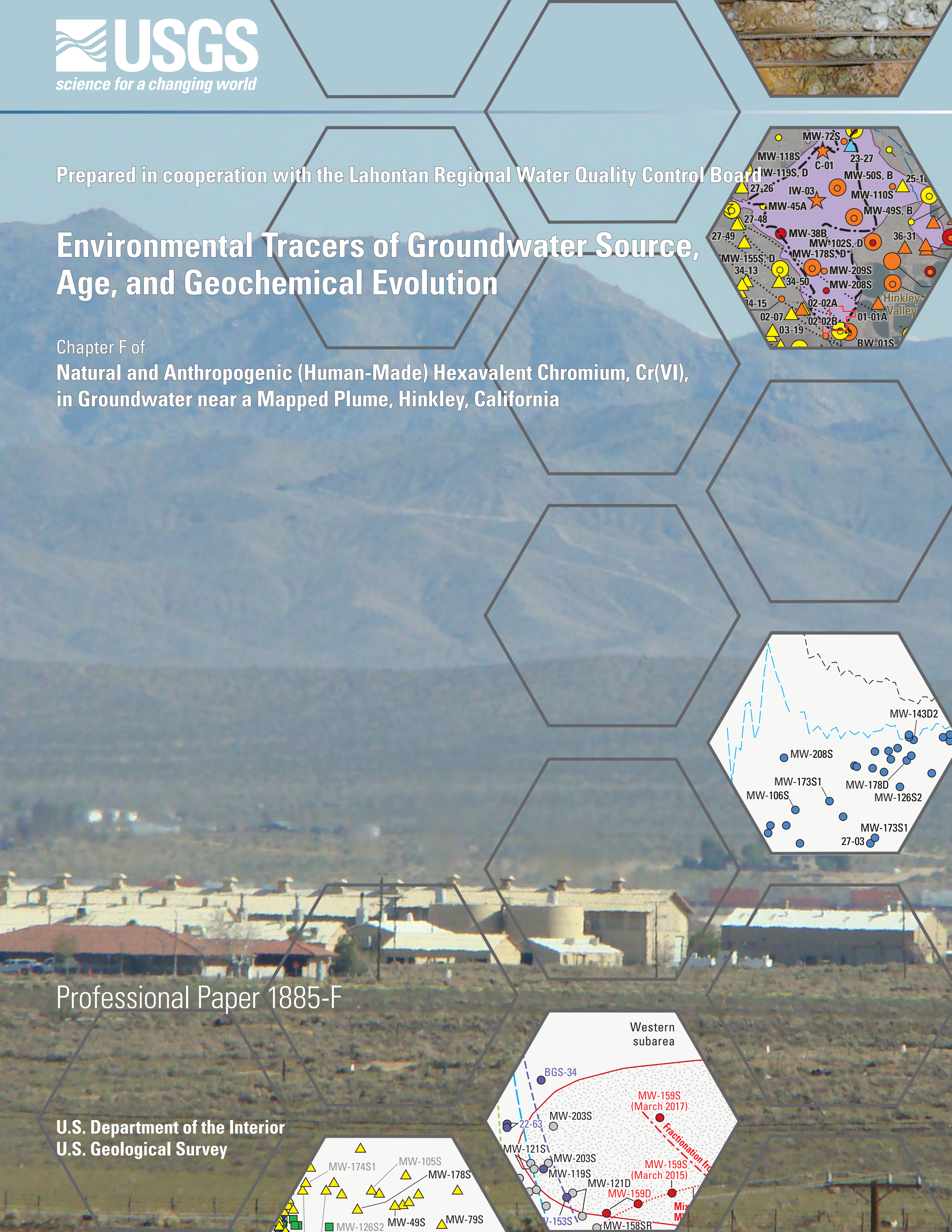

Prepared in cooperation with the Lahontan Regional Water Quality Control Board

Environmental Tracers of Groundwater Source, Age, and Geochemical Evolution

Chapter F of

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

Professional Paper 1885-F

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

Front cover

Chromium-containing oxides and other surface coatings on the surfaces of mineral grains with alluvium.

Delta deuterium concentration in water from wells.

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.

Tritium and decay-corrected tritium concentrations in precipitation at Santa Maria, California.

Delta chromium-53 isotopic composition as a function of hexavalent chromium concentration in the western subarea.

Tritium with depth below land surface in water from monitoring wells in Hinkley and Water Valleys.

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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	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
acre-foot (acre-ft)	1,233	cubic meter (m^3)
acre-foot (acre-ft)	0.001233	cubic hectometer (hm^3)
	Flow rate	
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)

International System of Units to U.S. customary units

Multiply	By	To obtain
Length		
micrometer (µm)	3.937×10^{-5}	inch (in.)
	Volume	
milliliter (mL)	0.0338	ounce, fluid (fl. oz)
liter (L)	33.81402	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
liter (L)	61.02	cubic inch (in^3)
cubic centimeter (cm^3)	0.06102	cubic inch (in^3)
	Mass	
milligram (mg)	3.527×10^{-5}	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

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

$$°F = (1.8 \times °C) + 32.$$

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 report, refers to distance above the vertical datum.

Supplemental Information

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

Tritium concentrations are given in tritium units (TU).

The natural logarithm of a number (ln) is its logarithm to the base of the mathematical constant *e*, which is an irrational and transcendental number approximately equal to 2.718281828459.

Isotopes are atoms of an element having the same number of protons but a different number of neutrons within the atomic nucleus. This difference may cause differences in the physical and chemical behavior of less abundant isotopes when compared to the more commonly abundant isotope; these differences can be used to understand the physical movement of water or constituents dissolved in water within the environment. Isotopic abundances are commonly expressed as ratios of the isotope of interest to the more abundant isotope in a sample to the ratio of those isotopes in a standard. The values are expressed in delta notation as parts per thousand differences between the isotopic ratios in the sample and standard. Some isotopes are stable and do not change (decay) over time; other isotopes are unstable (radioactive) and change (decay) into different elements or isotopes over time. Radiogenic isotopes are produced by the decay of unstable (radioactive) isotopes.

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.

A water year is the period from October 1 to September 30 and is designated by the year in which it ends.

Abbreviations

±	plus or minus
^{14}C	carbon-14
^{3}H	tritium
^{3}He	helium-3
^{4}He	helium-4
A_o	initial carbon-14 activity of dissolved inorganic carbon in the water sample at the time of recharge
CFC	chlorofluorocarbon
CFC-11	trichlorofluoromethane
CFC-113	trichlorotrifluoroethane (the 1,1,2-trichloro-1,2,2-trifluoroethane isomer)
CFC-12	dichlorodifluoromethane
Cr(III)	trivalent chromium having an oxidation state of +3
Cr(VI)	hexavalent chromium having an oxidation state of +6
DGMETA	Dissolved Gas Modeling and Environmental Tracer Analysis
DIC	dissolved inorganic carbon
Fe^{2+}	ferrous iron
GMWL	Global Meteoric Water Line
HDPE	high-density polyethylene
LMWL	Local Meteoric Water Line
LRL	laboratory reporting level
MCL	maximum contaminant level
ORP	oxidation reduction potential
per mil	parts per thousand (‰) difference
PG&E	Pacific Gas and Electric Company
pM	percent modern

pmc	percent modern carbon
pptv	parts per trillion by volume
p-value	probability value
Q4 2015	October–December 2015
R^2	coefficient of determination
RSD	relative standard deviation
R_{terr}	helium-3/helium-4 ratio of terrigenic helium
RWQCB	Regional Water Quality Control Board
SLAP	Standard Light Antarctic Precipitation
SRL	study reporting level
TU	tritium unit
USGS	U.S. Geological Survey
VPDB	Vienna PeeDee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
ybp	years before present
α	significance criterion
δ	used to denote isotopic differences as ratios relative to a standard ratio
$\delta^{18}O$	oyygen-18 to oxygen-16 ratio relative to the standard concentration in seawater
δD	deuterium to hydrogen ratio relative to the standard concentration in seawater
ε	fractionation factor
ε_{app}	apparent fractionation factor

Environmental Tracers of Groundwater Source, Age, and Geochemical Evolution

By John G. Warden,[1] John A. Izbicki,[1] Jürgen Sültenfuß,[2] Kathleen Scheiderich,[1] and John Fitzpatrick[3]

Abstract

Hexavalent chromium, Cr(VI), was discharged in cooling wastewater to unlined surface ponds from 1952 to 1964 and reached the underlying unconsolidated aquifer at the Pacific Gas and Electric Company (PG&E) Hinkley compressor station in the Mojave Desert, 80 miles northeast of Los Angeles, California. A suite of environmental tracers was analyzed in water samples collected from more than 100 wells to characterize the source, age, and geochemical evolution of groundwater within and near the Cr(VI) plume in Hinkley and Water Valleys. This information was used to help determine the extent of Cr(VI) associated with releases from the Hinkley compressor station and to identify Cr(VI) associated with natural sources.

The source of water in most wells, indicated by stable oxygen and hydrogen isotope values for water, delta oxygen-18 and delta deuterium, was recharge by infiltration of intermittent surface flows in the Mojave River. With the exception of small flows in 1958, the Mojave River was largely dry between 1952 and 1969. This dry period spans the period of Cr(VI) releases from the Hinkley compressor station; 1952–69 also spans the period of high tritium levels in precipitation resulting from the atmospheric testing of nuclear weapons and, as a consequence, tritium concentrations in groundwater in Hinkley Valley were comparatively low. Groundwater ages (time since recharge) increased downgradient from the Mojave River and with depth. Tritium, measured by helium ingrowth with a study reporting level of 0.05 tritium unit, was detected in water from 51 percent of wells, with detectable tritium as far as 7 miles downgradient from the Mojave River. Tritium concentrations were higher, and tritium/helium-3 groundwater ages younger, in water from wells near the Mojave River and in water from shallower wells downgradient. Agricultural pumping has decreased groundwater levels as much as 60 feet since 1952. As a result of this pumping, some groundwater containing tritium, and presumably anthropogenic Cr(VI), has been removed from the aquifer. The distribution of wells having carbon-14 activities near or greater than 100-percent modern carbon, consistent with post-1952 recharge water, was similar to the distribution of wells containing detectable tritium. Carbon-14 activities as low as 8.9-percent modern carbon, with carbon-14 ages (unadjusted for reactions with aquifer materials) of almost 20,000 years before present (ybp), were sampled in water from some deep wells. Hexavalent chromium concentrations in older groundwater were as high as 11 micrograms per liter but did not exceed 3.6 micrograms per liter in older water from wells completed in "Mojave-type" deposits (composed of felsic Mojave River stream and near-shore lake deposits sourced from the Mojave River); this value may represent an upper limit on Cr(VI) concentrations in groundwater within Mojave-type deposits that likely approximates background Cr(VI) concentrations in the study area. Chlorofluorocarbons were released to the atmosphere and hydrologic cycle as a result of industrial activity beginning in the 1930s. Chlorofluorocarbon data were not generally suitable for groundwater-age dating in Hinkley and Water Valley because of nonatmospheric contributions from local sources.

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[2] University of Bremen.

[3] U.S. Geological Survey, retired.

Strontium-87/86 isotope ratios and stable chromium isotopes, delta chromium-53, provide information on the geochemical evolution of groundwater in the aquifer. Highly radiogenic strontium-87/86 ratios greater than 0.71000 were present in water from wells completed in coarse-textured Mojave-type deposits having low chromium concentrations but were not diagnostic of these materials. Nonradiogenic strontium-87/86 ratios less than 0.70950 were diagnostic of weathered materials in the northern subarea of Hinkley and in Water Valley that were eroded from Miocene (23–5 million ybp) deposits east of the study area. Values for delta chromium-53 ranged from near 0 to 2.8 parts per thousand (‰) difference. The extent of reductive fractionation, mixing with native groundwater, and longitudinal dispersion within the October–December 2015 (Q4 2015) regulatory Cr(VI) plume can be estimated on the basis of the delta chromium-53 isotope composition of groundwater within the plume. Reduction of Cr(VI) to trivalent chromium, Cr(III), can occur in the presence of natural reductants in oxic groundwater. Although not diagnostic of anthropogenic chromium at the concentrations of interest near the Q4 2015 regulatory Cr(VI) plume margin, delta chromium-53 data indicate anthropogenic Cr(VI) within the plume is not conservative and has reacted with aquifer materials; these reactions have removed some anthropogenic Cr(VI) from groundwater.

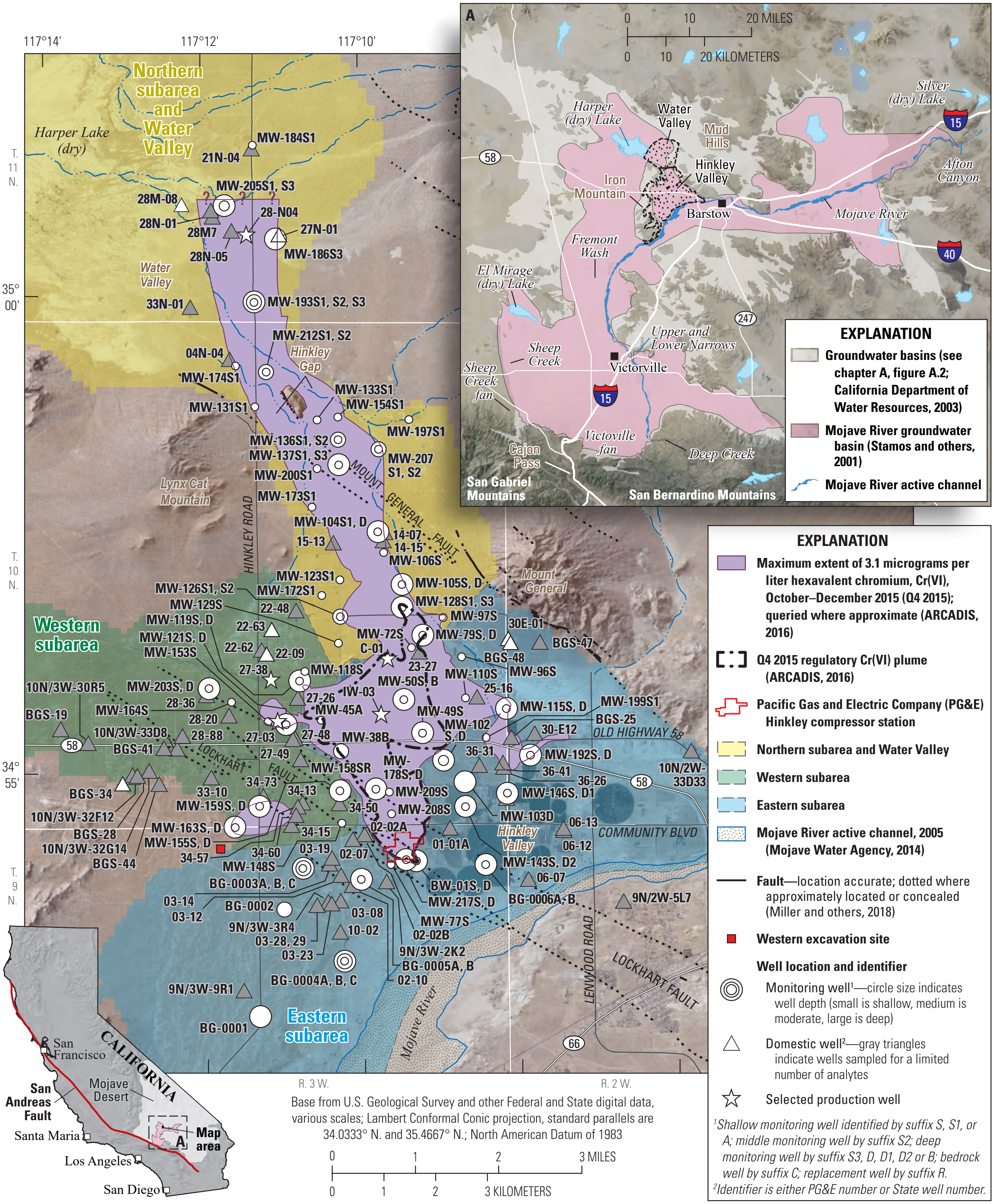
Environmental tracers, and the distribution of modern (post-1952) and premodern (pre-1952) groundwater, inform understanding of the extent of anthropogenic and naturally occurring Cr(VI) near the Q4 2015 regulatory Cr(VI) plume and the understanding of geochemical processes occurring in and near the margins of the Cr(VI) plume. The oxygen and hydrogen isotope compositions of water, tritium/helium-3 groundwater-age data, and carbon-14 data were used with mineralogy and chemistry data as part of a summative-scale analysis to determine the Cr(VI) plume extent later in this professional paper (chapter G).

F.1. Introduction

The Pacific Gas and Electric Company (PG&E) Hinkley compressor station, in the Mojave Desert, 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 (fig. F.1). 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 in the compressor station. Cooling wastewater containing Cr(VI) was discharged to unlined ponds, releasing Cr(VI) to soil and groundwater in the underlying unconsolidated aquifer (Lahontan Regional Water Quality Control Board, 2013). Since 1964, cooling-water management practices that do not release chromium into groundwater have been used at the site.

In 2007, a PG&E study of the background Cr(VI) concentrations in groundwater estimated the average Cr(VI) concentration in the Hinkley area to be 1.2 micrograms per liter (µg/L), with a 95-percent upper-tolerance limit of 3.1 µg/L (CH2M Hill, 2007). The 3.1 µg/L upper-tolerance limit was subsequently adopted by the Lahontan Regional Water Quality Control Board (RWQCB) as the maximum background Cr(VI) concentration. This concentration was used to map the Cr(VI) plume extent for regulatory purposes (ARCADIS, 2016). In response to limitations of the CH2M Hill (2007) study methodology (Lahontan Regional Water Quality Control Board, 2011), and in response to an increase in the mapped extent of Cr(VI) greater than 3.1 µg/L between 2008 and 2012 (chapter D, fig. D.2), the Lahontan RWQCB agreed with staff recommendations (Lahontan Regional Water Quality Control Board, 2012) that the 2007 background Cr(VI) concentration study be updated. The U.S. Geological Survey was requested by the Lahontan Regional Water Quality Control Board to complete the updated background study of Cr(VI) concentrations in Hinkley and Water Valleys.

This chapter reports the results of an environmental tracer study evaluating the sources, movement, and age (time since recharge) of groundwater, as well as chemical reactions and environmental processes occurring in groundwater, in and near the mapped 3.1-µg/L Cr(VI) regulatory plume. This chapter is part of the U.S. Geological Survey (USGS) background Cr(VI) study developed in collaboration with a technical working group composed of community members, the Independent Review Panel Manager (Project Navigator, Ltd.), the Lahontan RWQCB, PG&E, and consultants for PG&E. Plans for the USGS background study and midterm progress are available in USGS Open-File Reports (Izbicki and Groover, 2016, 2018).



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 F.1. Location of Hinkley and Water Valleys, western Mojave Desert, California. Well location data are available in U.S. Geological Survey (2021) and chapter E (appendix E.1, tables E.1.1, E.1.3).

Environmental tracers are constituents that can be used to understand the hydrologic history of water, including the source, movement, and age of groundwater within an aquifer, and the chemical reactions or environmental processes that affect constituents within groundwater (Cook and Herczeg, 1999). Tracers of the source and movement of water include the stable isotopes of oxygen and hydrogen in the water molecule and dissolved atmospheric gases. These tracers provide information on the source of recharge (for example, the Mojave River or runoff from local streams), information on the evaporative history of water, and on processes that occur at the water table during recharge. Tracers of the age (time since recharge) of groundwater include (1) the radioactive isotope of hydrogen, tritium (^{3}H), and the daughter product of tritium decay, helium-3 (^{3}He); (2) the radioactive isotope carbon-14 (^{14}C); and (3) dissolved industrial gases, including chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6). The combination of these age tracers is effective for evaluating the movement and age of water in arid environments, evaluating the mixing of water from different sources, and estimating the percentage of modern water in a sample (defined as water recharged after 1952; Cook and Herczeg, 1999). Tracers of environmental processes and chemical reactions measured as part of this study include the stable, radiogenic isotope of strontium (strontium-87) and the stable isotopes of chromium (chromium-52 and chromium-53). These tracers can be used to evaluate geologic material with which water has been in contact and processes that control the reduction of Cr(VI) to trivalent chromium, Cr(III).

F.1.1. Site Description

Hinkley Valley is about 62 square miles (mi^2; fig. F.1). The climate is arid with cool winters and hot summers. Average annual precipitation is less than 4.4 inches per year (Western Regional Climate Center, 2019). Hinkley Valley is bounded by the Mojave River to the south, Iron Mountain and Lynx Cat Mountain to the west, Mount General to the east, and Hinkley Gap and Water Valley to the north.

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 and basalt in Water Valley (chapter B, table B.3) and in local alluvium eroded from those materials. Chromium concentrations in unconsolidated materials are higher in fine-textured silt and clay and lower in coarse-textured sand and gravel (chapter B, fig. B.8; chapter C, fig. C.6). Chromite is not generally present, and most chromium is substituted within magnetite that is fairly resistant to weathering (chapter C, fig. C.7). Some more easily weathered chromium-containing minerals, including actinolite in older alluvium deposited by the ancestral Mojave River and hornblende in weathered bedrock and local alluvium eroded from Iron Mountain (chapter C, fig. C.9), also are present.

Hinkley Valley contains about 36 mi^2 of unconsolidated deposits that were saturated under predevelopment conditions (pre-1930, chapter H, fig. H.8*A*). Aquifers of interest in Hinkley and Water Valleys are composed primarily of unconsolidated deposits consisting of Mojave River stream (alluvium) and lake-margin deposits sourced from the Mojave River (Miller and others, 2018, 2020), referred to as "Mojave-type" deposits for the purposes of this professional paper (chapter A, table A.1). "Non-Mojave-type" deposits including locally derived alluvium, lacustrine (lake deposits), groundwater-discharge deposits, and weathered bedrock (chapter A, table A.1) also are important aquifers or confining units in some areas.

On the basis of differences in geology and hydrology, the study area was divided into the eastern, western, and northern subareas in Hinkley Valley and Water Valley (fig. F.1). 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 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). Fine-textured deposits, generally described as "brown clay," are interspersed throughout unconsolidated deposits and, in places, separate 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 present at land surface near Mount General and at depth in the eastern subarea also are commonly described as brown clay.

The Hinkley compressor station and the highest Cr(VI) concentrations within the October–December 2015 (Q4 2015) regulatory Cr(VI) plume are in the eastern subarea, with concentrations greater than 1,000 µg/L remaining near the Hinkley compressor station (ARCADIS, 2016; chapter D, fig. D.2; chapter E, fig. E.11). The western subarea consists of Mojave-type deposits overlying lacustrine deposits, 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 in 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) containing basalt and weathered material eroded from Miocene (23–5 million years before present, ybp) deposits east of the study area (Miller and others, 2018, 2020).

In the Mojave Desert, little or no groundwater recharge occurs from direct infiltration of precipitation (Izbicki, 2004) or from infiltration of runoff within small intermittent streams draining desert mountains (Izbicki and others, 2007). The primary source of recharge to the unconsolidated aquifer underlying Hinkley Valley is infiltration of intermittent surface flows within the Mojave River (Thompson, 1929; Stamos and others, 2001; Izbicki, 2004; Seymour, 2016; Jacobs Engineering Group, Inc., 2019). Surface flows in the Mojave River originate mainly from runoff of winter precipitation near Cajon Pass and the San Bernardino Mountains (Izbicki, 2004), about 40 mi south of Hinkley Valley (fig. F.1). The Mojave River through Hinkley Valley is normally dry but flows on average once every 5 to 7 years (U.S. Geological Survey, 2019b); consequently, recharge to the unconsolidated aquifer in Hinkley Valley is intermittent, and many years can pass without substantial recharge (Stamos and others, 2001; chapter A, fig. A.3). Annual recharge to the alluvial aquifer has exceeded 20,000 acre-feet only 12 times since 1950 (Stamos and others, 2001; Jacobs Engineering Group, Inc. 2019), with recharge exceeding 80,000 acre-feet in water years 1969, 1980, 1983, and 1993 (fig. F.2).

During predevelopment, groundwater flow was from the Mojave River north toward Hinkley Gap and Water Valley where groundwater discharged by evaporation along the margins of Harper (dry) Lake (Thompson, 1929; chapter H, fig. H.8*A*). The Lockhart fault impedes groundwater flow in Hinkley Valley. During predevelopment, groundwater was within 15 ft of land surface in much of Hinkley Valley, and many wells in Water Valley had water levels above land surface (Thompson, 1929; chapter H, fig. H.8*A*). Water-level declines as a result of agricultural pumping since the early 1950s have been as great as 60 ft (Stone, 1957; California Department of Water Resources, 1967; Seymour and Izbicki, 2018; chapter H, fig. H.8*B*). As a consequence of water-level declines, saturated alluvium in much of the western subarea downgradient from the Lockhart fault is a thin veneer (commonly less than 10 ft thick) overlying weathered bedrock (CH2M Hill, 2013), and saturated alluvium in much of the northern subarea is a thin veneer overlying fine-textured lacustrine and mudflat/playa deposits (Stantec, 2013). 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 lacustrine or mudflat/playa deposits. Lake-margin deposits in much of Water Valley, sourced from the ancestral Mojave River, were above the water table at the time of this study (2017; Stamos and others, 2001; Miller and others, 2018, 2020; chapter H, fig. H.8). Groundwater levels near the Mojave River can increase rapidly as a result of recharge, with increases of as much as 87 ft in parts of the valley during the 1993 water year (Lines, 1996). Predevelopment (pre-1930) and water level maps prepared at the time of this study (2017) are available in chapter H within this professional paper (fig. H.8).

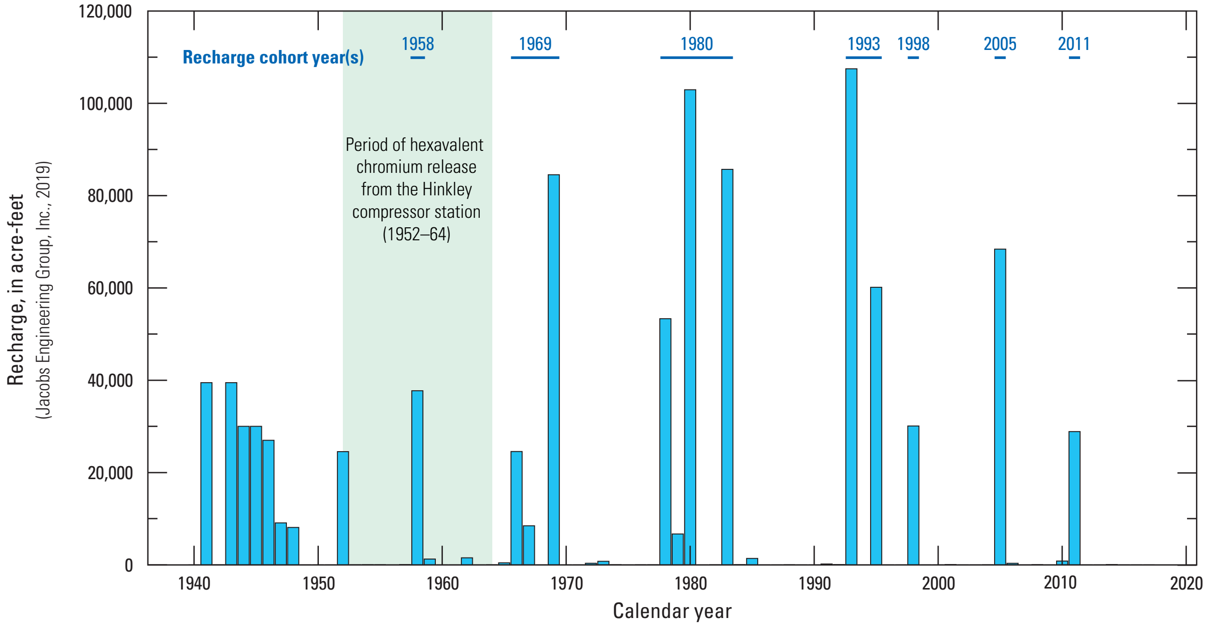


Figure F.2. Annual recharge of the unconsolidated aquifer in Hinkley Valley, western Mojave Desert, California, 1940 to 2017. Data modified from Stamos and others (2001) andJacobs Engineering Group, Inc., (2019).

Cooling wastewater containing Cr(VI) was discharged to unlined surface ponds from 1952 to 1964. At the time, groundwater levels were about 27 ft bls near the Hinkley compressor station (Seymour and Izbicki, 2018). In Q4 2015, the regulatory Cr(VI) plume extended about 3 mi downgradient from the historical release point within the Hinkley compressor station (ARCADIS, 2016). However, the actual extent of the Cr(VI) release was uncertain, and Cr(VI) concentrations in water from wells greater than the interim regulatory background of 3.1 µg/L were present in water from wells in Water Valley, more than 8 mi downgradient from the Hinkley compressor station (ARCADIS, 2016). Remediation of Cr(VI) released from the Hinkley compressor station began in 1992 and, depending on the option selected, site cleanup was projected to require 10 to 95 years (Haley and Aldrich, Inc., 2010; Pacific Gas and Electric Company, 2011).

Monitoring wells installed for regulatory purposes by PG&E were most commonly identified by the prefix MW, with sites numbered sequentially in the order they were drilled. Shallow wells, commonly screened across or just below the water table, were identified with the suffix S or S1. 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. The suffix C is used for wells completed in consolidated rock, and the suffix R is added if the well is a replacement for a well that was destroyed. Wells installed by PG&E as part of the USGS Cr(VI) background study were identified with the prefix BG; the BG sites were numbered sequentially in the order they were permitted, and 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. Beginning in 2011, core material at well sites was commonly collected and archived by PG&E from near the water table to below the depth of the deepest well at a site.

F.1.2. Purpose and Scope

The purpose of this chapter is to evaluate the source(s), movement, and age of groundwater relative to the timing of Cr(VI) releases and migration downgradient from the Hinkley compressor station. The scope of the study included collection and interpretation of multiple environmental tracers. The tracers included (1) the stable isotopes of oxygen and hydrogen (delta oxygen-18 and delta deuterium, respectively) within the water molecule to evaluate sources of groundwater recharge; (2) neon, argon, and nitrogen gases to evaluate recharge processes, including temperature and excess air at the time of recharge; (3) tracers of the age of groundwater including tritium (^{3}H) and its decay product helium-3 (^{3}He), carbon-14 (^{14}C), and industrial gases including chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6); (4) strontium isotopes (strontium-87/86 ratios) and (5) chromium isotopes (delta chromium-53) to evaluate reactions between aquifer materials, groundwater, and dissolved constituents. The use of multiple environmental and isotopic tracers to evaluate the source, movement, and age of groundwater and constituents within groundwater is an increasingly common approach in the study of complex hydrogeologic systems (Hatzinger and others, 2018; Kaown and others, 2018; Wilske and others, 2019; Vengosh and others, 2002). Interpretation of tracers of groundwater age using lumped parameter models (Jurgens and others, 2012) to evaluate groundwater-age distributions with respect to simplified analyses of aquifer geometry, recharge processes, and mixing as proposed by Izbicki and Groover (2016, 2018) was not possible within the scope of this study. The stable isotopes of oxygen and hydrogen and age tracer results were used as inputs to the summative-scale analyses (chapter G) to determine the spatial extent of anthropogenic (human-made) Cr(VI) and natural background Cr(VI) in Hinkley and Water Valleys.

F.2. Field and Laboratory Methods and Quality Assurance Data

Water samples were collected from more than 100 monitoring, domestic, and production wells in Hinkley and Water Valleys, Calif., from March 2015 to November 2017 and analyzed for chemical data (chapter E) and a suite of environmental tracers. The suite of tracers included the stable isotopes of oxygen and hydrogen within the water molecule, dissolved atmospheric gases, and tracers of young and old groundwater (table F.1). Tracers of young and old groundwater included tritium and its decay product helium-3, carbon-14, and industrial gases including CFCs and sulfur hexafluoride. The environmental tracer samples were collected at the same time as samples for water chemistry, including Cr(VI), using field protocols developed for this project (chapter E).

Environmental tracer data were interpreted using standard techniques and computer programs appropriate for each tracer. These techniques are discussed with the background and results for each tracer rather than as part of the methods to simplify the presentation for the reader.

Table F.1. Methods of analysis for water samples and constituents sampled for environmental tracers of groundwater source, age, and geochemical evolution, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through March 2017.

[**Abbreviations**: USGS, U.S. Geological Survey; RSIL, Reston Stable Isotope Laboratory, Reston, Virginia; RGDL, Reston Groundwater Dating Laboratory, Reston, Va.; NOSAMS, National Ocean Sciences Accelerator Mass Spectrometry Facility, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts; HELIS, Helium Isotope Studies Laboratory, University of Bremen, Germany; NSRIL, Nontraditional Stable and Radiogenic Isotope Laboratory, Menlo Park, California]

Constituent	Filtered (dissolved concentration) or unfiltered	Analyzing laboratory	Reference(s)
Oxygen and hydrogen isotopes of water	Unfiltered	USGS RSIL	Révész and Coplen, 2008a, 2008b
Dissolved nitrogen and argon gasses	Unfiltered	USGS RGDL	U.S. Geological Survey, 2018
Carbon-14 and carbon-13	Filtered	NOSAMS	National Ocean Sciences Accelerator Mass Spectrometry Facility, 2018
Tritium, helium, helium-3, helium-4, and neon	Unfiltered	HELIS	Sültenfuß and others, 2009
Chlorofluorocarbons	Unfiltered	USGS RGDL	Bullister, 1984; Bullister and Weiss, 1988
Sulfur hexafluoride	Unfiltered	USGS RGDL	Law and others, 1994; Busenberg and Plummer, 2000
Strontium isotopes	Filtered	USGS NSRIL	Bullen and others, 1996
Chromium isotopes	Filtered	USGS NSRIL	Scheiderich and others, 2015; Larsen and others, 2016

F.2.1. Field Methods

Pacific Gas and Electric Company contract sample-collection crews worked with USGS field crews to pump groundwater from PG&E monitoring wells. For most monitoring wells, three casing volumes were purged before sample collection using submersible pumps with the same equipment and similar procedures used by PG&E contractors to collect quarterly samples for regulatory purposes (chapter E). Field parameters, including water levels, pH, temperature, specific conductance, dissolved oxygen, and oxidation reduction potential (ORP), were monitored during well purging prior to sample collection. Samples were collected after a minimum of three casing volumes were purged from the well and field parameters stabilized. Where possible, drawing the water level into the well screen was avoided. Aeration of water within the well screen during purging and sample collection would potentially compromise samples for tritium/helium-3, noble gases, and industrial gas analyses. Water samples were collected and processed in the field by USGS sample-collection crews. Additional details on sample collection from low-yielding wells, domestic wells, and production wells are provided in chapter E within this professional paper.

Water samples for analyses of oxygen and hydrogen isotopes in the water molecule, carbon isotopes, tritium, strontium isotopes, and chromium isotopes were collected by routing well water through dedicated plastic tubing used at each well for regulatory sample collection to an enclosed sample-collection chamber. Samples were filtered using a 0.45-micrometer filter, if required; bottled within the sample-collection chamber; and then shipped to the appropriate laboratories (table F.1). Filtration was required for analyses of carbon, strontium, and chromium isotopes.

Water for analyses of oxygen and hydrogen isotopes was collected in unrinsed 60-milliliter (mL) glass bottles. Water for analyses of carbon isotopes was collected by bottom filling 1-liter (L) plastic coated glass bottles after flushing three bottle volumes with sample water. Water for analysis of tritium was collected in 1-L high-density polyethylene (HDPE) bottles after flushing one bottle volume with sample water. Water for analysis of strontium and chromium isotopes was collected in 250-mL and 1-L HDPE bottles rinsed three times with sample water before filling. Samples for environmental tracers were stored in cool, dry conditions and shipped to analytical laboratories at the end of each field trip.

Water samples for analyses of dissolved gases (nitrogen, argon, helium, and neon), industrial gases (CFCs and sulfur hexafluoride), and helium isotopes were collected by routing water through inline copper tubes. The copper tubing was attached directly to submersible pumps and was intended to isolate sample water from the atmosphere, thereby preventing gas exsolution (loss) during sample collection (Solomon and Cook, 1999). Hexavalent chromium contamination issues associated with fittings used to attach the copper tubing to submersible pumps in 2015 are discussed in chapter E within this professional paper. Water samples for analysis of nitrogen and argon were collected in duplicate by bottom filling 125-mL glass bottles submerged in sample water. Water samples for analyses of CFCs were collected in triplicate by bottom filling 125-mL glass bottles submerged in sample water after flushing three bottle volumes. Water for analysis of sulfur hexafluoride was collected in duplicate by bottom filling 1-L amber glass bottles after flushing three bottle volumes.

Water samples for analysis of helium and neon concentrations and helium isotope ratios were collected in duplicate in copper tubing sealed at both ends using metal pinch clamps (Weiss, 1968; Solomon and Cook, 1999). The pinch clamps did not provide an adequate seal for some samples collected during March 2015 and March 2016, and those wells were resampled in March 2017 to obtain dissolved helium and neon data. Selected wells were sampled more than one time to evaluate potential changes in tracer concentrations and groundwater chemistry that may have occurred during the study (chapter E).

In addition to samples analyzed for the suite of environmental isotopes, more than 70 domestic and agricultural wells were sampled between January 21 and 31, 2016. In addition to chemical data (discussed in chapter E within this professional paper), samples from those wells were analyzed for the stable isotopes of oxygen and hydrogen in the water molecule. Domestic wells were purged and sampled using the installed pump by USGS field personnel.

F.2.2. Laboratory Methods

The stable isotopes of oxygen and hydrogen within the water molecule were analyzed by dual-inlet mass spectrometry at the USGS Reston Stable Isotope Laboratory in Reston, Virginia (Révész and Coplen, 2008a, b). Oxygen-18 and deuterium abundances are reported as ratios with the more abundant isotopes oxygen-16 and hydrogen-1, relative to those ratios in the Vienna Standard Mean Ocean Water–Standard Light Antarctic Precipitation scale (commonly known as VSMOW–SLAP; Coplen and others, 1999). The ratios are reported in delta (δ) notation as delta oxygen-18 ($\delta^{18}O$) and delta deuterium (δD), in units of per mil (‰) differences. The VSMOW and SLAP water isotope standards are assigned delta oxygen-18 values of 0 and −55.5 per mil and delta deuterium values of 0 and −428 per mil, respectively. Laboratory precision is plus or minus (±) 0.1 per mil for $\delta^{18}O$ and ±1 per mil for delta deuterium (Révész and Coplen, 2008a, b).

Dissolved nitrogen and argon gases were analyzed by gas chromatography with a thermal conductivity detector at the USGS Groundwater Dating Laboratory in Reston, Va. (U.S. Geological Survey, 2018). Laboratory precision is ±0.001 milligram per liter (mg/L) for nitrogen and ±0.003 mg/L for argon (U.S. Geological Survey, 2018). Each bottle collected in the field for dissolved nitrogen and argon gases was analyzed at the laboratory, and multiple results are available (appendix F.1, table F.1.1; U.S. Geological Survey, 2021).

Tritium was analyzed by helium-3 ingrowth (Clarke and others, 1976) at the University of Bremen, Germany, Department of Oceanography, Helium Isotope Studies Laboratory (commonly known as HELIS). About 9 months is required for enough tritium to decay to measurable concentrations of helium-3 within sealed sample containers. Concentrations were then measured by sector field mass spectrometry with a laboratory reporting level (LRL) of 0.01 tritium unit (TU) and a precision of ±3 percent (Sültenfuß and others, 2009). In comparison, tritium measurement by liquid scintillation (Thatcher and others, 1977) with electrolytic enrichment (Ostlund and Werner, 1962), a method that is commonly used in studies of groundwater age, typically has an LRL of 0.2 TU (Izbicki and Michel, 2004). Helium-4, neon-20, and neon-22 data required to interpret tritium/helium-3 ages were measured by quadrupole mass spectrometry at the Helium Isotope Studies Laboratory. Ratios of helium-3/helium-4 and helium/neon are accurate within 0.4 and 0.5 percent, respectively.

The radioactive isotope of carbon (carbon-14, ^{14}C) and the stable isotopes of carbon (carbon-12 and carbon-13) in dissolved inorganic carbon (DIC) were measured at the National Ocean Sciences Accelerator Mass Spectrometry Facility (commonly known as NOSAMS) in Woods Hole, Massachusetts, through a contract with the USGS National Water Quality Laboratory (NWQL). Carbon dioxide gas was stripped from water samples and reacted with an iron catalyst to form graphite that was then analyzed for carbon-14 by continuous-flow accelerator mass spectrometry. The stable isotopes of carbon in DIC were measured as the ratio of the rarer to more common isotope (carbon-13/carbon-12) by analyzing a split of the stripped carbon dioxide gas by stable isotope mass spectrometry (National Ocean Sciences Accelerator Mass Spectrometry Facility, 2018). Abundances of carbon-13 and carbon-12 isotopes are expressed in delta (δ) notation as per mil differences in the carbon-13/carbon-12 ratio ($\delta^{13}C$) of a sample relative to the carbon-13/carbon-12 ratio in the Vienna PeeDee Belemnite carbon isotope standard (commonly known as VPDB; Gonfiantini, 1978). Standard laboratory convention is to report carbon-14 data as percent modern (pM) by normalizing carbon-14 measurements for isotope fractionation to a common delta carbon-13 value of −25 per mil (Stuiver and Polach, 1977). Although this convention is useful for providing conformity in reporting units across different laboratories and for studies of carbon-14 in the biological sciences (for example, tree rings), carbon-14 dating in the hydrologic sciences is based on nonnormalized activities (Kalin, 1999; Mook and van der Plicht, 1999). For the purposes of this study, normalized carbon-14 activities reported by the laboratory in units of percent modern were converted to nonnormalized units of percent modern carbon (pmc) using the delta carbon-13 value measured in each sample and equations described by Plummer and Glynn (2013).

Chlorofluorocarbons (trichlorofluoromethane [CFC-11], dichlorodifluoromethane [CFC-12], and trichlorotrifluoroethane [CFC-113]) and sulfur hexafluoride were analyzed by gas chromatography with an electron capture detector (commonly known as ECD) at the USGS Groundwater Dating Laboratory in Reston, Va. (U.S. Geological Survey, 2018). Laboratory precision for CFCs is about 3 percent or less (U.S. Geological Survey, 2016), and precision for sulfur hexafluoride is about 0.75 percent or less (U.S. Geological Survey, 2019a), with greater values near the LRLs. Each bottle collected in the field for CFCs was analyzed at the laboratory, and multiple results are available (appendix F.1, table F.1.1; U.S. Geological Survey, 2021).

Strontium and chromium isotopes were analyzed by thermal ionization mass spectrometry (commonly known as TIMS) at the USGS Nontraditional Stable and Radiogenic Isotope Laboratory in Menlo Park, Calif. (Bullen and others, 1996; Scheiderich and others, 2015; Larsen and others, 2016). Strontium isotope data are expressed as the ratio of strontium-87 to strontium-86; this ratio can be measured accurately to within 0.00001. Abundances of chromium-52 and chromium-53 isotopes are expressed in delta (δ) notation as per mil differences in the chromium-53/chromium-52 ratio (δ^{53}Cr) within a sample relative to the chromium-53/chromium-52 ratio in the National Institute of Science and Technology (NIST) chromium isotope standard NIST979 (National Institute of Health, 2014). A double spike was added to chromium isotope samples before purification to allow for correction of isotopic fractionation that is known to occur during sample processing or analysis (Fantle and Bullen, 2009). Precision of chromium isotope analyses is about 0.15 per mil (Izbicki and others, 2008).

Selected samples of rock, minerals, and aquifer material also were analyzed for chromium isotopes. Solid samples were powdered by hand, weighed, and spiked with a chromium double spike before acid digestion at 115 degrees Celsius (°C) until visual inspection indicated no obvious particles remaining (this step can take hours to days). After digestion, samples were evaporated until dry, and an additional digestion with aqua regia at 115 °C was repeated for 24 hours. The samples were again evaporated until dry; if a siliceous residue was present, it was eliminated by refluxing with hydrochloric acid. The processed sample was then analyzed for the chromium-53/chromium-52 ratio by thermal ionization mass spectrometry.

Groundwater isotopic and chemical data are available from the USGS National Water Information System (NWIS; U.S. Geological Survey, 2021) and are provided with chemical data in chapter E (appendix E.1) within this professional paper. The delta oxygen-18 and delta deuterium values for additional domestic wells sampled as part of this study between January 21 and 31, 2016, are provided in appendix E.1, table E.1.3. Dissolved gas (nitrogen and argon), CFC, and sulfur hexafluoride data are provided in appendix F.1, table F.1.1. Chromium concentrations in core material, measured using portable X-ray fluorescence, and textural descriptions of core material are discussed in chapter B within this professional paper, and data are available in Groover and Izbicki (2018). Geologic provenance data were interpreted as part of this study from descriptions of core material (Miller and others, 2018, 2020) collected during drilling and installation of wells for regulatory purposes.

F.2.3. Quality Assurance Data

As many as 11 sequential replicates were collected between March 2015 and March 2017 (table F.2) to assess variability of analytical results for environmental tracers used in this study. Sequential replicates are a suite of samples collected as close in time as possible after a suite of environmental samples were collected (Spahr and Boulger, 1997; Wilde, 2006; Mueller and others, 2015). Sequential replicate data provide information on the variability introduced during sample collection, processing, transport, laboratory procedures, and variability introduced from natural variability in the sampled medium (Wilde, 2006; Geboy and Engle, 2011; Mueller and others, 2015). Replicate data for most constituents are available in chapter E within this professional paper (appendix E.1, table E.1.2). Replicate data for dissolved nitrogen, argon, CFC, and sulfur hexafluoride gas data are available in appendix F.1 (table F.1.1). Replicate data for delta oxygen-18 and delta deuterium for domestic wells are provided in chapter E within this professional paper (appendix E.1, table E.1.3 but have not been summarized in table F.2. Blank samples are generally not applicable for isotopic and other tracer data, and study reporting levels (SRLs) for isotopic and other tracer data were estimated on the basis of other data.

The ranges of concentrations and isotopic compositions for most environmental samples were generally comparable to those of sequential replicate data (table F.2). For the purposes of this professional paper, the relative standard deviation (RSD) between environmental and replicate analyses is defined as the ratio (in percent) of the standard deviation to the absolute value of the median concentration (Hyslop and White, 2009). The RSD provides an indication of whether the standard deviation is small or large compared to the median concentration. The RSD was less than 5 percent for most sets of replicate samples. The median RSD for delta helium-3 of 19 percent seems large because of the large positive and negative range of values from 5.8 to −47 percent, with a small magnitude median value of −6.83 percent. The median standard deviation for delta helium-3 of 1.2 percent was acceptable precision for this constituent.

F.2.4. Statistical Methods

Most statistics in this chapter were calculated using the computer program Statistical Analysis System (SAS Institute, Cary, North Carolina). Regression analysis was done using method of least squares (Neter and Wasserman, 1974) and regression statistics including slope, intercept, and coefficient of determination (R^2) were computed using SAS. Comparisons 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 (α) of 0.05, unless otherwise stated. Probability distributions were computed using the computer program Microsoft Excel (Microsoft Corp., Redmond, Washington)

Table F.2. Quality control results for constituents sampled for environmental tracers of groundwater source, age, and geochemical evolution, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through March 2017.

[Data are available in chapter E within this professional paper (appendix E.1, table E.1.2), appendix F.1 (table F.1.1), and U.S. Geological Survey (2021). Quality control results were analyzed by comparing environmental samples to sequential replicates. Each replicate set contained at least one environmental sample and at least one sequential replicate. The standard deviation and relative standard deviation of each replicate set were calculated. Reported values in the table are the median value of all replicate sets for each constituent. Relative standard deviation is the ratio of standard deviation to the absolute value of mean concentration. **Abbreviations**: σ, standard deviation; fg/kg, femtogram per kilogram; pg/kg, picogram per kilogram; mg/L, milligram per liter; δ, delta, used to denote differences in the isotopic ratio of the sample relative to differences in a standard; per mil, parts per thousand, differences relative to a standard; pmc, percent modern carbon; TU, tritium unit; cm³ at STP/kg of water, cubic centimeter at standard temperature and pressure per kilogram of water; E, denotes exponentiation]

Constituent	Number of replicate sets	Median value of replicate sets	Median standard deviation of replicate sets (1σ)	Median relative standard deviation of replicate sets, in percent
Sulfur hexafluoride (SF_6), fg/kg	10	88.5	4.7	3.3
Trichlorofluoromethane (CFC-11), pg/kg	10	358.8	9.0	4.1
Dichlorodifluoromethane (CFC-12), pg/kg	10	194.0	1.8	1.0
Trichlorotrifluorethane (CFC-113), pg/kg	10	45.7	1.1	3.0
Nitrogen (N_2), mg/L	11	17.05	0.08	0.5
Argon (Ar), mg/L	11	0.60	0.01	1.0
delta Chromium-53 ($\delta^{53}Cr$), per mil	5	0.791	0.045	5.7
delta Deuterium (δD), per mil	11	−61.10	0.28	0.5
delta Oxygen-18 ($\delta^{18}O$), per mil	11	−8.64	0.04	0.4
Strontium-87/86 ($^{87}Sr/^{86}Sr$), ratio	10	0.71027	0.00001	0.002
delta Carbon-13 ($\delta^{13}C$), per mil	10	−10.98	0.02	0.2
Carbon-14 (^{14}C), pmc	10	92.93	0.28	0.3
Carbon-14 (^{14}C) counting error, pmc	10	0.21	0.01	3.6
Tritium (^3H), TU	6	0.30	0.01	5.1
Helium-4 (^4He), cm³ at STP/kg of water	6	6.75E−05	1.42E−06	2.1
Neon (Ne), cm³ at STP/kg of water	6	2.48E−04	4.66E−06	2.0
delta Helium-3 (δ^3He), percent	6	−6.83	1.2	19

F.3. Tracers of the Source and Recharge History of Groundwater

Between March 2015 and November 2017, 132 samples from more than 100 wells were collected and analyzed for a suite of environmental tracers. These tracers included (1) the stable isotopes of oxygen and hydrogen (delta oxygen-18 and delta deuterium, respectively), to evaluate the source and evaporative history of water, and (2) noble gases to evaluate recharge processes including recharge temperature and entrainment of excess air during recharge. Samples included (1) water from monitoring wells and domestic wells selected with input from the technical working group and collected in March 2015, March 2016, and March 2017, with additional wells sampled in November 2017 to fill data gaps; (2) water collected in May 2016 from 12 monitoring wells installed as part of this study; and (3) water from the surface discharge of 5 selected production wells sampled between June 2015 and March 2016 (depth-dependent data collected within these production wells are discussed in greater detail in chapter H within this professional paper). The delta oxygen-18 and delta deuterium values of water from 69 domestic wells in Hinkley and Water Valleys sampled on January 27–31, 2016, also are discussed.

F.3.1. Oxygen-18 and Deuterium

Oxygen-18 and deuterium are naturally occurring stable isotopes of oxygen and hydrogen. Atoms of oxygen-18 and deuterium have more neutrons and a greater atomic mass than the more common isotopes, oxygen-16 and hydrogen-1. Differences in atomic mass result in differences in the physical and chemical behavior of the heavier, less abundant isotopes within the water molecule through a process known as fractionation in which lighter isotopes are enriched in the product, whereas heavier isotopes are enriched within the remaining reactant. Oxygen-18 and deuterium abundances are reported as ratios with the more abundant isotopes oxygen-16 and hydrogen in delta notation as per mil (parts per thousand) differences relative to the isotopic ratios in the standards (VSMOW–SLAP; Coplen and others, 1999). Samples that contain more of the lighter isotope have more negative values and are often referred to as lighter; samples that contain more of the heavier isotope have less negative values and are often referred to as heavier.

The oxygen and hydrogen isotope composition of precipitation throughout the world is linearly correlated in a relation known as the Global Meteoric Water Line (GMWL; Craig, 1961). In a given area, samples may plot slightly above or below the GMWL along a line known as the Local Meteoric Water Line (LMWL). The oxygen and hydrogen isotope composition of a water sample can be compared to the GMWL or LMWL and to the oxygen and hydrogen isotope compositions of water from different sources to infer the source and evaporative history of the sample.

Previous studies measured the delta oxygen-18 and delta deuterium values of precipitation and groundwater to determine the sources of recharge to alluvial aquifers along the Mojave River from its source near the San Bernardino Mountains to near Afton Canyon (fig. F.1; Friedman and others, 1992; Smith and others, 1992; Gleason and others, 1994; Izbicki and others, 1995, 2002; Williams and Rodoni, 1997; Kulongoski and others, 2003, 2009; Izbicki, 2004). The delta oxygen-18 and delta deuterium values are relatively constant in water from wells along the length of the Mojave River, with median values of −8.8 and −62 per mil (Izbicki, 2004) that are similar to the composition of winter precipitation near Cajon Pass that has volume-weighted delta oxygen-18 and delta deuterium values of −9.1 and −63 per mil (Izbicki, 2004). The delta oxygen-18 and delta deuterium data indicate groundwater along the river is primarily recharged from stormflows derived from runoff of winter precipitation near Cajon Pass (Izbicki, 2004). Water from wells in agricultural areas along the river has heavier (less negative) delta oxygen-18 and delta deuterium values that are associated with partial evaporation of irrigation return water (Izbicki, 2004).

Groundwater within older deposits that surround and underlie alluvial deposits along the river upstream from Hinkley Valley is recharged mostly from infiltration of small streams near the flanks of the San Bernardino and San Gabriel Mountains, with stream water derived from runoff of high-altitude precipitation. Typical delta oxygen-18 and delta deuterium values of −10.5 and −78 per mil for water from wells in those deposits are similar to volume-weighted values of −11.5 and −79 per mil (fig. F.3*A*) for high-altitude precipitation in the San Bernardino and San Gabriel Mountains (Kulongoski and others, 2003; Izbicki, 2004). Some areas contain groundwater with lighter (more negative) delta oxygen-18 and delta deuterium values than present-day high-altitude precipitation in the San Bernardino and San Gabriel Mountains (Izbicki, 2004). These values were measured in water from deep wells at the downgradient ends of long flow paths through aquifers. Carbon-14 and helium-4 measurements in water from these deep wells indicate groundwater ages of more than 10,000 ybp (Izbicki and others, 1995; Kulongoski and others, 2003, 2009). The difference in delta oxygen-18 and delta deuterium values between precipitation and water from deep wells near the end of long flow paths, combined with the old age of the water, indicates that groundwater in these locations was recharged at a time when the climate was cooler than present-day conditions (Izbicki, 2004; Kulongoski and others, 2009).

Groundwater recharged by runoff and infiltration from small streams draining the higher altitudes of the San Bernardino and San Gabriel Mountains is not present in Hinkley Valley. Infiltration of runoff from local mountains surrounding Hinkley Valley or direct infiltration of precipitation over the valley floor is not a substantial source of present-day groundwater recharge in the Mojave Desert (Izbicki and others, 2000, 2002). However, recharge from these sources may have been present in the past when the climate was cooler and wetter than the conditions at the time of this study and delta oxygen-18 and delta deuterium values from these sources would be lighter (more negative) than precipitation at the time of this study.

F.3.1.1. Oxygen-18 and Deuterium Results

The delta oxygen-18 and delta deuterium values in water from sampled wells in Hinkley and Water Valleys ranged from −10.1 to −6.9 per mil and from −79 to −53 per mil, respectively (fig. F.3*A*; chapter E, appendix E.1, table E.1.1). Median delta oxygen-18 and delta deuterium values of −8.6 and −61 per mil were similar to volume-weighted values for winter precipitation near Cajon Pass of −9.1 and −63 per mil (fig. F.3*A*) and to median values for water from wells in aquifers recharged by the Mojave River of −8.8 and −62 per mil (Izbicki, 2004). These results are consistent with regional data (Izbicki, 2004) that indicate most water from wells in Hinkley and Water Valleys was recharged by infiltration of surface flows in the Mojave River that originated from runoff of winter precipitation near Cajon Pass.

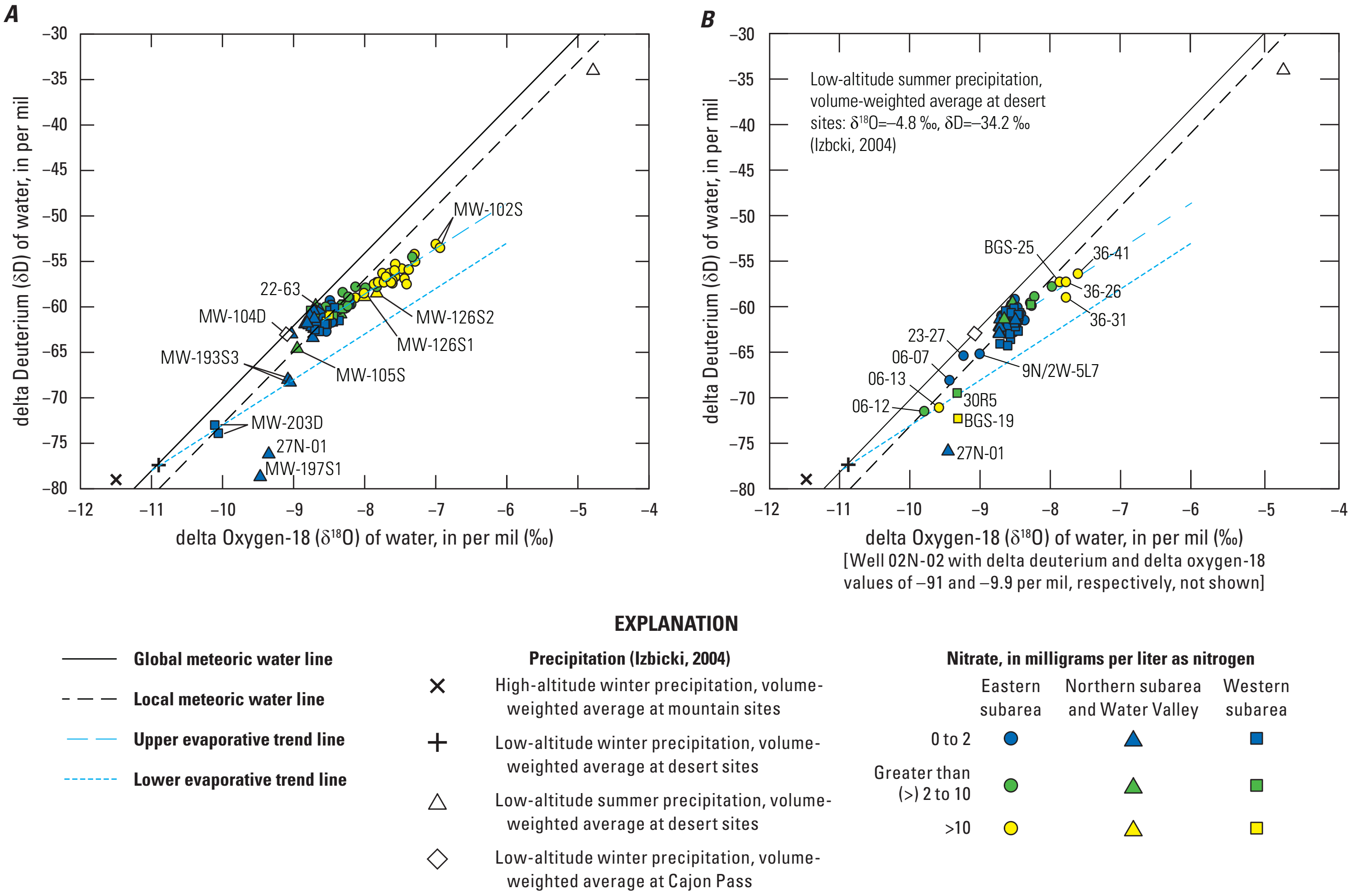


Figure F.3. Values of delta oxygen-18 as a function of delta deuterium in water from *A*, wells sampled March 2015 through November 2017 and *B*, selected domestic wells sampled January 27–31, 2016, Hinkley and Water Valleys, western Mojave Desert, California. Data are available in chapter E (appendix E.1, tables E.1.1, E.1.3.) and U.S. Geological Survey (2021).

Precipitation collected at desert sites near Hinkley and Water Valleys has volume-weighted average delta oxygen-18 and delta deuterium values of −4.8 and −34 per mil, respectively, during the summer and −10.9 and −77 per mil, respectively, during the winter (Izbicki, 2004); summer precipitation delta oxygen-18 and delta deuterium values are heavier (less negative) and winter precipitation delta oxygen-18 and delta deuterium values are lighter (more negative) than the ranges of delta oxygen-18 and delta deuterium values measured in water from most wells (fig. F.3*A*). The relatively large differences in delta oxygen-18 and delta deuterium values between water from most wells and desert precipitation indicate infiltration of precipitation falling directly over the study area and infiltration of runoff from local mountains are not substantial contributors to recharge in Hinkley and Water Valleys. This is consistent with the low average annual precipitation of less than 4.4 inches per year and average precipitation of only 0.7 inch during the summer (Western Regional Climate Center, 2019). However, water from some wells including MW-193S3, MW-197S1, MW-203D, and 27N-01 had lower (more negative) delta oxygen-18 and delta deuterium values outside the range of values in water from wells within aquifers along the Mojave River, indicating small amounts of locally recharged water (not sourced from the Mojave River) are present in some areas within Hinkley and Water Valleys (fig. F.3*A*).

The delta oxygen-18 and delta deuterium values in water from wells within and downgradient from agricultural areas in Hinkley Valley plot to the right of the GMWL on the upper evaporative trend line through the main body of data composed of water from wells recharged from Mojave River streamflows (fig. F.3*A*). Evaporative enrichment of oxygen-18 and deuterium in groundwater near agricultural areas in Hinkley Valley is consistent with irrigation return water. The slope of the evaporative trend line is about 5. Evaporative slopes commonly range from 3 to 6 (Coplen and others, 1999) with lower values representing evaporation under arid conditions and higher values representing evaporation under more humid conditions (Benettin and others, 2018).

Water samples having heavier delta oxygen-18 and delta deuterium values also had nitrate concentrations greater than the typical background concentration of 2 mg/L as nitrogen in the Mojave Desert (Christensen and Fields-Garland, 2001; Izbicki and others, 2015; Metzger and others, 2015), with many samples having nitrate concentrations greater than 10 mg/L as nitrogen. The trend of increasing nitrate with evaporative enrichment of oxygen-18 and deuterium is consistent with nitrate sourced from agricultural activities; however, agricultural activity is not the only source of nitrate in the study area. For example, water from domestic well 22-63 had nitrate concentrations greater than 10 mg/L as nitrogen and oxygen-18 and deuterium values that were not enriched by evaporation (fig. F.3*A*), indicating a nonagricultural source of nitrate. Domestic well 22-63 is in a residential area within the community of Hinkley, and the source of nitrate in water from this well is probably septic discharge.

The delta oxygen-18 and delta deuterium values in water from well MW-203D in the western subarea and in water from wells MW-193S3, MW-197S1, and 27N-01 in the northern subarea and Water Valley were highly negative (fig. F.3*A*). These delta oxygen-18 and delta deuterium values were outside the measured range of water from wells within aquifers along the Mojave River and indicate that infiltration of modern surface flows within the river was not the source of recharge for these wells. The delta oxygen-18 and delta deuterium values for water from wells MW-193S3, MW-197S1, and 27N-01 plot to the right of the LMWL, and the water may have been partly evaporated before recharge. The lower evaporative trend line (fig. F.3*A*) intercepts the GMWL near the delta oxygen-18 and delta deuterium values of winter precipitation and passes through values from MW-203D and MW-193S3. The data indicate that infiltration of winter precipitation could be a source of water from these wells; however, groundwater-age data (presented later in this chapter) indicate water from these wells may have been recharged more than 15,000 years ago at a time when the climate was cooler and wetter than at the time of this study. Water from wells MW-197S1 and 27N-01 would fall on an evaporative trend line (not shown in fig. F.3*A*) that intersects the GMWL at values that are more negative than values associated with present-day precipitation. Groundwater-age data (presented later in this chapter) indicate the water was recharged between 7,350 and 9,000 years ago and also are consistent with recharge at a time when the climate was cooler and wetter—from sources that may not be present in Hinkley and Water Valleys under the conditions at the time of this study.

F.3.1.2. Oxygen-18 and Deuterium Results from Domestic Wells

The delta oxygen-18 and delta deuterium values of water from 69 domestic wells sampled in Hinkley and Water Valleys between January 27 and 31, 2016, ranged from −9.9 to −7.6 per mil and from −91 to −56 per mil, respectively (fig. F.3*B*; chapter E, appendix E.1, table E.1.3). Similar to samples from monitoring wells (fig. F.3*A*), most domestic wells contain water having delta oxygen-18 and delta deuterium values consistent with recharge from infiltration of surface flows in the Mojave River. Consistent with monitoring well data, most samples with nitrate concentrations greater than 10 mg/L as nitrogen plot along the upper evaporative trend line through the main body of data having a slope of about 5 (fig. F.3*B*) and have been affected by evaporative enrichment associated with agricultural activity.

The delta oxygen-18 and delta deuterium values of water from domestic wells 06-07, 06-12, 06-13, and 9N/2W-5L7 are more negative than median values for water from wells in aquifers recharged by the Mojave River of −8.8 and −62 per mil (Izbicki, 2004; fig. F.3*B*). These wells are near ponds used to recharge imported water (fig. F.4), and the lighter (more negative) values are consistent with imported water from northern California. Water from domestic wells 10N/3W-30R5 and BGS-19, in the western subarea near the margins of the aquifer (fig. F.4), also have lighter (more negative) delta oxygen-18 and delta deuterium values, indicating that water from these wells was not recharged by infiltration of surface flows in the Mojave River under present-day climatic conditions. Nitrate concentrations greater than background nitrate concentrations in water from wells 06-12, 06-13, and 30R5 along the GMWL that have not been affected by evaporative enrichment (fig. F.3*B*) are consistent with a septic source of nitrate.

F.3.1.3. Discussion of Oxygen-18 and Deuterium Results

Most Mojave River streamflow originates from winter precipitation falling near Cajon Pass—a low-altitude gap between the San Bernardino and San Gabriel Mountains, about 40 mi southwest of Hinkley Valley—rather than as runoff from precipitation or snowmelt from the higher altitudes within the mountains or from local precipitation within the desert (Izbicki, 2004). The delta deuterium values in water from most wells (less negative than about −65 per mil) is consistent with groundwater recharged from the Mojave River (fig. F.4).

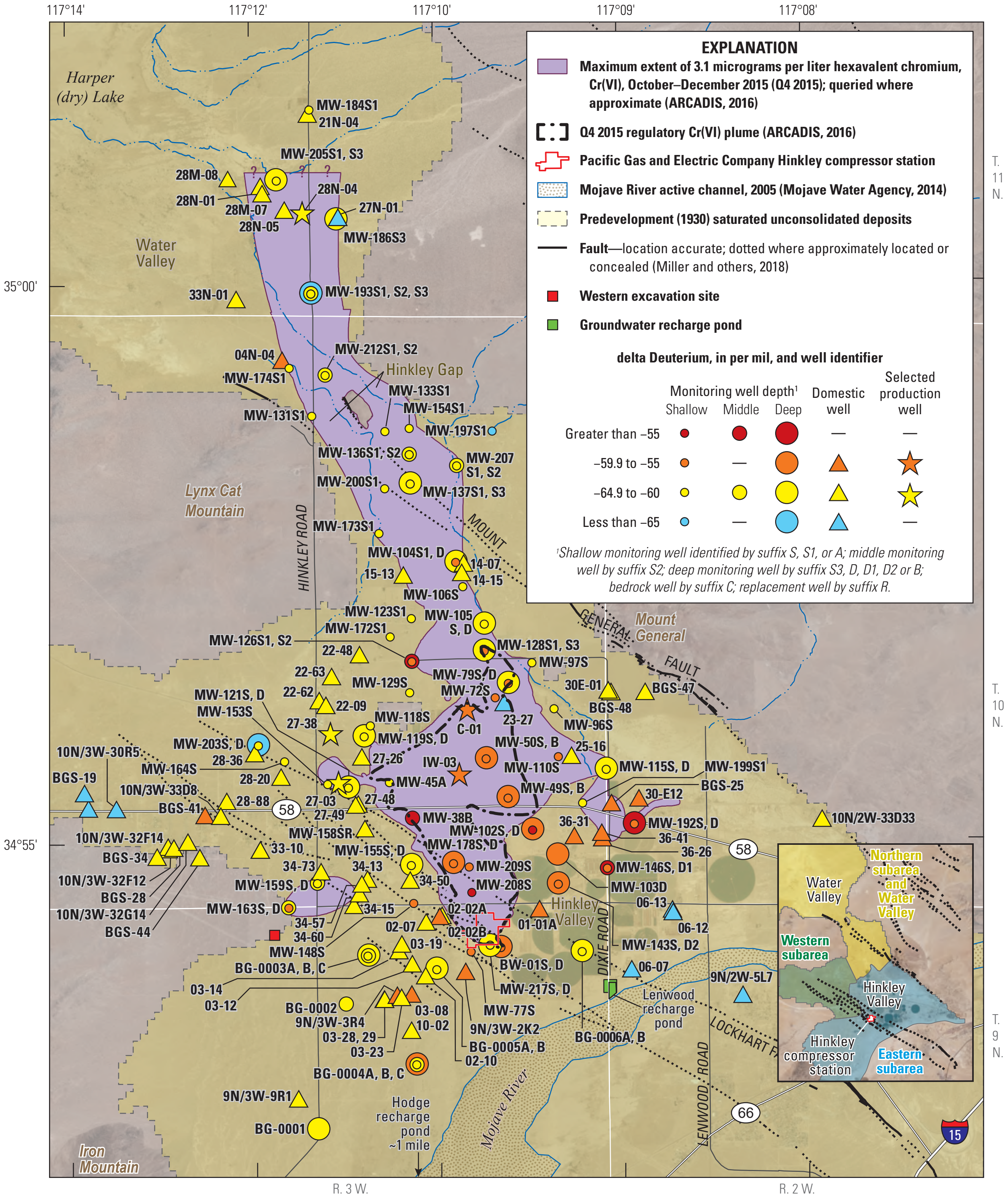
Water from some deep wells and some wells along the margins of the study area (MW-203D, MW-193S3, MW-197S1, and domestic wells 27N-01, BGS-19 and 30R5) have delta deuterium values more negative than −65 per mil that are consistent with a local source of recharge other than the Mojave River. Water from several domestic wells (06-07, 06-12, 06-13, and 9N/2W-5L7) near groundwater recharge ponds along the Mojave River have delta deuterium values more negative than −65 per mil (fig. F.4) and may have been partly sourced from water imported from northern California. Imported water from northern California has been used in the past to recharge aquifers along the Mojave River and typically has delta deuterium values more negative than water recharged from the Mojave River (Izbicki, 2004).

Most samples having delta deuterium values less negative than −60 per mil have likely been affected by evaporative enrichment of irrigation return water (fig. F.3*A*). In the eastern subarea, water from many wells has been affected by irrigation return, including deep and shallow wells within and directly downgradient from agricultural areas. Although water recharged from the Mojave River was present throughout Hinkley and Water Valleys, highly evaporated irrigation water was not present farther downgradient than well MW-104S1, about 1 mi downgradient from the mapped Q4 2015 regulatory Cr(VI) plume (fig. F.4). Specific conductance and major-ion chemistry data indicate a similar distribution of irrigation return water (chapter E, figs. E.6, E.8, respectively). Groundwater pumping for agricultural purposes created a local pumping depression beginning in the early 1950s (Stone, 1957; California Department of Water Resources, 1967; Stamos and others, 2001; Jacobs Engineering Group, 2019) that persisted until groundwater-level declines limited agricultural pumping in the early 1990s. The pumping depression likely limited groundwater movement downgradient from the eastern subarea into the northern subarea and may have limited the downgradient movement of Cr(VI) released from the Hinkley compressor station.

F.3.2. Noble Gases, Recharge Temperature, and Excess Air

Noble gases, including neon and argon, are not chemically reactive but do dissolve in groundwater. Similar to noble gases, atmospheric nitrogen gas (dinitrogen or N_2) also dissolves in groundwater, although additional nitrogen may be added to groundwater through denitrification (reduction of nitrate to nitrogen gas) during reduced conditions. Nitrogen gas added to groundwater from denitrification is known as excess nitrogen (Vogel and others, 1981).

The solubility of neon, argon, and nitrogen in water is a function of the temperature of groundwater at the time of recharge (recharge temperature; Weiss, 1970, 1971), which can be determined from the concentrations of these gases in groundwater (Mazor, 1972; Stute and others, 1995). In groundwater, gas concentrations often exceed their solubility equilibrium at the recharge temperature because of entrainment of atmospheric gases during recharge, a phenomenon known as excess air (Heaton and Vogel, 1981). Excess air in groundwater is generally thought to be related to trapping and dissolution of air bubbles at the water table during rapid recharge events or from fluctuations of the water table associated with pumping (Stute and Talma, 1998; Stute and Schlosser, 1999; Kulongoski and others, 2009). Recharge temperature, excess air, and excess nitrogen were used to evaluate hydrologic processes controlling recharge in Hinkley and Water Valleys in California and for calculating tracer concentrations for estimation of groundwater age.



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 F.4. Values of delta deuterium in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, tables E.1.1, E.1.3.) and U.S. Geological Survey (2021).

The concentrations of dissolved noble gases and nitrogen gas in groundwater are primarily governed by solution of these gases at the water table during recharge. The solubility of gases at the water table can be estimated using Henry's law and depends on temperature, salinity, and the partial pressure of the gas at the time of recharge. Henry's law can be written as follows:

$$C_s = \beta(T,S)\frac{P_x}{P_o} \qquad \text{(F.1)}$$

where

C_s is the concentration of the gas in water;

β is the Bunsen coefficient, which is experimentally derived in controlled laboratory experiments and is a function of temperature (T) and salinity (S);

P_x is the partial pressure of the gas at the water table, which is a function of recharge elevation (and associated barometric pressure), the partial pressures of other major gases in the unsaturated zone, and relative humidity (in most cases, the relative humidity near the water table is constant and near 100 percent); and

P_o is the standard sea-level atmospheric pressure at a temperature of 0 °C (Stute and Schlosser, 1999).

Recharge temperature, excess air, and excess nitrogen were calculated using concentrations of dissolved argon, neon, and nitrogen gas in groundwater with the Excel-based computer program Dissolved Gas Modeling and Environmental Tracer Analysis (DGMETA; Jurgens and others, 2020). The DGMETA calculations assumed complete dissolution of unfractionated excess air (Heaton and Vogel, 1981; Aeschbach-Hertig and others, 1999, 2000). As many as five models were computed for each sample using different combinations of dissolved argon, neon, and nitrogen gas and fit to parameters of recharge temperature, excess air, and excess nitrogen. Samples not having neon data were modeled in DGMETA using argon and nitrogen gas data. DGMETA models assumed excess air amounts between 1 and 4 cubic centimeters (cm^3) at standard temperature and pressure per kilogram of water for estimation of excess nitrogen. For each sample, a single model that best described the set of gas concentrations for that sample was chosen.

The model calculations used a recharge elevation of 2,100 ft, the approximate elevation of the water table underlying the Mojave River streambed for the reach through Hinkley Valley. This elevation was chosen because recharge to the unconsolidated aquifer underlying Hinkley Valley is primarily sourced from infiltration of intermittent surface flows along the river within Hinkley Valley (Thompson, 1929; Stamos and others, 2001; Izbicki, 2004; Seymour, 2016; Jacobs Engineering Group, Inc., 2019). Salinity values for solubility calculations were estimated from field measurements of specific conductance using an empirical equation describing the relation between specific conductance and salinity (Pickering, 1981). The use of measured data incorporates the effect of salinity solubility calculations, including water from wells affected by irrigation return water in some wells.

Gas solubility is dependent on salinity, but the effect of salinity is small in fresh groundwater (Plummer and Busenberg, 1999; Stute and Schlosser, 1999). Sensitivity analyses comparing recharge temperatures calculated from measured salinity (specific conductance) data with recharge temperatures calculated from the minimum salinity measured as part of this study (a proxy for freshwater recharge from the Mojave River) indicate a difference in recharge temperature attributable to salinity from irrigation return less than 0.1 °C for most samples.

F.3.2.1. Recharge Temperature and Excess Air Results

Dissolved-argon and nitrogen gas concentrations ranged from about 0.50 to 0.77 mg/L and from 13.7 to 24.6 mg/L, with median concentrations of 0.56 and 16.3 mg/L, respectively (appendix F.1, table F.1.1). Neon concentrations ranged from 1.78×10^{-4} to 4.48×10^{-4} cm^3 at standard temperature and pressure per kilogram of water with a median of 2.10×10^{-4} cm^3 at standard temperature and pressure per kilogram of water (chapter E, appendix E.1, table E.1.1).

The calculated recharge temperatures for water from sampled wells in Hinkley and Water Valleys ranged from 9.8 to 23.3 °C, with a median recharge temperature of 18.1 °C. The median recharge temperature is similar to the average annual air temperature of 17.7 °C measured at a weather station in Barstow, about 5 mi east of the study area (Western Regional Climate Center, 2019). The calculated excess air values in water from sampled wells in Hinkley and Water Valleys ranged from 0.5 to 8.9 cm^3 at standard temperature and pressure per kilogram of water, with a median excess air value of 1.9 cm^3 at standard temperature and pressure per kilogram of water. Excess nitrogen concentrations ranged from 0 to 4.7 mg/L, with a median concentration of 0.15 mg/L. Excess nitrogen concentrations consistent with denitrification within the aquifer were present in water from only two wells, MW-193S3 and domestic well 22-09. Well MW-193S3 in Water Valley has low dissolved-oxygen concentrations of 0.3 mg/L, and well 22-09 is in a residential area receiving septic discharge.

Dissolved-gas data were used to evaluate the consumption of dissolved oxygen in water from wells. Argon has a Henry's law constant (unitless) of 3.4×10^{-2} (Ozima and Podosek, 2002), which is similar to the constant for oxygen of 3.2×10^{-2} (Sander, 2015). Dissolved oxygen is reactive in groundwater and was not used to calculate recharge temperature or excess air. Measured dissolved oxygen, measured argon concentrations, and the initial dissolved-oxygen concentration in the sample at the time of recharge (estimated from recharge temperature and excess air data) were used to calculate dissolved oxygen consumed since recharge. Consumption of dissolved oxygen is a measure of reduction that has occurred within the groundwater since recharge that is potentially important in evaluating the reduction of Cr(VI) to Cr(III) under natural conditions.

Measured dissolved-oxygen concentrations did not exceed initial dissolved-oxygen concentrations in water from sampled wells, with the exception of water from MW-143S (fig. F.5*A*). In water from most wells, measured dissolved-oxygen concentrations were less than the initial concentration at the time of recharge, which is consistent with consumption of dissolved oxygen by microbial respiration and other natural processes (fig. F.5*A*). Consumption of dissolved oxygen was less in water from wells near recharge areas along the Mojave River and was correlated with increasing groundwater age and inversely correlated with carbon-14 activities described later in this chapter, although the correlation is low with a coefficient of determination (R^2) of 0.20 (fig. F.5*B*).

F.3.2.2. Discussion of Recharge Temperature and Excess Air

In most settings, seasonal temperature variations at the water table are small, and groundwater temperature approximates the average annual air temperature (Heaton and Vogel, 1981). Exceptions include areas where a large quantity of water infiltrates rapidly through the unsaturated zone from focused sources of recharge such as streams (Stute and Schlosser, 1999; Kulongoski and Izbicki, 2008).

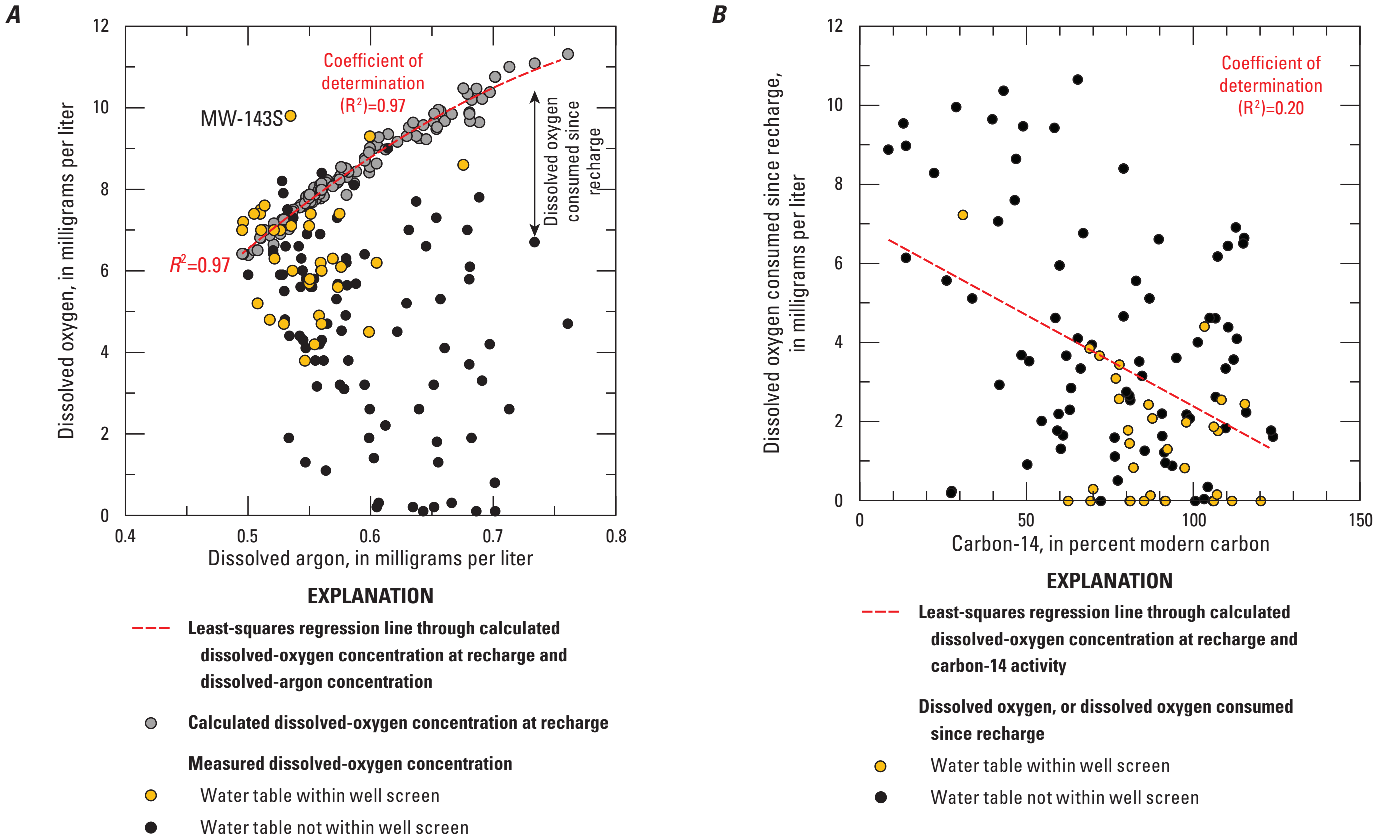


Figure F.5. Dissolved atmospheric gases in water from wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 to November 2017. *A*, Initial and measured dissolved oxygen as a function of measured argon and *B*, dissolved oxygen consumed since recharge as a function of carbon-14 activity. Data are available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

The median recharge temperature of 18.1 °C in water from sampled wells (fig. F.6*A*) in Hinkley and Water Valleys, calculated using the computer program DGMETA (Jurgens and others, 2020), approximates the average annual air temperature in the study area of 17.7 °C (Western Regional Climate Center, 2019). For purposes of visualization, recharge temperatures are shown graphically as a function of dissolved-argon and nitrogen gas concentrations (fig. F.7). Recharge temperatures within the nomograph in the interior of figure F.7 differ slightly from values calculated on the basis of dissolved-argon, neon, and nitrogen gas data using DGMETA; however, both the DGMETA and graphical results indicate lower recharge temperatures in the eastern subarea compared to other areas within Hinkley and Water Valleys (figs. F.6*A*, F.8). The median DGMETA recharge temperature for water from monitoring wells in the eastern subarea was 16.1 °C (fig. F.6*A*). In contrast, the median recharge temperatures for water from monitoring wells in the northern subarea (including Water Valley) and the western subarea were 19.0 and 19.9 °C, respectively (fig. F.6*A*). The median recharge temperature for water from wells in the eastern subarea is similar to the average spring air temperature of 16.6 °C (Western Regional Climate Center, 2019), and water from wells MW-115D, BG-0006B, and MW-143D2 (fig. F.7) has DGMETA recharge temperatures of 9.8, 11.3, and 11.1 °C, respectively, approaching the average winter air temperature of 8.5 °C (Western Regional Climate Center, 2019). Lower recharge temperatures in the eastern subarea are consistent with recharge as infiltration of streamflow in the Mojave River derived from runoff of winter precipitation. Wells MW-115D, BG-0006B, and MW-143D2 and other wells in the eastern subarea having recharge temperatures less than 14.0 °C, consistent with winter recharge, are deeper wells that are isolated from irrigation return water. Consistent with major-ion (chapter E, fig. E.8) and delta oxygen-18 and delta deuterium compositions, water from shallower wells in the eastern subarea has mixed with some fraction of water recharged from irrigation return and has higher recharge temperatures greater than 20 °C.

Excess air values in water from wells in Hinkley and Water Valleys, calculated using the computer program DGMETA (Jurgens and others, 2020), ranged from 0.5 to 8.9 cm^3 at standard temperature and pressure per kilogram of water (fig. F.6*B*), with a median concentration of 1.9 cm^3 at standard temperature and pressure per kilogram of water. The median excess air values were 3.4, 1.9, and 1.5 cm^3 at standard temperature and pressure per kilogram of water from monitoring wells in the eastern, western, and northern (including Water Valley) subareas, respectively (fig. F.6*B*). Graphical analyses of argon and nitrogen concentrations show similar results with higher excess air values in the eastern subarea and lower values elsewhere in Hinkley and Water Valleys (fig. F.7).

In arid and semiarid environments, intermittent recharge that causes rapid rises of the water table favors entrapment of air bubbles (Heaton and Vogel, 1981). The higher excess air values in the eastern subarea are consistent with water from wells having a greater percentage of water infiltrated as focused recharge from intermittent surface flows of the Mojave River. The highest DGMETA excess air values of 8.4 and 8.9 cm^3 at standard temperature and pressure per kilogram of water were calculated for deep wells BG-0006B and MW-143D2, which are near recharge areas along the Mojave River and isolated from irrigation return. Samples having specific conductance, delta oxygen-18 and delta deuterium values, and recharge temperatures consistent with irrigation return had lower excess air values.

Water from most sampled wells in Hinkley and Water Valleys was oxic with dissolved-oxygen concentrations greater than 0.5 mg/L. Denitrifying bacteria require low oxygen concentrations to reduce nitrate to nitrogen. Small amounts of dissolved nitrogen gas possibly from denitrification were present in water from well MW-193S3 in Water Valley (fig. F.7), which had a dissolved-oxygen concentration of 0.3 mg/L. Excess nitrogen gas, potentially indicative of denitrification, also was measured in water from well 22-09 in a formerly residential area served by septic systems in Hinkley Valley. In addition to well 22-09, other wells, including 27N-01 and MW-121D in areas potentially receiving septic or animal waste, also have excess nitrogen concentrations, although dissolved-oxygen concentrations in these wells indicate oxic conditions.

Differences in recharge temperature and excess air of water from wells result from changes in groundwater recharge processes along the Mojave River since the onset of agricultural pumping and water-level declines beginning in the early 1950s. Before agricultural development, infiltration and groundwater recharge from the river likely occurred as a result of warmer, sustained streamflows through a comparatively thin unsaturated zone underlying the river. Agricultural pumping lowered the water table and created additional storage for recharge water infiltrated from the river. Infiltration and groundwater recharge after agricultural development reflect recharge from colder winter stormflows infiltrated through thicker unsaturated zones. After agricultural development, excess air data indicate recharge was rapid. Winter streamflows that resulted in groundwater recharge in Hinkley Valley needed to be of sufficient magnitude to flow from the mountain front across largely dry stream reaches along the river to reach Hinkley Valley. These winter streamflows were able to reach Hinkley Valley while losing water through infiltration along upstream reaches of the Mojave River channel. These winter streamflows were likely larger than the average streamflows during predevelopment, and they were likely less frequent.

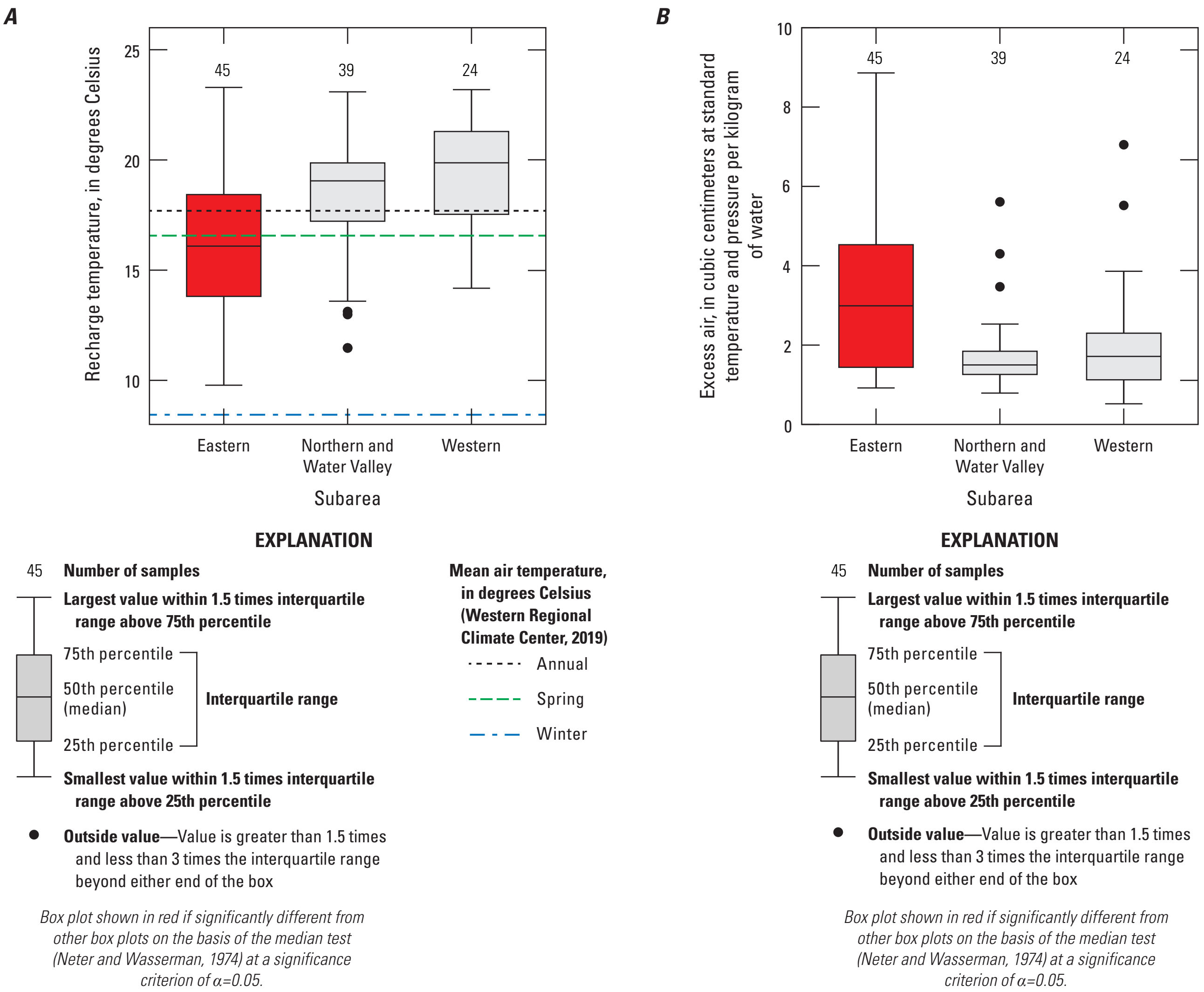


Figure F.6. *A*, Recharge temperatures and *B*, excess air concentrations calculated from dissolved atmospheric gas (argon, neon, and nitrogen) concentrations in water from sampled monitoring wells in the eastern subarea, the northern subarea and Water Valley, and the western subarea, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Values are available in appendix F.2 (table F.2.1) and were calculated from data available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

Recharge from the Mojave River was ultimately inadequate to meet water supply demands in the area, resulting in water-level declines beginning in the early 1950s in Hinkley and Water Valleys and regionally in the adjudication of groundwater in the Mojave River groundwater basin in 1996 (California Superior Court, 1996). The warmer groundwater recharge temperatures and lower excess air values in the western and northern subareas (including Water Valley) of Hinkley Valley compared to the eastern subarea are consistent with more sustained recharge from surface flows in the Mojave River that occurred through a thinner unsaturated zone. Recharge under these conditions is characteristic of predevelopment (pre-1930) and would predate Cr(VI) releases from the Hinkley compressor station between 1952 and 1964.

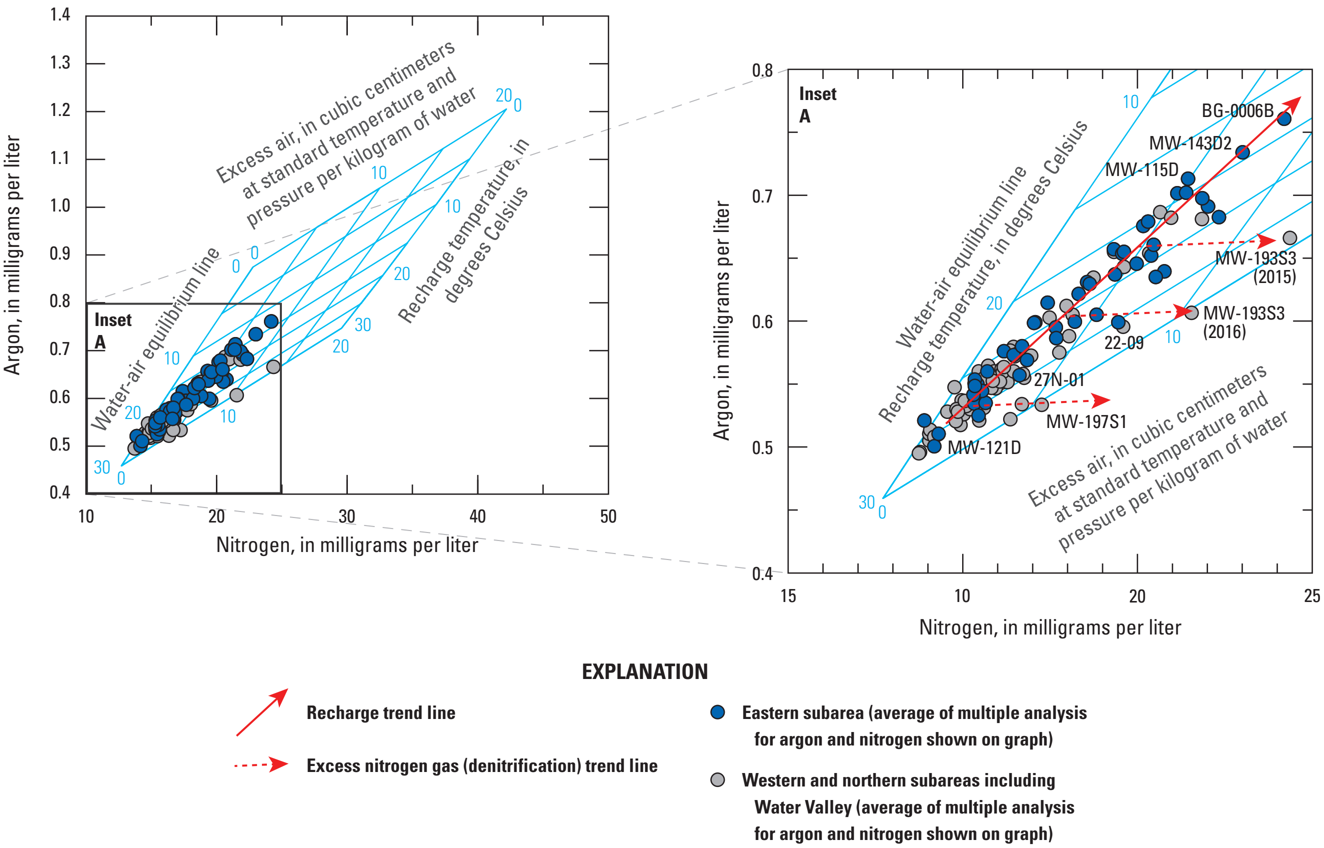
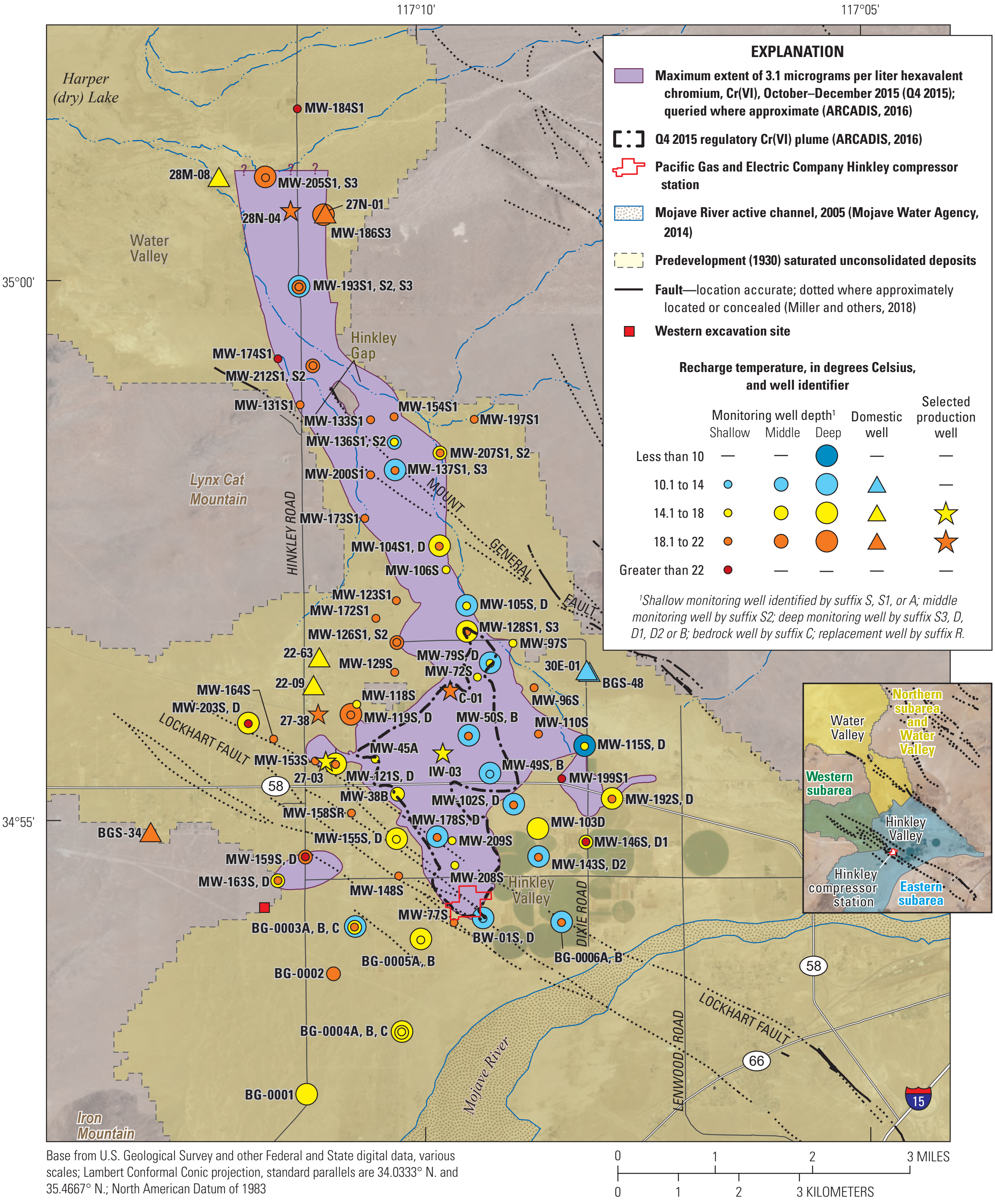


Figure F.7. Dissolved-argon concentrations as a function of dissolved-nitrogen gas concentrations with a nomograph showing recharge temperatures and excess air concentrations in water from sampled wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

F.3.3. Summary of the Source and Recharge History of Groundwater

The stable isotopes of oxygen and hydrogen within the water molecule, delta oxygen-18 and delta deuterium, indicate almost all groundwater in Hinkley and Water Valleys was recharged as infiltration of intermittent streamflow in the Mojave River. Streamflow in the river originates primarily as precipitation in Cajon Pass more than 40 mi south of the study area. The delta deuterium values, of about -65 per mil, in water from most wells in Hinkley and Water Valleys are consistent with groundwater recharged from the Mojave River, with heavier (less negative) values resulting from evaporation. Water from wells underlying agricultural areas within Hinkley Valley that has been affected by evaporation and irrigation return, has high nitrate concentrations associated with agricultural activities, while some other wells having high nitrate concentrations are affected by septic discharges.

The delta oxygen-18 and delta deuterium composition of water from a few deep wells and some wells along the margins of the unconsolidated aquifer in Hinkley Valley (MW-203D, MW-193S3, MW-197S1, and domestic wells 27N-01, BGS-19 and 30R5) is consistent with a local source of recharge other than the Mojave River. Water from several domestic wells (06-07, 06-12, 06-13, and 9N/2W-5L7) near groundwater recharge ponds along the Mojave River, may have been partly sourced from water imported from northern California.



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 F.8. Groundwater recharge temperatures calculated from dissolved-atmospheric gas (argon, neon, and nitrogen) data, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Values are available in appendix F.2 (table F.2.1) and were calculated from data available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

Groundwater pumping for agricultural purposes created a local pumping depression beginning in the early 1950s that persisted until the early 1990s. The pumping depression likely limited groundwater movement downgradient from the eastern subarea into the northern subarea and may have limited the downgradient movement of Cr(VI) released from the Hinkley compressor station. Recharge temperature and excess air values (calculated from dissolved-argon, neon, and nitrogen gas data) indicate recharge processes along the Mojave River have changed since predevelopment. As agricultural pumping lowered the water table along the river, groundwater recharge to Hinkley Valley was derived from fewer large winter stormflows that were sufficient in magnitude to reach Hinkley Valley compared to more sustained streamflows before development. Recharge from the Mojave River was ultimately inadequate to meet water supply demands in the area, resulting in water-level declines beginning in the early 1950s in Hinkley and Water Valleys and regionally in the adjudication of groundwater in the Mojave River groundwater basin in 1996 (California Superior Court, 1996). The warmer groundwater recharge temperatures and lower excess air values in water from wells in the western and northern subareas of Hinkley Valley and Water Valley compared to the eastern subarea are consistent with recharge from sustained surface flows in the Mojave River that occurred through a thinner unsaturated zone. Recharge under these conditions are characteristic of predevelopment (pre-1930) and would predate Cr(VI) releases from the Hinkley compressor station between 1952 and 1964.

F.4. Tracers of the Age of Groundwater

In addition to tracers of the source and recharge history of groundwater, samples also were analyzed for tracers of groundwater age. Groundwater age is the time since groundwater was recharged (entered the saturated zone) and became isolated from the atmosphere. Estimates of groundwater age are useful for tracing the movement of modern (post-1952) and older (pre-1952) water in groundwater-flow systems.

Cooling wastewater containing Cr(VI) was discharged to unlined ponds at the Hinkley compressor station between 1952 and 1964 (Lahontan Regional Water Quality Control Board, 2013), and tracers of modern and older groundwater can help in understanding the movement of Cr(VI) released from the Hinkley compressor station. Tracers of groundwater age measured as part of this study include (1) tritium and its decay product helium-3 (tritiogenic helium), (2) carbon-14, and (3) industrial gases. Each tracer has a different history of anthropogenic releases to the environment (fig. F.9) and different reactions within groundwater that may affect the interpretation of groundwater age.

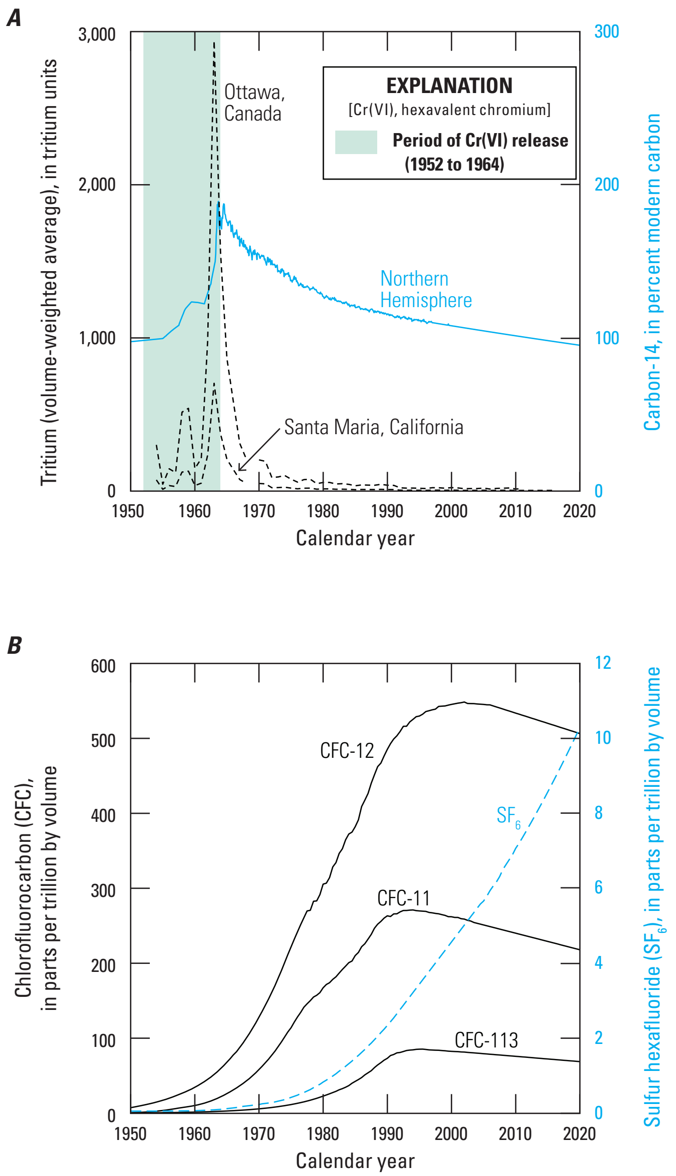


Figure F.9. Groundwater-age tracer input histories. *A*, Carbon-14 (^{14}C) and tritium atmospheric input histories and *B*, industrial gases (chlorofluorocarbons [CFCs] including trichlorofluoromethane [CFC-11], dichlorodifluoromethane [CFC-12], and trichlorotrifluoroethane [CFC-113] and sulfur hexafluoride [SF_6]) atmospheric input histories. Data are modified from Plummer and Friedman (1999).

Tritium and carbon-14 are naturally occurring but also were released in large quantities to the atmosphere beginning in 1952 as a result of the atmospheric testing of nuclear weapons. Tritium and carbon-14 reached peak concentrations in the atmosphere in the early 1960s and began to decline with the signing of the Nuclear Test Ban Treaty in 1963 (U.S. National Archives, 2022), which prohibited the atmospheric testing of nuclear weapons. Terrigenic helium from the decay of naturally occurring uranium and thorium radionuclides within aquifer materials and from mantle outgassing is accounted for in tritium and helium-3 groundwater-age dates. Industrial gases, including chlorofluorocarbons, were first released to the atmosphere in the early 1930s. Chlorofluorocarbon concentrations in the atmosphere began to decline with the signing of the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987 (United Nations, 2020), which limited releases of ozone-depleting gases. Industrial gases also include sulfur hexafluoride; sulfur hexafluoride was not regulated by the Montreal Protocol, and atmospheric concentrations continued to increase after 1987 (Plummer and Busenberg, 1999).

Groundwater-age estimates and the fraction of modern (post-1952) water within a sample, known as the “mixing fraction,” were evaluated relative to the timing of Cr(VI) releases from the Hinkley compressor station to determine whether or not groundwater was of the appropriate age to contain anthropogenic Cr(VI). However, not all modern groundwater recharged from the Mojave River after 1952 passed near the Hinkley compressor station and would contain anthropogenic Cr(VI).

F.4.1. Tritium and Tritium/Helium-3 Age Dating

Tritium is a radioactive isotope of hydrogen with a half-life of 12.3 years (Lucas and Unterweger, 2000). In this study, tritium is reported in tritium units; 1 TU is equivalent to one tritium atom in 10^{18} atoms of hydrogen (Taylor and Roether, 1982). Before 1952, the only source of tritium in the atmosphere was natural production from the bombardment of nitrogen by cosmic radiation (Solomon and Cook, 1999). Atmospheric testing of nuclear weapons from 1952 to 1963 released about 800 kilograms (kg) of tritium to the atmosphere (Michel, 1976), causing a large increase in the tritium concentration of precipitation (fig. F.9*A*). After the end of atmospheric testing of nuclear weapons in 1963, tritium concentrations in precipitation decreased, and by the time of this study (2015–17) tritium concentrations in precipitation were near pre-1952 levels (International Atomic Energy Agency, 2020).

Tritium deposition at selected sites throughout the world has been measured since the 1950s by the International Atomic Energy Agency (1981) and has been estimated at unmeasured sites in the United States (Michel, 1989; Michel and others, 2018). The tritium concentration of precipitation in coastal California before 1952 was about 2 TU (International Atomic Energy Agency, 1981; Michel, 1989) and reached a peak of about 700 TU in 1963 (fig. F.9*A*) at a site near Santa Maria, Calif., about 140 mi northwest of Los Angeles, California (fig. F.1). Based on a pre-1952 tritium concentration of 2 TU and calculations of subsequent decay, groundwater recharged in the early 1950s before the atmospheric testing of nuclear weapons would have a tritium concentration of about 0.05 TU in 2016. This study therefore adopts an SRL of 0.05 TU for tritium, which is consistent with the methodology for defining the cutoff between detectable and nondetectable tritium by other studies (Bexfield and others, 2012).

Tritium decays to helium-3, a stable isotope of helium. After recharge and isolation from the atmosphere, dissolved helium-3 concentrations increase as tritium decays with time. The helium-3 produced from radioactive decay of tritium is referred to as “tritiogenic helium-3.” Tritium/helium-3 age dating of groundwater calculates the age of groundwater from measured tritium and its decay product tritiogenic helium-3. The tritium/helium-3 age of a water sample is defined as follows:

$$t = \frac{t_{1/2}}{\ln 2} \times \ln\left(1 + \frac{{}^{3}He_{trit}}{{}^{3}H}\right) \qquad (F.2)$$

where

t is the tritium/helium-3 (${}^{3}H/{}^{3}He$) age (time since recharge) of groundwater;

$t_{1/2}$ is the half-life of tritium, equal to 12.3 years;

${}^{3}He_{trit}$ is the measured tritiogenic helium-3 in the water sample; and

${}^{3}H$ is the measured tritium in the water sample.

For the purposes of tritium/helium-3 age-dating calculations, the amount of tritiogenic helium-3 must be estimated separately from other sources of helium-3 in groundwater. Groundwater can contain additional helium-3 derived from sources other than the decay of tritium, including (1) atmospheric sources (solubility equilibrium with the atmosphere), (2) excess air entrapped during recharge, and (3) terrigenic sources (radiogenic production in aquifer solids or crustal and mantle sources of helium-3). In this study, the concentration of tritiogenic helium-3 in water samples was separated from other sources of helium-3 by mass-balance calculations done using the computer program DGMETA (Jurgens and others, 2020). The computer program DGMETA uses dissolved gas modeling results described previously to constrain recharge temperatures and excess air concentrations and calculates tritiogenic helium-3 according to Schlosser and others (1989):

$$^{3}\mathrm{He}_{trit}={}^{4}\mathrm{He}_{s}R_{s}-({}^{4}\mathrm{He}_{s}-{}^{4}\mathrm{He}_{terr})R_{air}+{}^{4}\mathrm{He}_{eq}R_{air}(1-\alpha)-{}^{4}\mathrm{He}_{terr}R_{terr} \qquad (F.3)$$

and

$$^{4}\mathrm{He}_{terr}={}^{4}\mathrm{He}_{s}-{}^{4}\mathrm{He}_{eq}-{}^{4}\mathrm{He}_{exc} \qquad (F.4)$$

where

$^{3}\mathrm{He}_{trit}$ is the helium-3 produced by radioactive decay of tritium (tritiogenic helium-3);
$^{4}\mathrm{He}_{s}$ is the measured total dissolved helium-4 in the sample;
R_{s} is the measured helium-3/helium-4 ratio of the sample;
$^{4}\mathrm{He}_{terr}$ is the dissolved helium-4 originating from terrigenic sources, equal to the amount of helium-4 in excess of helium-4 originating from the solubility equilibrium with the atmosphere and excess air;
R_{air} is the atmospheric helium-3/helium-4 ratio, equal to 1.384×10^{-6} (Clarke and others, 1976);
$^{4}\mathrm{He}_{eq}$ is the dissolved helium-4 in solubility equilibrium with the atmosphere;
α is the helium equilibrium isotope fractionation factor between air and the dissolved phase (Benson and Krause, 1980);
R_{terr} is the terrigenic helium-3/helium-4 ratio; and
$^{4}\mathrm{He}_{exc}$ is the dissolved helium-4 originating from excess air.

As indicated in equation F.3, the determination of tritiogenic helium-3 requires knowledge of the ratio of helium-3 to the more abundant isotope helium-4. The helium-3/helium-4 ratio of the sample can be measured, and the helium-3/helium-4 ratio of terrigenic helium (R_{terr}) can be estimated using graphical methods (Weise and Moser, 1987; Stute and others, 1992) or estimated from knowledge of the groundwater-flow system. Graphical routines for estimating R_{terr} and the percentages of terrigenic helium derived from mantle and radiogenic sources are included in DGMETA. Estimates of R_{terr} used in this study were 2×10^{-8} (83 percent of samples), 3.31×10^{-7} (12 percent of samples), and 1.06×10^{-6} (5 percent of samples); these R_{terr} estimates indicate 0, 3, and 10 percent of terrigenic helium derived from mantle sources.

The tritium/helium-3 age-dating method is applicable for groundwater that contains tritium. If the tritiogenic helium-3 concentration is not known, or the contributions of helium-3 from other sources cannot be quantified, water samples having tritium concentrations greater than the SRL are interpreted as containing a fraction of water recharged after 1952, and water samples having tritium concentrations less than the SRL are interpreted as containing water recharged before 1952. Tritium/helium-3 ages are accurate to within ±2 years and accurate to within ±5 years where large concentrations of excess air are present (Solomon and Cook, 1999).

Terrigenic helium concentrations increase with groundwater residence time within the aquifer as a result of radiogenic decay and mantle degassing and provide a means to estimate the age of groundwater recharged thousands of ybp (Solomon, 1999). Terrigenic helium groundwater-age estimates may be qualitative or quantitative if accumulation rates from radiogenic decay and fluxes of mantle degassing can be estimated. In this study, terrigenic helium concentrations are expressed as a percentage of the total dissolved helium in the sample according to

$$\textit{Percentage of terrigenic helium} = \left(\frac{^{4}\mathrm{He}_{terr}}{^{4}\mathrm{He}_{s}-{}^{4}\mathrm{He}_{exc}}\right)100 \qquad (F.5)$$

where terms are defined as previously described. The abundances of helium-3 and helium-4 are reported in delta notation as delta helium-3, in units of percentage relative to an air standard having a helium-3/helium-4 ratio of 1.384×10^{-6} (Clarke and others, 1976). The values will be negative if the helium-3/helium-4 in the sample is less than the helium-3/helium-4 air standard.

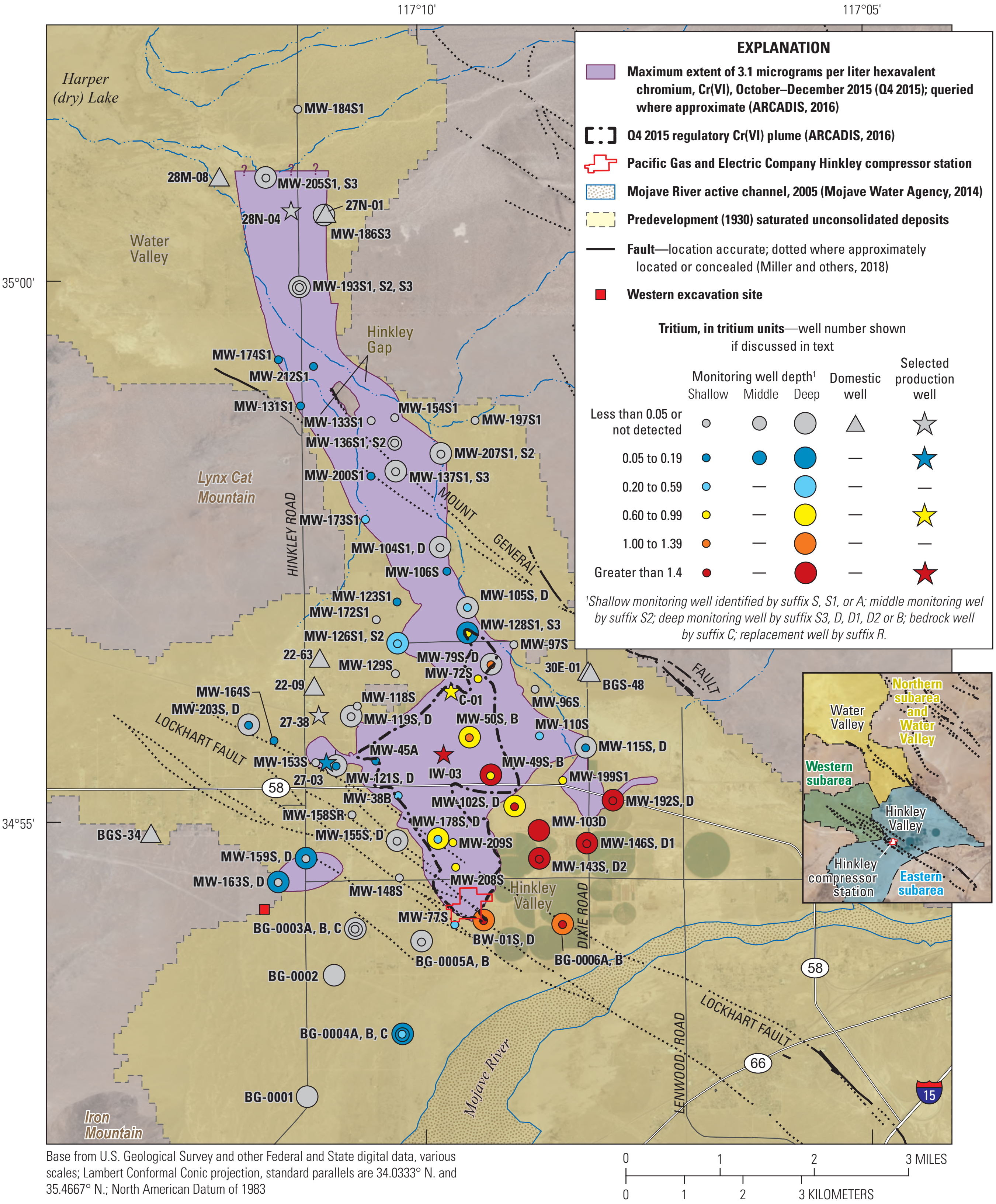
F.4.1.1. Tritium Results

Tritium concentrations ranged from less than the SRL of 0.05 to 1.89 TU (chapter E, appendix E.1, table E.1.1; fig. F.10). Tritium was detected in water from 53 wells in Hinkley and Water Valleys, or almost 50 percent of sampled wells. Tritium concentrations were higher in water from wells near recharge areas along the Mojave River and decreased downgradient (fig. F.10). Low levels of tritium, 0.17 TU, were detected in water from well MW-174S1 in Water Valley, 6 mi downgradient from the Mojave River. Tritium concentrations and detection frequency were generally higher in shallower wells, but some deep wells in the eastern subarea contained measurable tritium (fig. F.11). Tritium was not generally detected in water from deeper wells in the western subarea or in the northern subarea farther downgradient than well MW-128S3, about 3.5 mi from the Mojave River (fig. F.10). Tritium was not detected in water from the seven domestic wells sampled and analyzed for tritium. These wells were generally screened in weathered bedrock or locally derived alluvium near the margins of the aquifer (fig. F.10). Wells MW-137S1, MW-159D, and MW-193S3, which were sampled in March 2015 and resampled March 2017, had low-level tritium detections. Low levels of tritium were considered representative of modern (post-1952) water if the measured carbon-14 activity exceeded the initial activity of post-1952 recharge water (A_o value) in the Mojave Desert of 84 pmc estimated by Izbicki and Michel (2004). For example, well MW-163D, which was sampled in March 2015, had a low-level tritium value of 0.07 TU and a measured carbon-14 activity of 69 pmc. On the basis of the carbon-14 data, the low-level tritium value of 0.07 TU may not accurately represent post-1952 recharge water. In contrast water from well MW-121S, also sampled in March 2015, had a low-level tritium value of 0.07 TU and a measured carbon-14 activity of 98 pmc; the low-level tritium value of 0.07 TU likely represents some fraction of post-1952 recharge water within the sample.

Cooling wastewater containing Cr(VI) was discharged from the Hinkley compressor station to unlined ponds between 1952 and 1964 (Lahontan Regional Water Quality Control Board, 2013). Large amounts of recharge from infiltration of Mojave River streamflow containing tritium associated with the atmospheric testing of nuclear weapons did not occur until 1969, after Cr(VI) releases from the Hinkley compressor station ended, although some recharge from the Mojave River occurred in 1958 (fig. F.2). Hexavalent chromium from the Hinkley compressor station was initially released into older pre-1952 groundwater containing low tritium concentrations that would have decayed to less than the SRL by the time of this study; consequently, the leading edge of the Cr(VI) plume may precede the leading edge of groundwater containing measurable tritium (fig. F.10).

Tritium was detected most frequently in water from wells in the eastern subarea, with detectable tritium in water from 36 of 48 wells, or 75 percent of sampled wells in the eastern subarea (fig. F.10). Tritium was detected in water from most wells within the mapped Q4 2015 regulatory Cr(VI) plume, although tritium was not detected in some deeper wells within the footprint of the plume. Tritium concentrations greater than 1.0 TU were measured in water from wells screened within the shallow and deep zones composing the upper aquifer in the eastern subarea. Although the higher tritium concentrations were near recharge areas along the Mojave River, tritium concentrations greater than 1 TU were measured in water from shallow wells as far downgradient as MW-79S within the Q4 2015 regulatory Cr(VI) plume (fig. F.10). Tritium was not detected in water from 12 wells in the eastern subarea, including well MW-96S completed in weathered bedrock, deep well MW-79D within the footprint of the Q4 2015 regulatory plume, and well MW-115D underlying mudflat/playa deposits in the eastern subarea. Tritium was not generally detected in water from shallow or deep wells upgradient (southwest) from the Lockhart fault, except in water from wells BG-0004A, B, and C along the Mojave River (fig. F.10).

Tritium was detected in water from 6 of 22 sampled wells, or 27 percent of wells, in the western subarea. Tritium concentrations in the western subarea were low, with concentrations of less than 0.1 TU. The low concentrations and the low frequency of tritium detection indicate groundwater in the western subarea was mostly recharged before 1952 and largely predates releases from the Hinkley compressor station. Tritium was present in water from shallow monitoring wells MW-121S, MW-164S, and MW-203S and from production well 27-03 (fig. F.10). Carbon-14 activities in water from these wells were 99, 69, 28, and 82 pmc, respectively (chapter E, appendix E.1, table E.1.1), only water from one of these wells contained tritium and carbon-14 activities consistent with post-1952 recharge. These wells are north of and nominally downgradient from the Lockhart fault (fig. F.10; chapter H, fig. H.8); however, tritium was generally absent in water from sampled wells within mapped strands and upgradient from the Lockhart fault (fig. F.10). Historical water-level data (Stone, 1957; California Department of Water Resources, 1967) and more recent water-level data (CH2M Hill, 2013) indicate the Lockhart fault impedes groundwater flow through Hinkley Valley, and the distribution of low-level tritium concentrations within the western subarea is consistent with movement of groundwater along the downgradient side of the fault from the eastern subarea, or water from septic sources in the westernmost wells MW-164S and MW-203S. Measurable tritium at concentrations of 0.09 and 0.07 TU also was detected in water from wells MW-159D and MW-163D, respectively, downgradient from the “western excavation site,” in March 2015; carbon-14 activities in water from these wells ranged from 80 to 69 pmc (chapter E, appendix E.1, table E.1.1); well MW-159D did not contain measurable tritium when it was resampled in March 2017. Shallow wells at these sites, MW-159S and MW-163S, did not contain measurable tritium (fig. F.10).



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 F.10. Tritium concentrations in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

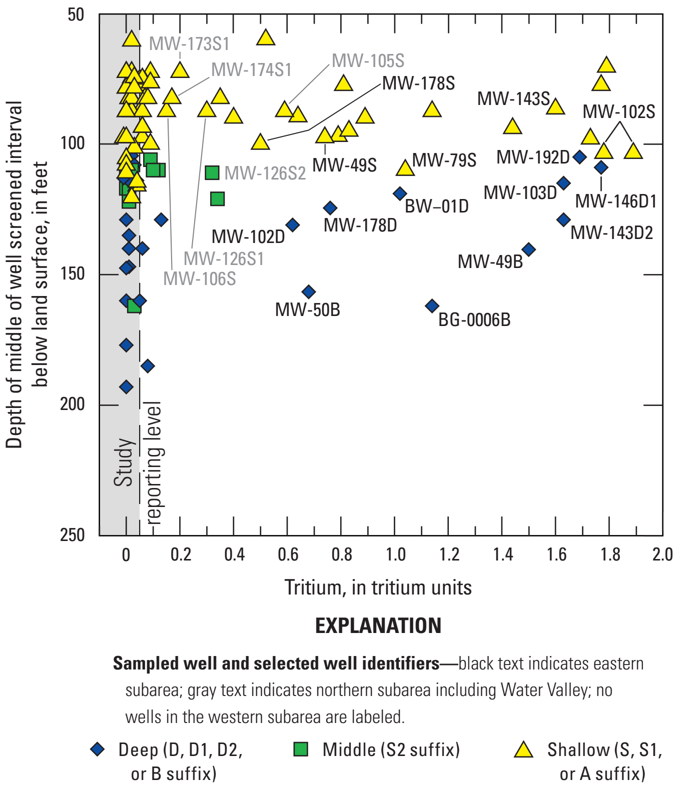


Figure F.11. Tritium with depth below land surface in water from monitoring wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

Tritium was detected in 6 of 8 (75 percent) sampled shallow wells upgradient from (south of) the Mount General fault (fig. F.10; chapter H, fig. H.8). Tritium concentrations were as high as 0.59 TU in water from well MW-105S. The distribution of tritium-containing groundwater indicates post-1952 groundwater, recharged after Cr(VI) releases from the Hinkley compressor station, in water from shallow wells upgradient from the Mount General fault (fig. F.10). These shallow wells are downgradient from the Q4 2015 regulatory Cr(VI) plume. Tritium was not detected in water from deeper wells north of the Q4 2015 regulatory Cr(VI) plume, with the exception of MW-126S2, which is not isolated from the surface by a hydrologically important clay layer (fig. F.10). Tritium also was not detected in water from wells downgradient from (north of) the Mount General fault (fig. F.10).

Tritium was detected in water from shallow wells MW-131S1, MW-174S1, and MW-212S1 in the southern part of Water Valley at concentrations of 0.05, 0.17, and 0.06 TU, respectively (chapter E. appendix E.1, table E.1.1; fig. F.10). Carbon-14 activities in water from wells MW-131S1, MW-174S1, and MW-212S1 were 0.56, 95, and 84 pmc, respectively (chapter E. appendix E.1, table E.1.1). Water in wells MW-174S1 and MW-212S1 have tritium and carbon-14 activities consistent with post-1952 water. Tritium was not detected further downgradient in Water Valley than well MW-174S1.

Tritium concentrations in water from wells in the study area were lower than what would be expected for water recharged at the time of peak atmospheric tritium concentrations. In 1963, the peak tritium concentration in precipitation at Santa Maria, Calif., was about 700 TU (fig. F.9*A*), with a 2016 decay-corrected concentration of about 35 TU. Tritium concentrations in water from sampled wells are consistent with the intermittent recharge history of the Mojave River, with streamflow and large amounts of recharge from the river not occurring until 1969, 6 years after the peak tritium concentration in precipitation at Santa Maria, Calif. (figs. F.2, F.9*A*). By 1969, tritium concentrations in precipitation at Santa Maria had declined to 50 TU (estimated by correlation with data from Ottawa, Canada), with a 2016 decay-corrected concentration of 3.5 TU; about two times higher than the highest measured tritium concentration in Hinkley or Water Valleys. Low-tritium concentrations in water from sampled wells are consistent with the timing of groundwater recharge, radioactive decay since recharge, and mixing of pre-1952 and post-1952 water within the aquifer underlying Hinkley and Water Valleys. In addition, agricultural pumping and subsequent water-level declines, commonly more than 60 ft, may have removed tritium-containing groundwater from aquifers within Hinkley and Water Valleys.

F.4.1.2. Tritium/Helium-3 Ages and Modern Groundwater

Tritium and helium-3 concentrations were used to calculate tritium/helium-3 ages (eq. F.2) of groundwater recharged after 1952 in Hinkley and Water Valleys. Tritiogenic helium-3 concentrations from the decay of tritium ranged from 0.01 to 37.9 TU (calculated from data in chapter E, appendix E.1, table E.1.1). The highest tritiogenic helium-3 concentration of 37.9 TU was measured in water from well MW-50B and is in the range of concentrations estimated for 1969 recharge from precipitation data at Santa Maria, Calif. The second highest concentration of 12.7 TU was measured in water from well MW-208S, about 0.6 mi downgradient from the Hinkley compressor station. Well MW-208S had the highest Cr(VI) concentration measured as part of this study, 2,500 µg/L (chapter E, appendix E, table E.1.1). A feature of the Q4 2015 regulatory Cr(VI) plume is that more than 60 years after the initial Cr(VI) release, high Cr(VI) concentrations remain near the Hinkley compressor station. High tritiogenic helium-3 concentrations in water from well MW-208S are consistent with slow movement of water within splays of the Lockhart fault in this part of Hinkley Valley.

Comparison of the reconstructed initial tritium (tritium + tritiogenic helium-3) in samples at the time of recharge to historical records of tritium precipitation indicates water from many wells contains mixtures of pre-1952 and post-1952 water. In these mixtures, the apparent tritium/helium-3 age calculated as part of this study applies to the post-1952 fraction of water (Aeschbach-Hertig and others, 1998; Plummer and others, 1998). Tritium/helium-3 ages for the modern (post-1952) fraction of water from sampled wells ranged from less than 1 year to greater than 50 years.

The tritium/helium-3 recharge date of the modern fraction of water within each sample was calculated as the sample date minus the tritium/helium-3 age. The fraction of modern water was estimated by dividing the tritium concentration in the sample by the historical tritium concentration in precipitation at the time of recharge (the tritium/helium-3 recharge date). Volume-weighted measurements of tritium (decay corrected to 2016) in precipitation at Santa Maria, Calif., were used for mixing fraction calculations (fig. F.12). These mixing fraction calculations assume binary mixing of post-1952 water with older groundwater recharged before the advent of the atmospheric testing of nuclear weapons. If groundwater was not affected by mixing, all sample points would plot on the 2016 decay-corrected input history (fig. F.12) and the samples would contain 100-percent post-1952 water. Although water from a few wells near the Mojave River plot on the decay-corrected line, most samples plot below the decay-corrected input history and are affected by either mixing with older water that does not contain tritium or mixing with water having lower concentrations of tritium. No samples plot above the decay-corrected line, indicating that the local tritium input history is reasonably approximated by tritium data from the precipitation site at Santa Maria, Calif.

The history of intermittent streamflow in the Mojave River and subsequent groundwater recharge to Hinkley and Water Valleys is known (fig. F.2; Lines, 1996; Stamos and others, 2001). On the basis of these data, tritium/helium-3 recharge dates were grouped into recharge cohorts corresponding to measured Mojave River streamflows and recharge between 1958 and 2011. Large streamflows and subsequent groundwater recharge occurred in 1969, 1980, 1993, 1998, 2005, and 2011 (fig. F.2). Recharge from some smaller streamflows that were closely spaced in time was grouped with larger streamflows into recharge cohorts spanning several years to simplify data analyses (fig. F.2). Recharge from small flows in 1958 was treated as a separate recharge cohort, and streamflows in 2005 and 2011 also were treated as separate recharge cohorts. Percentages of modern, post-1952, water were calculated using the assigned recharge cohort date. Within the scope of this study, it was not possible to interpret tracers of groundwater age using lumped parameter models (Jurgens and others, 2012) to evaluate groundwater-age distributions with respect to simplified analyses of aquifer geometry, recharge processes, and mixing as proposed by Izbicki and Groover (2016, 2018).

Wells in the eastern subarea contained water from all recharge cohorts that occurred in the Mojave River between 1958 and 2011; water from 31 wells, about 65 percent of sampled wells in the eastern subarea, contained more than 10-percent modern water (figs. F.13*A*, *B*). Tritium/helium-3 ages were younger, and fractions of modern water greater, in water from wells in the eastern subarea near recharge areas along the Mojave River than elsewhere in the study area (figs. F.13*A*, *B*). Water from shallow wells along the river contained more than 50-percent modern water recharged as recently as 2011. Tritium/helium-3 ages increased and the percentage of modern water generally decreased with distance from the river. The highest fractions of modern water in the study area, near 100-percent modern water, were estimated in water from wells MW-146D1, MW-143D2, and MW-49B (fig. F.12). Water from these wells was recharged in 1993, which was the most commonly measured recharge cohort.

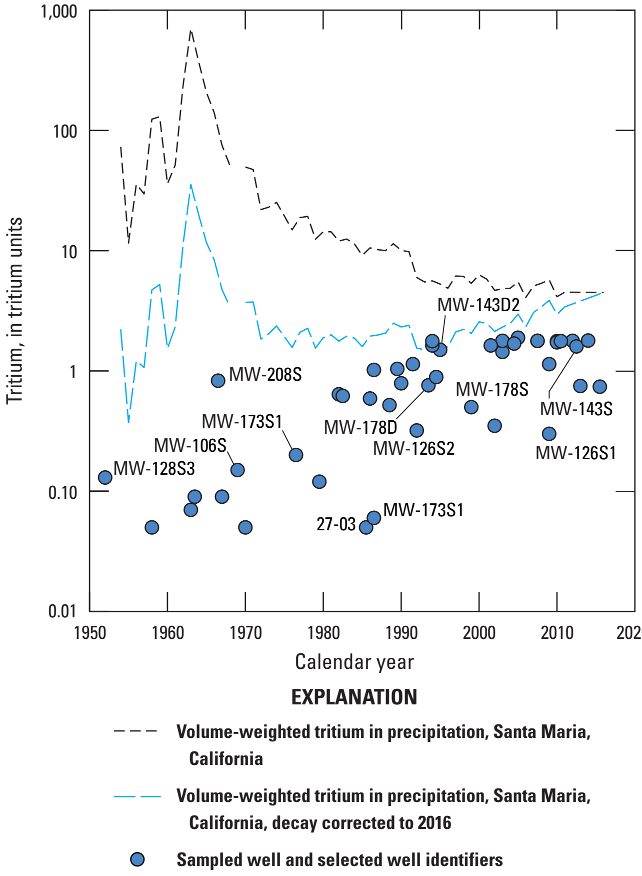
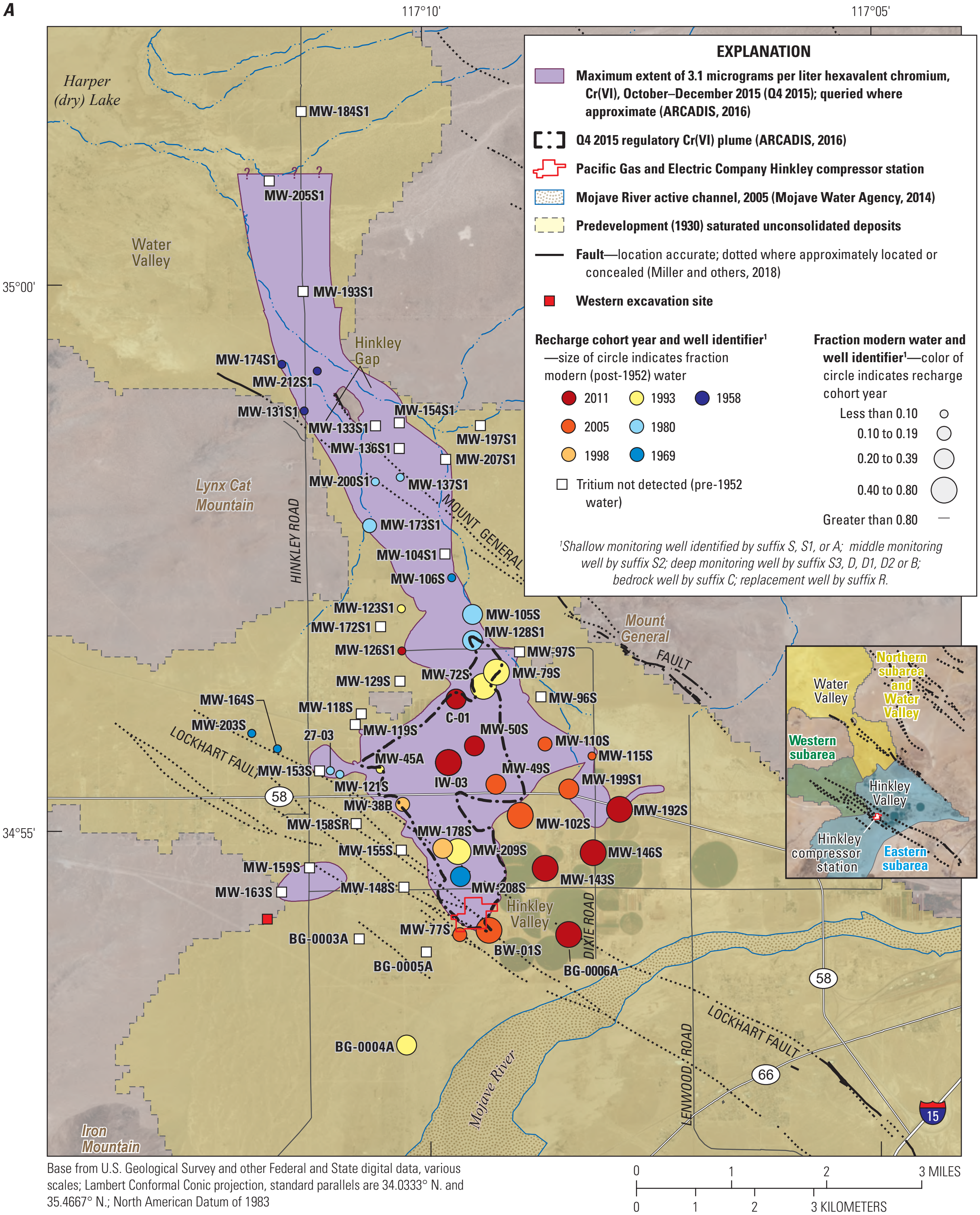
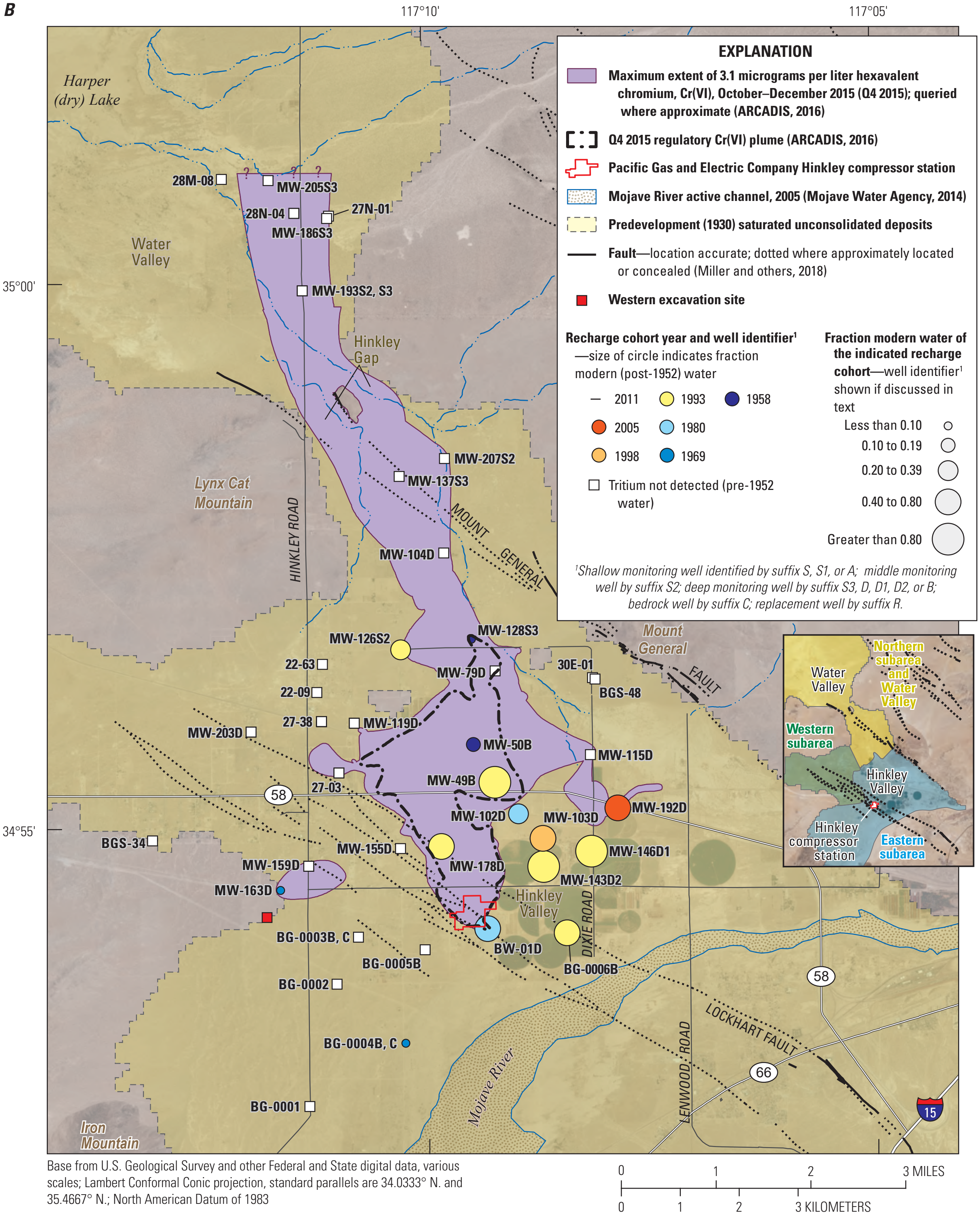


Figure F.12. Tritium and decay-corrected tritium concentrations in precipitation at Santa Maria, California, and tritium concentrations and apparent tritium/helium-3 ages (year of recharge) in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data from Santa Maria, California, are available in International Atomic Energy Agency (2020). Site data are available in chapter E (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 F.13. Recharge cohorts and fraction of post-1952 water in *A,* shallow wells and *B*, deep wells, Hinkley and Water Valleys, western Mojave Desert, California, November 2015 through March 2017. Values are available in appendix F.2 (table F.2.1) and were calculated from data available in chapter E (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 F.13.—Continued

Streamflow in 1993 produced the largest volume of recharge from the Mojave River (fig. F.2; Stamos and others, 2001; Jacobs Engineering Group, Inc. 2019). Less than 10-percent modern water was present in water from deeper wells BG-0004B and BG-0004C (fig. F.13*B*) along the Mojave River, indicating limited movement of water from the river to deeper aquifers along the river upgradient from the Lockhart fault. Less than 10-percent modern water also was measured in well MW-128S3 (fig. F.13*B*) near the leading edge of the regulatory Cr(VI) plume. Low percentages of modern water were generally associated with older recharge cohorts, consistent with the removal of water recharged during these cohorts by agricultural pumping.

Water from 11 wells screened in the shallow zone within the upper aquifer in the eastern subarea had tritiogenic helium-3 concentrations of less than 1 TU. Most of these wells were near the Mojave River, and the tritiogenic helium-3 data are consistent with recently recharged water having limited time for decay of tritium and accumulation of tritiogenic helium-3. Water from wells IW-03 and C-01 (fig. F.13*A*), farther downgradient from the river, also had low tritiogenic helium-3 concentrations and contained as much as 50-percent modern water estimated to have been recharged in 2011. Wells IW-03 and C-01 are extraction wells used by PG&E to pump chromium-containing groundwater to agricultural fields for remediation within the underlying soil. Younger groundwater could have moved rapidly through permeable deposits within the aquifer toward these pumping wells. However, it also is possible that helium may have been lost to the atmosphere when water was pumped to the surface for irrigation, resulting in younger tritium/helium-3 ages in irrigation return water that do not accurately reflect the time since recharge from the Mojave River.

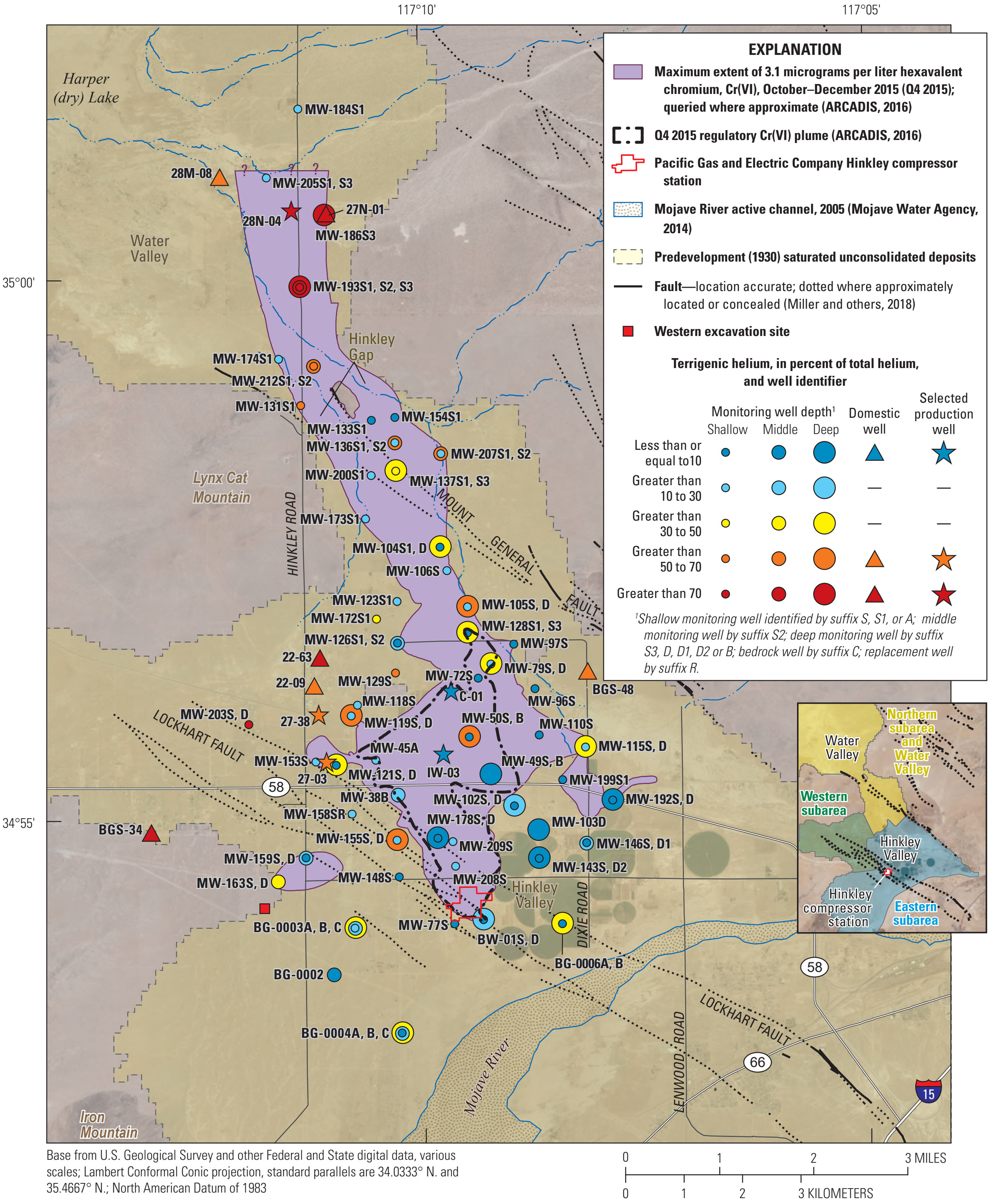
In the western subarea, water recharged in 1980 was present in wells MW-121S and 27-03, and water recharged in 1969 was present in wells MW-164S and MW-203S (figs. F.13*A*, *B*). None of these wells contained greater than 10-percent modern water (figs. F.13*A*, *B*).

In the northern subarea, water recharged after 1980 was present in most shallow wells upgradient from the Mount General fault. Water from wells MW-105S and MW-173S1 had modern water fractions greater than 10 percent (fig. F.13*A*). Shallow monitoring well MW-105S is just north of the leading edge of the mapped Q4 2015 regulatory plume and contained 31-percent modern water recharged in 1980, which is similar to the 34-percent modern water recharged in 1980 in nearby well MW-128S1 within the Q4 2015 regulatory Cr(VI) plume (fig. F.13*A*). Water from well MW-126S1, just north of the Q4 2015 regulatory plume, had 2011 water. The young apparent age is likely related to loss of helium in irrigation return water within the well. In contrast, water from deeper well MW-126S2 at the same site contained 21-percent modern water recharged in 1993 and did not seem to be affected by helium loss, although it also contained irrigation return water (fig. F.13*B*). Well MW-126S2 is not isolated from the surface by an intervening clay layer and was the only deeper well in the northern subarea containing post-1952 water. Small fractions of modern water (less than 10 percent) recharged in 1958 were present in water from wells MW-131S1, MW-174S1, and MW-212S1 in the southern part of Water Valley (fig. F.13*A*).

F.4.1.3. Terrigenic Helium

Terrigenic helium originates from the decay of uranium and thorium in aquifer solids, or from the upward migration of helium from deep crustal or mantle sources (Andrews and Lee, 1979; Stute and others, 1992). Terrigenic helium was estimated as part of the tritium/helium-3 groundwater-age calculations. Previous investigations have determined that terrigenic helium from radiogenic, crustal, and mantle sources is present in groundwater within the Mojave River groundwater basin with concentrations increasing along groundwater-flow paths and as mantle-derived helium migrates through faults (Kulongoski and others, 2003). Terrigenic helium can be used to estimate the age of older groundwater if radiogenic, crustal, and mantle accumulation rates can be quantified (Solomon, 1999). In this study, terrigenic helium was used qualitatively to compare relative ages of older groundwater recharged before the release of Cr(VI) from the Hinkley compressor station.

Total dissolved helium concentrations ranged from 4.6×10^{-5} to 2.6×10^{-3} cm^3 at standard temperature and pressure per kilogram of water, and delta helium-3 values ranged from −83.9 to 12.2 percent (chapter E, appendix E, table E.1.1), relative to an air standard having a helium-3/helium-4 ratio of 1.384×10^{-6} (Clarke and others, 1976). Both values fall within the ranges of concentrations and delta helium-3 values measured elsewhere in the Mojave River groundwater basin (Kulongoski and others, 2003). Terrigenic helium concentrations, calculated as helium exceeding contributions from atmospheric equilibrium and excess air during recharge (eqs. F.3, F.4), are expressed as a percentage of the total helium in the sample (eq. F.5). Terrigenic helium ranged from less than 10 percent to greater than 70 percent of total helium in water from sampled wells in Hinkley and Water Valleys, Calif. (fig. F.14).



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 F.14. Terrigenic helium, as a percentage of total helium, in water from wells, Hinkley and Water Valleys, California, March 2015 through November 2017. Values are available in appendix F.2 (table F.2.1) and were calculated from data available in chapter E (appendix E.1, table E.1.1.) and U.S. Geological Survey (2021).

Terrigenic helium was generally lower in the eastern subarea, which had a median value of 7.6 percent. The lowest percentages were measured in water from wells near recharge areas along the Mojave River. All samples with less than 5-percent terrigenic helium had detectable tritium. Terrigenic helium percentages were higher in the western subarea, deep wells in the northern subarea, and in Water Valley, with median values of 45, 54, and 71 percent, respectively. Water having greater than 50-percent terrigenic helium was present in 8 of 19 sampled wells in the western subarea, 3 of 6 deep wells in the northern subarea, and 10 of 12 sampled wells in Water Valley (42, 50, and 83 percent, respectively.) The highest terrigenic helium percentages were measured in water from wells MW-193S1, MW-193S2, MW-193S3, MW-186S3, 27N-01, and 28N-04 in Water Valley; MW-203S (helium concentrations in MW-203D were not measured because of laboratory issues) and domestic well BGS-34 in the western subarea; and domestic well BGS-48 in the eastern subarea. High terrigenic helium percentages result from accumulation of helium as groundwater age increases and where present are indicative of older water in wells.

In contrast to previous work near active faults in the Mojave Desert (Kulongoski and others, 2003), terrigenic helium percentages were not elevated in water from wells near the Lockhart or Mount General faults. The data reflect the relative inactivity (and limited outgassing of mantle volatiles) along these faults. Consistent with accumulation of terrigenic helium in older groundwater, terrigenic helium percentages were significantly correlated to carbon-14 activities (discussed in the following section), with terrigenic helium increasing as carbon-14 activities decreased (Kendall's tau [β] = −0.58, p-value <0.001; fig. F.15).

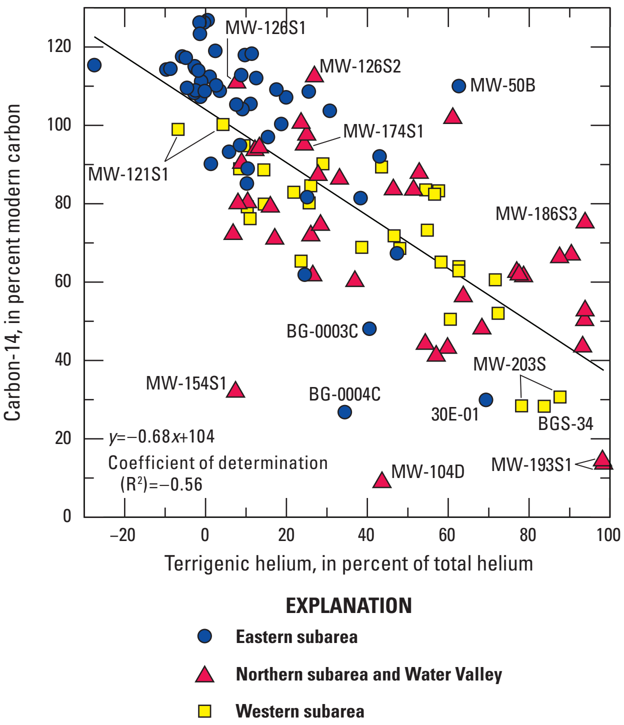


Figure F.15. Carbon-14 activities as a function of percentage of terrigenic helium in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Values are available in appendix F.2 (table F.2.1) and were calculated from data available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

F.4.2. Carbon-14 and Carbon-13 Age Dating

Carbon-14, a radioactive isotope of carbon produced naturally by interactions of cosmic rays and nitrogen gas in the atmosphere, has a half-life of about 5,730 years (Godwin, 1962; Mook, 1980). Carbon-14 is oxidized to carbon dioxide in the atmosphere, dissolves in precipitation, and enters Earth's hydrologic and biologic cycles. Unlike tritium, carbon is not part of the water molecule; however, carbon-14 is incorporated into groundwater as dissolved carbonate species during recharge. After recharge, carbon-14 is isolated from the atmosphere and decays with time.

The carbon-14 activity of DIC in groundwater is expressed as pmc relative to the carbon-14 activity in the standard National Bureau of Standards Oxalic Acid I (Stuiver and Polach, 1977, formerly known as National Bureau of Standards OxI, prepared in 1958). Modern carbon is defined as 95 percent of the carbon-14 activity in National Bureau of Standards Oxalic Acid I in the year 1950, which is equal to 0.95 multiplied by 13.56 disintegrations per minute per gram of carbon or 12.88 disintegrations per minute per gram of carbon (Kalin, 1999; Plummer and Glynn, 2013). This value is equal to 100 pmc. Samples that have a carbon-14 activity of less than 12.88 disintegrations per minute per gram of carbon have less than 100 pmc. National Bureau of Standards Oxalic Acid I is no longer available, and the National Institute of Standards and Technology New Oxalic Acid standard SRM-4990C (Stuiver and Polach, 1977, formerly known as National Bureau of Standards OxII, prepared in 1974) was used.

Testing of nuclear weapons beginning in 1952 produced carbon-14 in addition to tritium in the atmosphere (fig. F.9*A*; Solomon and Cook, 1999), and carbon-14 activities may exceed 100 pmc in aquifers where modern-age groundwater is present. Carbon-14 activities are used to estimate the age of DIC in groundwater on scales ranging from recent to more than 20,000 ybp.

The carbon-14 age of DIC in groundwater can be estimated from the equation for radioactive decay according to

$$t = -\frac{t_{1/2}}{\ln 2}\ln\left(\frac{A}{A_o}\right) \qquad \text{(F.6)}$$

where

t is the carbon-14 age (time since recharge) of DIC in groundwater, in ybp;

$t_{1/2}$ is the half-life of carbon-14, equal to 5,730 years;

A is the measured carbon-14 activity of DIC in the water sample; and

A_o is the initial carbon-14 activity of DIC in the water sample at the time of recharge.

Uncertainties in carbon-14 dating originate from (1) determining the initial carbon-14 activity of DIC in the water sample at the time of recharge (A_o) and (2) determining the extent that the carbon-14 activity of DIC in groundwater has been altered by chemical reactions (including isotopic exchange) between constituents dissolved in groundwater and aquifer materials.

The initial carbon-14 activity of DIC in groundwater at the time of recharge is rarely equal to 100 pmc because of reactions that occur between infiltrating water, soil gases (primarily carbon dioxide), and carbonate minerals in the unsaturated zone (Mook, 1980; Kalin, 1999). To account for reactions that alter the initial carbon activity, A_o is typically estimated using either mass-balance approaches that adjust for geochemical reactions affecting carbon-14 (Plummer and others, 1991; Han and Plummer, 2016) or using empirical approaches that determine A_o from the maximum carbon-14 activity of the youngest samples recharged before the advent of the atmospheric testing of nuclear weapons (Verhagen and others, 1974; Geyh, 2005; Plummer and Glynn, 2013). Using an empirical approach, Izbicki and Michel (2004) reported an A_o value of 84 pmc for the Mojave River groundwater basin from measurements of the maximum carbon-14 activity of water from wells not having detectable tritium. In this study, carbon-14 ages calculated assuming radioactive decay and an initial carbon-14 activity of 100 pmc are referred to as “unadjusted ages” and represent a maximum groundwater age. Adjusted carbon-14 ages also were calculated assuming an A_o value of 84 pmc for modern groundwater recharge (Izbicki and Michel, 2004) and using isotope mass-balance approximations with carbon-13.

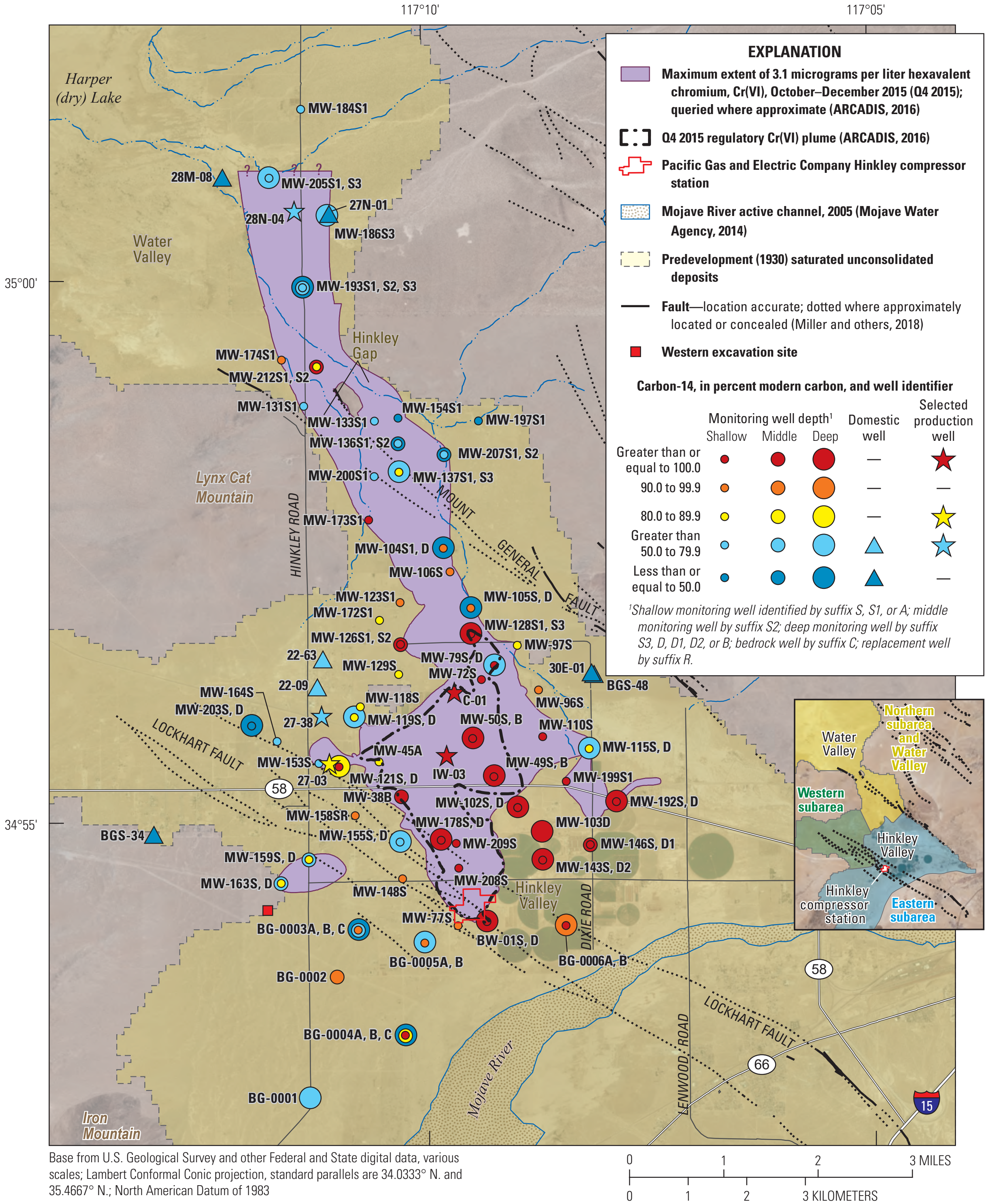
Chemical reactions between constituents dissolved in groundwater and aquifer materials may add carbon that does not contain carbon-14 to the dissolved phase or remove carbon that may contain carbon-14 from the dissolved phase. In both cases, these reactions result in a reduction of the carbon-14 activity originally present in the sample, which results in a calculated carbon-14 age that is older than the actual age of the groundwater. In this study, carbon-13, a naturally occurring stable isotope of carbon, was used to evaluate chemical reactions that occur within the aquifer.

F.4.2.1. Carbon-14 and Carbon-13 Results

Dissolved inorganic carbon-14 activities ranged from 8.9 to 127 pmc in water from sampled wells in Hinkley and Water Valleys (fig. F.16; chapter E, appendix E.1, table E.1.1). The spatial distribution of carbon-14 activities was similar to the distribution of tritium with generally higher activities, commonly exceeding 100 pmc, associated with post-1952 water from wells near the Mojave River. Like tritium, carbon-14 activities decreased with increasing distance from the river. Water from wells within the footprint of the Q4 2015 regulatory Cr(VI) plume had carbon-14 activities greater than 100 pmc, with the exception of MW-45A and deep well MW-79D, which had activities of 89 and 67 pmc, respectively. Several deeper wells within the footprint of the Q4 2015 regulatory Cr(VI) plume including MW-49B, MW-50B, and MW-128S3 had carbon-14 activities greater than 100 pmc. Carbon-14 activities greater than 100 pmc also were present in water from wells MW-126S1 and S2 downgradient from the Q4 2015 regulatory Cr(VI) plume.

The delta carbon-13 values of DIC in water from sampled wells ranged from −16 to −5.6 per mil (fig. F.17; chapter E, appendix E.1, table E.1.1). Carbon-13 is an indicator of processes affecting the groundwater carbonate system because of large differences in the carbon isotope composition of carbonate minerals and organic matter within aquifer materials relative to the initial groundwater DIC. An initial delta carbon-13 value of about −12.5 per mil is typical for DIC in recently recharged groundwater (Clark and Fritz, 1997).

Dissolution of carbonate minerals, or isotopic exchange of DIC with minerals, tends to increase delta carbon-13 values because carbonate minerals generally have delta carbon-13 values greater than (less negative than) −12.5 per mil. The estimated delta carbon-13 value of carbonate minerals in Hinkley and Water Valleys is −4.1 per mil. This value is based on the average of four samples of core material having delta carbon-13 values ranging from −4.7 to −3.7 per mil measured as part of this study (table F.3). Core materials from sites MW-119 (at 107.5 ft bls composed of groundwater-discharge deposits) and MW-154 (at 85 ft bls composed of mudflat/playa deposits) were not used to calculate the average delta carbon-13 value of aquifer materials. The delta carbon-13 value of −4.1 per mil is similar to the −4.5 per mil value of aquifer carbonates in the Mojave River groundwater basin (Izbicki and others, 1995) and to the carbon isotope composition of aquifer materials elsewhere in the southwestern United States (Robertson, 1992).



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 F.16. Measured carbon-14 activities in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

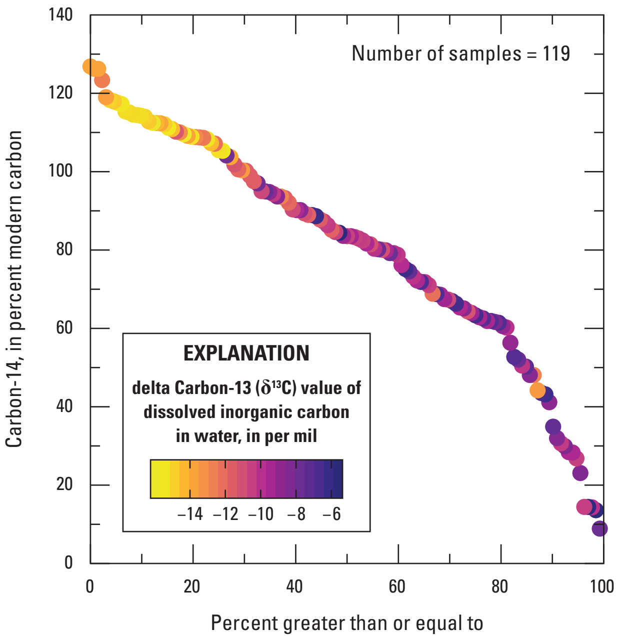


Figure F.17. Carbon-14 and delta carbon-13 values of dissolved inorganic carbon in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. (VPDB, Vienna PeeDee Belemnite carbon isotope standard; Gonfiantini, 1978). Data are available in chapter E (appendix E.1, table E.1.1.) and U.S. Geological Survey (2021).

Table F.3. The inorganic delta carbon-13 values of core material from selected well sites, Hinkley Valley, western Mojave Desert, California.

[Data are available in U.S. Geological Survey (2021). Locations are shown in figure F.1. Analysis by U.S. Geological Survey, Reston Stable Isotope Laboratory, Reston, Virginia. **Abbreviations**: PG&E, Pacific Gas and Electric Company; USGS, U.S. Geological Survey; per mil, parts per thousand (‰) difference]

PG&E site name	State well number	USGS site number	Sample depth, in feet below land surface	Core material delta carbon-13/carbon-12, in per mil
MW-203S	010N003W28F033S	345552117115703	84	−3.7
MW-153S	010N003W27N011S	345531117111201	109	−3.9
MW-121D	010N003W27P005S	345529117105801	119	−4.0
MW-119	010N003W27G010S	345557117104801	107.5	0.4
MW-119	010N003W27G010S	345557117104801	120	−4.7
MW-154	010N003W11D004S	345842117101702	85	−2.3

Carbon added to DIC in groundwater from respiration of organic matter, whether from autotrophic respiration by plant roots or heterotrophic respiration by microorganisms (Hanson and others, 2000), tends to decrease delta carbon-13 values because organic matter generally has values of less than (more negative than) −12.5 per mil. The delta carbon-13 of organic carbon in aquifer materials is about −21 per mil for marine deposits and −28 per mil for continental deposits (Izbicki and Michel, 2004).

In water from wells in Hinkley and Water Valleys, delta carbon-13 values of DIC were greater than and less than the typical value for DIC in recently recharged groundwater of −12.5 per mil. Samples containing modern water, based on carbon-14 activities greater than 100 pmc, were generally affected by microbial respiration of organic material within the aquifer. The median delta carbon-13 value of −14.4 per mil in water from wells having carbon-14 activities greater than 100 pmc is similar to the median delta carbon-13 value of −14.3 per mil reported in a global study of recently recharged groundwater (Gleeson and others, 2015; Jasechko, 2016). In contrast, samples having carbon-14 activities less than 100 pmc were generally affected by dissolution of carbonate minerals within the aquifer (fig. F.17). The results indicate that respiration of organic matter and reactions with carbonate minerals in aquifer material have altered groundwater carbon-14 activities, and actual groundwater ages are younger than unadjusted carbon-14 ages.

F.4.2.2. Carbon-14 Activities of Modern Groundwater

In 1963, after the peak of atmospheric testing of nuclear weapons in the northern hemisphere, carbon-14 activities in the atmosphere and precipitation were as high as 183 pmc (fig. F.9*A*). By 1969, when the first large modern (post-1952) Mojave River streamflows occurred, carbon-14 activities had decreased by 15 percent to 155 pmc. In contrast, there was a fourteenfold decrease in tritium concentrations in precipitation at Santa Maria, Calif., from 700 to 50 TU during the same period, and much of the tritium in precipitation associated with the atmospheric testing of nuclear weapons did not enter groundwater in Hinkley and Water Valleys because of limited streamflow and groundwater recharge from the Mojave River during this period (fig. F.2). In addition, because of its longer 5,730-year half-life, decay of carbon-14 between 1969 and sample collection was minimal. For these reasons, carbon-14 may be a more robust and easily detected tracer of modern-age groundwater in the study area than tritium. Tritium concentrations and carbon-14 activities in precipitation have decreased to near natural levels since the signing of the Nuclear Test Ban Treaty in 1963 (fig. F.9*A*).

Carbon-14 activities greater than 100 pmc in DIC (fig. F.18*A*) result solely from the presence of modern (post-1952) groundwater. Carbon-14 activities greater than 100 pmc were measured in water from 31 wells, including wells near recharge areas along the Mojave River, most wells within the Q4 2015 regulatory Cr(VI) plume, and wells in the northern subarea as far downgradient as wells MW-126S1 and MW-126S2 (fig. F.16). Water from most sampled wells having carbon-14 activities greater than 100 pmc had detectable tritium concentrations greater than 1 TU, although water from well MW-128S3 near the leading edge of the Q4 2015 regulatory Cr(VI) plume and associated with the 1958 recharge cohort (fig. F.13*B*) had a carbon-14 activity of 104 pmc and a tritium concentration of 0.13 TU (fig. F.18*A*). Similarly, in March 2015, well MW-121S in the western subarea had a carbon-14 activity of 100 pmc and a tritium concentration of 0.09 TU. Water from well MW-174S1 near the leading edge of the tritium front in the southern part of Water Valley had a tritium concentration of 0.17 TU and a carbon-14 activity of 95 pmc.

The initial carbon-14 activity of modern water recharged within the Mojave River groundwater basin (A_o) was 84 pmc based on a previous study (Izbicki and Michel, 2004). This value is consistent with data from Hinkley and Water Valleys, where most samples having a carbon-14 activity greater than 87 pmc also have detectable tritium greater than 0.1 TU (fig. F.18*A*). Water from wells having tritium concentrations between 0.1 TU and the SRL of 0.05 TU have a wide range of carbon-14 activities as low as 14 pmc (fig. F.18*A*). Water samples from 12 wells with tritium concentrations less than 0.1 TU have carbon-14 activities greater than the A_o of 84 pmc and contain at least some modern water (fig. F.18*A*). These wells include MW-45A within the Q4 2015 regulatory Cr(VI) plume, wells MW-121S and MW-121D in the western subarea near the margin of the regulatory Cr(VI) plume, and wells MW-123S1 and MW-104S1 in the northern subarea downgradient from the regulatory Cr(VI) plume, with the remaining wells largely upgradient from the Lockhart fault.

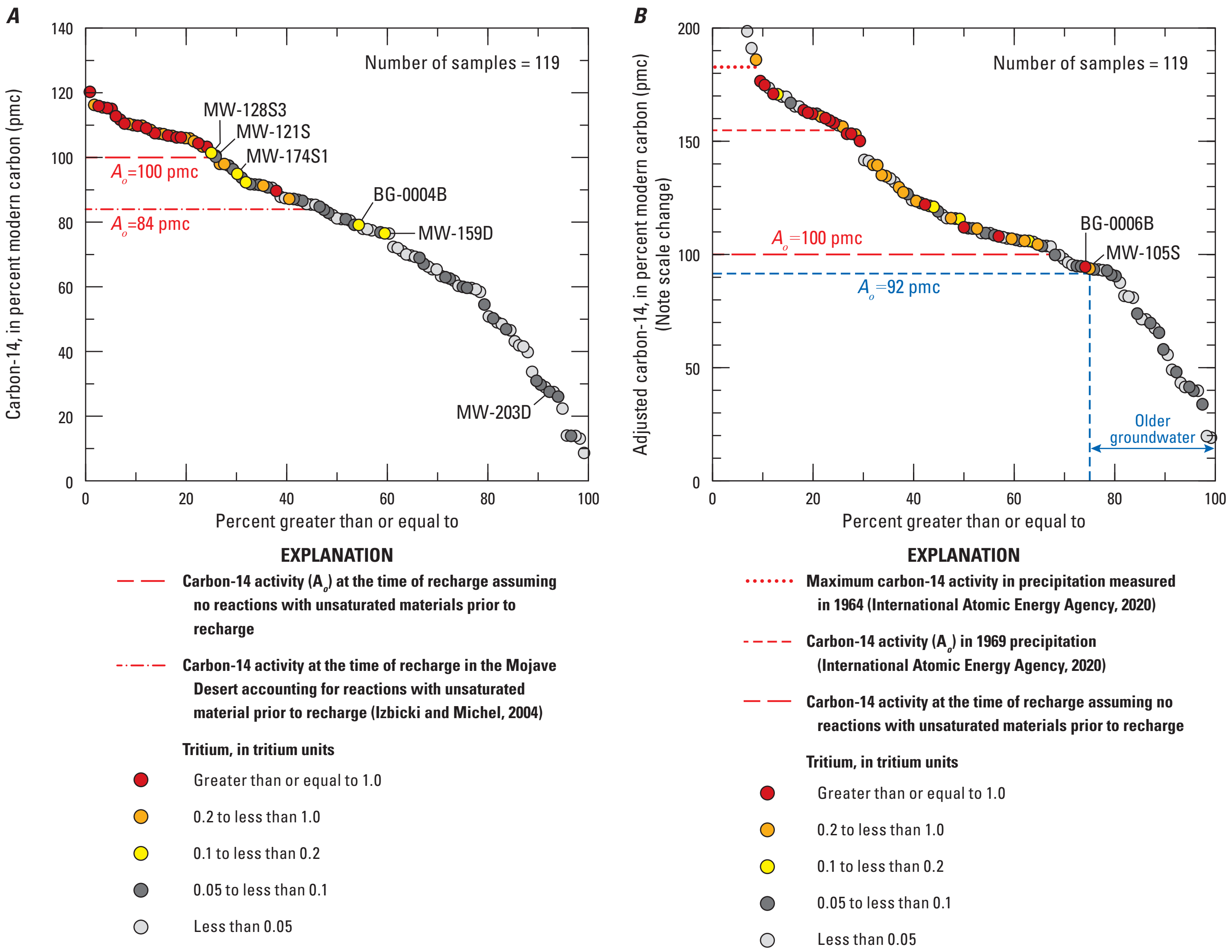


Figure F.18. Frequency distributions of carbon-14 activities. *A*, measured activities and *B*, adjusted activities, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1.) and U.S. Geological Survey (2021).

In addition to reactions with aquifer materials in the unsaturated zone before groundwater recharge, carbon-14 activities also are affected by reactions within the saturated zone after groundwater recharge. For the purposes of this study, the combined effect of reactions within the unsaturated and saturated zones on carbon-14 activities was addressed on the basis of simplified mass-balance calculations assuming (1) input of carbon from microbial respiration of organic carbon within aquifer materials having a delta carbon-13 value of −21 per mil or (2) contributions of inorganic carbon from carbonate minerals within aquifer solids having a delta carbon-13 value of −4.1 per mil. Based on measured carbon isotope compositions and the results of the mass-balance calculations, microbial respiration dominated in water from wells near recharge areas along the Mojave River, and reactions with inorganic carbonate minerals (including dissolution and isotopic exchange) dominated in water from wells farther from the river. The mass-balance calculation adjusted carbon-14 activities greater than 100 pmc for water from an additional 26 wells compared to measured carbon-14 activities. Water from all these wells has tritium concentrations of less than 0.09 TU, with water from only three wells having tritium greater than the SRL of 0.05 TU. Adjusted carbon-14 data (not shown in fig. F.16) indicate some fraction of post-1952 recharge could be present in water from shallow wells downgradient from the Q4 2015 regulatory Cr(VI) plume as far as MW-205S1, including domestic well 28M-8 along the margin of Harper (dry) Lake in Water Valley. However, comparisons of adjusted carbon-14 values with maximum carbon-14 activities in precipitation indicate that adjustments for reactions of groundwater with inorganic carbon from aquifer carbonates overestimate the extent of recent recharge in water from wells in Hinkley and Water Valleys and adjusted carbon-14 values were not used to estimate groundwater age in this professional paper.

F.4.2.3. Carbon-14 Activities and Chemistry of Older Groundwater

Water from 11 sampled wells had unadjusted carbon-14 ages greater than 10,000 ybp, and water from 24 wells had unadjusted carbon-14 ages greater than 5,000 ybp. Although the mass-balance adjustments for carbon-14 activities overestimate the presence of modern recharge in water from wells, the absence of tritium and the break in slope of the pmc frequency distribution at 92 pmc are consistent with changes in recharge patterns and indicative of older groundwater that has lower carbon-14 activities and is unlikely to contain a small fraction of modern water (fig. F.18*B*). The 92-pmc value is slightly higher than the regional A_o value of 84 pmc estimated by Izbicki and Michel (2004) and indicates that aquifer materials in Hinkley and Water Valleys are less reactive than aquifer materials regionally. Wells having adjusted carbon-14 activities less than 92 pmc include wells MW-155S and MW-155D within mapped strands of the Lockhart fault and MW-115S and MW-115D in mudflat/playa deposits in the eastern subarea. This group also includes deeper wells near the margin of the aquifer that were recharged from sources other than the Mojave River on the basis of delta oxygen-18 and delta deuterium data.

Water from 12 wells containing older groundwater based on adjusted carbon-14 activity measurements had low-level tritium activities between 0.05 and 0.09 TU. Samples that had low-level tritium activities in this range may have been affected by tritium sourced from septic discharges, agricultural activities, incomplete well development, and sample collection near the water table; therefore, these low-level tritium activities may not reflect the presence of post-1952 water. Additionally, water from well MW-193S3 may contain tritium sourced from tampering with bleach or some other unknown solution possibly poured into the well (Pacific Gas and Electric Company, 2013).

The oldest carbon-14 age was about 20,000 ybp (unadjusted for reactions with aquifer materials) in water from well MW-104D in the northern subarea about 1 mi downgradient from the Q4 2015 regulatory Cr(VI) plume (table F.4). Dissolved-oxygen concentrations in water from MW-104D were 0.2 mg/L, with correspondingly low Cr(VI) concentrations of 0.12 µg/L. The large difference in groundwater age in water from MW-104D (and in water from well MW-105D within 0.2 mi of the plume, having a carbon-14 activity of 44 pmc) compared to recent water from deeper wells within the leading edge of the Q4 2015 regulatory Cr(VI) plume may have resulted from agricultural pumping and the reversal of groundwater gradients between the early 1950s and early 1990s (Stone, 1957; California Department of Water Resources, 1967). Terrigenic helium concentrations greater than 30 percent in water from wells having older groundwater (table F.4) are consistent with accumulation of terrigenic helium from decay of uranium and thorium within aquifer solids (Solomon and Cook, 1999).

The chemistry of older water from selected wells is commonly alkaline, with pH values as high as 9.5. Although most water is oxic, older water from some wells is reduced and does not contain dissolved-oxygen concentrations greater than the SRL of 0.2 mg/L. Nitrate concentrations did not exceed 0.05 mg/L as nitrogen, except in water from sampled domestic wells that may be affected by residential septic discharges. Concentrations of Cr(VI) in older water from wells completed in Mojave-type deposits are as high as 3.5 µg/L in water from well MW-115D in the eastern subarea and as high as 3.6 µg/L in water from well MW-137S3 in the northern subarea (table F.4). Concentrations of Cr(VI) in water from these wells may represent an upper limit on Cr(VI) concentrations in groundwater within Mojave-type deposits that likely approximates background Cr(VI) concentrations in the study area.

Table F.4. Selected age-tracer data and hexavalent chromium and total dissolved-chromium concentrations in water from selected wells having older groundwater, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through March 2017.

[Data are available in U.S. Geological Survey (2021). Hexavalent chromium and total dissolved chromium are filtered through 0.45-micrometer pored-sized filters with analysis by Assett Laboratories, Las Vegas, Nevada. Values rounded for presentation. Unadjusted and adjusted radiocarbon ages were calculated using initial carbon-14 activities of 100 and 84 percent modern carbon, respectively. **Abbreviations**: PG&E, Pacific Gas and Electric Company; USGS, U.S. Geological Survey; mm/dd/yyyy, month/day/year; ft bls, feet below land surface; Cr(VI), hexavalent chromium; µg/L, microgram per liter; Cr(t), total dissolved chromium; mg/L as N, milligram per liter as nitrogen; δD, delta deuterium; per mil, parts per thousand (‰) difference; $\delta^{18}O$, delta oxygen-18; $\delta^{13}C$, delta carbon-13; ^{14}C, carbon-14; pmc, percent modern carbon denormalized from laboratory values in percent modern; ybp, years before present; —, no data; delta used to denote differences in the isotopic ratio of the sample relative to differences in a standard; <, less than the value shown]

PG&E site name	USGS site identification number	Date (mm/dd/yyyy)	Depth of well (ft bls)	Cr(VI) (µg/L)	Cr(t) (µg/L)	Total nitrogen (mg/L as N)	δD (per mil)	$\delta^{18}O$ (per mil)	$\delta^{13}C$ (per mil)	^{14}C (pmc)	Unadjusted age (ybp)	Adjusted age (ybp)	Terrigenic helium, in percent of total dissolved helium
						Eastern subarea							
BG-0005B	345352117100202	05/02/2016	182	1.1	1.1	0.17	−63	−8.5	−9.3	67	3,250	1,910	—
BG-0003C	345359117104602	05/04/2016	190	1.1	0.91	0.11	−60	−8.6	−12.7	48	6,050	4,710	40
MW-79D	345625117091301	03/03/2015	165	<0.06	0.13	0.05	−60	−8.7	−10.9	67	3,270	1,920	47
MW-115D	345539117081001	03/08/2017	113	3.5	3.9	0.42	−62	−8.6	−11.1	79	1,950	435	38.3
BGS-48	345620117080601	03/09/2016	258	0.44	0.11	0.59	−61	−8.7	−8.4	23	12,100	10,800	—
30E-01	345622117080801	03/11/2015	224	1.8	1.7	0.36	−62	−8.7	−8.5	30	9,970	8,630	69
						Western subarea							
MW-155D	345448117101801	03/09/2017	152	<0.06	0.42	0.15	−61	−8.6	−10.2	51	5,650	4,300	61
MW-203D	345552117115702	03/17/2015	118	8.9	9.1	0.12	−73	−10.1	−10.0	14	16,070	14,700	—
MW-203D	345552117115702	03/15/2017	118	5.4	8.2	0.14	−74	−10.1	−10.5	14	16,000	14,700	—
BGS-34	345453117130401	03/11/2016	147	2.3	2.4	0.18	−63	−8.6	−9.7	28	10,400	9,090	84
						Northern subarea and Water Valley							
MW-104D	345730117094701	03/18/2015	140	0.12	0.16	0.07	−63	−9.0	−7.9	8.9	20,000	18,700	44
MW-133S1	345841117103302	03/15/2016	80	8.0	8.2	0.44	−61	−8.7	−9.6	70	2,950	1,650	6.8
MW-136S2	345828117101701	03/09/2015	127	<0.06	0.55	0.22	−61	−8.6	−8.8	41	7,340	6,000	57
MW-137S3	345812117101601	03/10/2015	117	3.6	3.7	0.31	−60	−8.7	−10.2	60	4,190	2,850	37
MW-154S1	345842117101702	03/12/2015	85	11	9.8	0.56	−61	−8.7	−8.6	31	9,700	8,360	7.4
MW-193S3	345955117112002	03/12/2015	145	0.19	2.8	0.03	−68	−9.1	−5.6	14	16,490	15,100	98
MW-193S3	345955117112002	03/09/2016	145	0.48	0.61	0.06	−68	−9.1	−5.9	14	16,000	14,700	98
MW-197S1	345841117092303	03/16/2016	68.5	1.1	1.1	0.05	−79	−9.5	−7.6	35	8,700	7,360	—
MW-207S2	345822117094601	03/17/2016	109.5	3.5	3.5	0.19	−62	−8.7	−8.6	48	6,050	4,700	68
27N-01	350036117110301	03/09/2016	175	1.7	2	0.14	−76	−9.4	−6.6	44	6,880	5,540	93

F.4.3. Industrial Gas Age Dating

Chlorofluorocarbons (CFCs), marketed as Freons, are synthetic organic compounds that were produced commercially beginning in the 1930s for industrial and refrigerant applications. Trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) were used primarily as coolants for refrigeration and air conditioning and as propellants in aerosol cans, whereas trichlorotrifluoroethane (CFC-113) was used mainly as a solvent in the electronics industry (Plummer and Busenberg, 1999). Concentrations of CFCs in the atmosphere closely tracked commercial production, increasing until peak atmospheric concentrations were reached in the 1990s and decreasing thereafter (fig. F.9*B*). Chlorofluorocarbons are contributors to ozone depletion (Plummer and Busenberg, 1999). Decreases in atmospheric CFC concentrations since the 1990s were a result of decreases in CFC production beginning in 1987 after the signing of the Montreal Protocol (United Nations, 2020) and subsequent strengthening of the protocol in 1990 and 1992 (Plummer and Busenberg, 1999).

Chlorofluorocarbons dissolve in precipitation and are incorporated into groundwater during recharge. The development of techniques to measure low concentrations of CFCs in water within environmental ranges in equilibrium with atmospheric concentrations enabled the use of CFCs as tracers of young groundwater (Bullister, 1984; Bullister and Weiss, 1988; Busenberg and Plummer, 1992; Plummer and Busenberg, 1999, 2006). Using this approach, groundwater that has measurable CFC-12, CFC-11, and CFC-113 within environmental ranges in equilibrium with atmospheric concentrations was recharged or contains a fraction of water that was recharged after 1945, 1950, and 1957, respectively.

Sulfur hexafluoride is a stable gas with electrical insulating properties that are useful in high-voltage electrical switches and transformers (Plummer and Busenberg, 1999; Busenberg and Plummer, 2006). Sulfur hexafluoride has accumulated in the atmosphere since substantial industrial production began in the 1960s (fig. F.9*B*; Plummer and Busenberg, 1999; Busenberg and Plummer, 2006). Sulfur hexafluoride dissolves in precipitation and is incorporated into groundwater during recharge. Measurement of sulfur hexafluoride concentrations in water at low concentrations within environmental ranges in equilibrium with atmospheric concentrations enabled the use of sulfur hexafluoride as a tracer of young groundwater recharged since about 1970 (Busenberg and Plummer, 1997, 2006; Plummer and Busenberg, 1999). The use of sulfur hexafluoride as a tracer of young groundwater is complicated by the presence of geologic sources of sulfur hexafluoride derived from igneous rocks and minerals (Busenberg and Plummer, 2000; Deeds and others, 2008), but sulfur hexafluoride has successfully been used to estimate groundwater age in sandy and fractured-rock aquifers of the eastern United States and other areas (Busenberg and Plummer, 1997; Plummer and others, 2001; Lindsey and others, 2003). In contrast to sulfur hexafluoride, CFCs have no known geologic source.

Groundwater ages are determined from industrial gas data by converting measured groundwater concentrations to equilibrium concentrations in air (expressed as a dry air concentration, in parts per trillion by volume) based on Henry's law and comparing the dry air equilibrium concentrations to known historical atmospheric concentrations (fig. F.9*B*). The solubilities of CFCs depend on temperature, pressure, and salinity of water at the time of recharge, and groundwater concentrations also can be affected by entrapment of excess air. This study used recharge temperatures and excess air determined from dissolved gas measurements of neon, argon, and nitrogen in water from wells (see section "F.3.2 Noble Gases, Recharge Temperature, and Excess Air") to calculate equilibrium CFC and sulfur hexafluoride concentrations and correct for excess air.

In addition to atmospheric sources, CFCs and sulfur hexafluoride can be added to water from local anthropogenic sources. Local anthropogenic CFC sources include recharge from rivers carrying sewage effluent, leaking septic tanks or sewer lines, and leaking landfills. Local anthropogenic sulfur hexafluoride sources include high-voltage electrical supply equipment and landfills (Plummer and Busenberg, 1999; Cook and others, 2006; Darling and others, 2012).

In this study, the term "environmental concentrations" is used to refer to CFC or sulfur hexafluoride concentrations less than the dry air equilibrium concentration expected from the maximum atmospheric concentration. In groundwater age-dating studies, CFC concentrations expected from atmospheric concentrations rarely exceed a few parts per billion and are much lower than concentrations from other sources that have been identified as a human health concern in drinking water. For reference, the California maximum contaminant levels (MCLs) for CFC-11 and CFC-113 are 0.15 and 1.2 mg/L, respectively (State Water Resources Control Board, 2019). No MCL is defined by the State of California for CFC-12, but CFC-12 has a notification level of 1 mg/L (State Water Resources Control Board, 2018). Sulfur hexafluoride does not have an MCL or notification level defined by the State of California (State Water Resources Control Board, 2018, 2019). Sample concentrations exceeding the maximum dry air concentrations of 281, 564, and 89 parts per trillion by volume (pptv) for CFC-11, CFC-12, CFC-113, respectively, and 10.5 pptv for sulfur hexafluoride, are not suitable for comparison with atmospheric concentrations for groundwater age-dating purposes.

F.4.3.1. Chlorofluorocarbons

Chlorofluorocarbons were detected in water from all wells sampled in this study, including water from wells having no detectable tritium and low carbon-14 activities (appendix F.1, table F.1.1). Water samples that do not have detectable tritium contain water recharged before 1952. The maximum CFC-11 and CFC-12 concentrations in the atmosphere before 1952 were about 1 and 10 pptv (fig. F.9*B*), respectively, and CFC-113 was not present in quantities significant for groundwater-age dating before 1957. Of the samples in this study that did not have measurable tritium, none of the samples had CFC-11 concentrations of less than 1 pptv, and only three samples (from wells MW-136S2, MW-207S2, and domestic well 28M-08) had CFC-12 concentrations of less than 10 pptv. The presence of CFCs in older water, at concentrations higher than their maximum atmospheric concentrations before 1952, indicates that water from most wells in Hinkley and Water Valleys is affected to some degree by nonatmospheric sources of CFCs. The detection of CFCs in groundwater without measurable tritium and with low carbon-14 activities has been reported in other locations in California (Deeds and others, 2012) and the American Southwest (Bexfield and others, 2012).

Concentrations of CFC-11, CFC-12, and CFC-113 exceeded their respective maximum dry air equilibrium concentrations in 25, 9, and 11 percent of wells, respectively (appendix F.1, table F.1.1), and CFC concentrations in these wells were not suitable for groundwater-age dating. Possible sources contributing to CFC concentrations higher than expected on the basis of equilibrium with maximum atmospheric concentrations include CFCs from industrial activities, septic system discharges, sewage effluent, agrochemicals, and discarded refrigerators or aerosol cans (Busenberg and Plummer, 1992; Höhener and others, 2003; Darling and others, 2012). Small quantities of CFCs can greatly affect groundwater concentrations; for example, only 0.1 mL of CFC-12 would be required to raise concentrations to modern levels in a pristine aquifer 0.4 mi^2 in area with 500 ft of saturated thickness and a porosity of 0.2; standard domestic refrigerators of older design can contain as much as 1,000 mL of CFC-12 (Morris and others, 2006). Concentrations of CFCs within the environmental range that appear suitable for groundwater-age dating also may be affected by nonatmospheric sources.

To evaluate environmental concentrations and nonatmospheric CFC sources, SRLs were established following the approach of Deeds and others (2012). Empirical distribution functions of CFC concentrations were constructed for each CFC from a subset of samples of older groundwater collected from deep or intermediate short-screened monitoring wells (table F.4). These samples did not have detectable tritium, had nitrate concentrations less than the background concentration of 2 mg/L as nitrogen in the western Mojave Desert (Christensen and Fields-Garland, 2001; Izbicki and others, 2015; Metzger and others, 2015), and had CFC concentrations within environmental concentration ranges less than equilibrium with their maximum atmospheric concentrations. Data were ranked using the Blom formula (Blom, 1958), and SRLs were defined as the 95-percent confidence interval of each empirical distribution function (Deeds and others, 2012). This approach identified 19 samples, from 17 wells, as deep and old. Samples from water-table well MW-154S1, which was susceptible to atmospheric contributions of CFCs during sample collection, and samples from domestic wells, which may be susceptible to contributions of CFC from nearby septic systems, were not used to calculate SRLs. The CFC-11, CFC-12, and CFC-113 SRLs estimated using this approach were 187, 145, and 53 pptv, respectively; assuming piston flow, these concentrations correspond to recharge years of 1982, 1971, and 1986, respectively. Given these high SRLs, it is difficult to reliably estimate groundwater ages in Hinkley and Water Valleys; therefore, CFC-11, CFC-12, and CFC-113 concentrations greater than or less than the SRLs were used as a qualitative indicator of the presence or absence of modern recharge in groundwater. After applying SRLs to CFC concentrations, 9, 56, and 19 percent of sampled wells had CFC-11, CFC-12, and CFC-113 concentrations, respectively, within the environmental concentration range suitable for age-dating purposes. These results indicate that only CFC-12 had a substantial number of samples within the environmental concentration range after applying SRLs, indicating that CFC-12 may be the most reliable CFC for estimating groundwater age in Hinkley and Water Valleys.

Most wells with screened intervals deeper than 150 ft have low CFC-12 concentrations (fig. F.19), and CFC-11 and CFC-113 had similar distributions with depth. The median CFC-12 concentration in water from shallow monitoring wells was 310 pptv, whereas the median concentration in water from deep monitoring wells was 58 pptv, which is less than the SRL of 187 pptv. The trend of decreasing CFC concentrations with depth indicates that deeper groundwater is older than shallower groundwater and is consistent with tritium and carbon-14 depth trends. A subset of samples collected from deep and intermediate wells had CFC-12 values greater than 300 pptv (fig. F.19). These samples were collected from wells in the eastern subarea. In most cases, deeper wells sampled from the same site had lower CFC-12 concentrations, consistent with the trend of increasing groundwater age with depth.

Limited interpretation of the spatial distribution of CFC-12 concentrations in Hinkley and Water Valleys indicates pre-1971 water in most deep wells in the western and northern subareas and Water Valley—with the exceptions of wells MW-126S2, MW-212S2, and MW-186S3. Some water samples shallow wells MW-131S1, MW-174S1 and MW-212S1 in the northern subarea and Water Valley had CFC-12 concentrations in the environmental concentration range that were consistent with post-1971 water. Wells MW-131S1, MW-174S1 and MW-212S1 had detectable tritium concentrations consistent with post-1952 water.

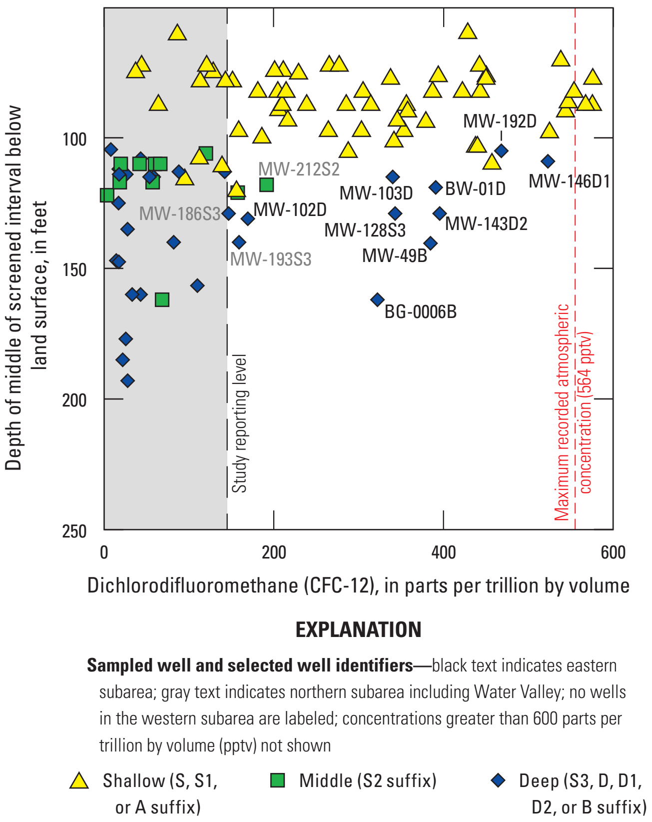


Figure F.19. Dichlorodifluoromethane (CFC-12) concentrations with depth below land surface in water from monitoring wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

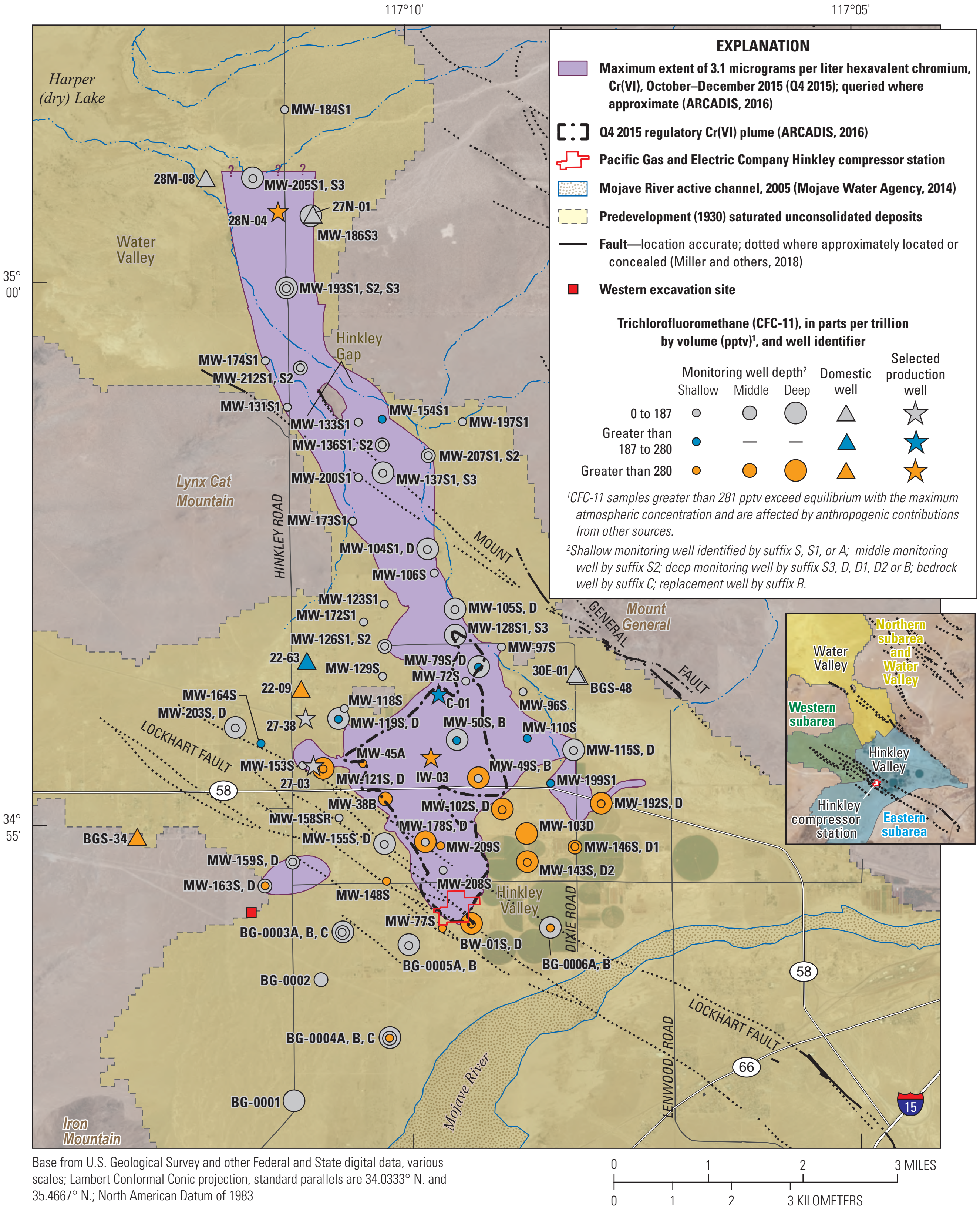
Water from 25 percent of sampled wells had high CFC-11 concentrations greater than the maximum atmospheric equilibrium concentration of 281 pptv. The spatial distribution of wells having high CFC-11 concentrations greater than 281 pptv was a contiguous mappable feature, extending from recharge areas along the Mojave River downgradient as far as production well IW-03 in the eastern subarea and wells MW-121S and MW-121D in the western subarea (fig. F.20). In addition, CFC-11 concentrations greater than the SRL of 187 pptv were present as far downgradient as well MW-79S and production well C-01 in the eastern subarea, and in water from well MW-119S in the western subarea. This spatially continuous distribution of high CFC-11 concentrations in water from wells is consistent with a common source of CFC-11 in recharge water from the Mojave River.

One possible source of these high CFC-11 concentrations is the discharge of treated sewage effluent to the Mojave River from upstream wastewater treatment plants. Previous studies have determined that sewage effluent discharged to rivers can contribute CFCs to groundwater systems recharged by infiltration of river water (Schultz and others, 1976; Busenberg and Plummer, 1992; Böhlke and others, 1997). Schultz and others (1976) determined that CFC-11 can be used as a tracer of treated sewage effluent in groundwater recharged from intermittent flows of the Santa Cruz River near Tucson, Arizona. A regional wastewater treatment plant along the Mojave River upstream from Hinkley Valley began operating in 1981. This plant treats as much as 4.5 million gallons per day of water and discharges most of the treated wastewater effluent to the Mojave River (Victor Valley Wastewater Reclamation Authority, 2017). As a consequence of these discharges, surface flows of the Mojave River would have contained treated wastewater effluent, and CFC-11 derived from treated wastewater. The high CFC-11 concentrations and tritium/helium-3 ages ranging from 1980 to 2011 for the fraction of modern water within wells MW-192S, MW-192D, MW-49B, IW-03, MW-45A, MW-121S, and MW-121D are largely consistent with groundwater containing treated wastewater recharged after 1983. The one exception is water from well MW-121D, which had CFC-11 concentrations consistent with treated wastewater discharges but did not have detectable tritium.

Uncertainty caused by CFCs associated with local anthropogenic sources limited the use of CFC data for estimating groundwater ages in this study. The CFC SRLs are high relative to environmental concentrations within dateable ranges, and some samples categorized as "deep and old" also may be affected by nonatmospheric CFC sources. However, the general spatial and depth distributions of CFC concentrations, in particular CFC-12, and high CFC-11 concentrations associated with recharge from the Mojave River containing treated wastewater after 1983 are generally consistent with the spatial and depth distributions of tritium and carbon-14. Collectively, these data indicate that groundwater near and downgradient from recharge areas along the Mojave River contains younger post-1971 water and that groundwater age increases with depth.

F.4.3.2. Sulfur Hexafluoride

Sulfur hexafluoride concentrations in water from wells in Hinkley and Water Valleys ranged from less than 0.3 to 47.9 pptv, with a median concentration of 2.1 pptv (appendix F.1, table F.1.1). The highest concentrations were measured in water from wells MW-197S1, MW-207S1, and MW-207S2 in the northern subarea downgradient from the Mount General fault. Sulfur hexafluoride concentrations greater than about 10.5 pptv exceed the maximum concentration recorded in the atmosphere and indicate that there is another source of sulfur hexafluoride in water from these wells.



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 F.20. Trichlorofluoromethane (CFC-11) concentrations in water from wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in appendix F.1 (table F.1.1) and U.S. Geological Survey (2021).

Field studies completed in volcanic (extrusive) and plutonic (intrusive) igneous settings have reported sulfur hexafluoride concentrations that in some cases exceed equilibrium with the modern atmosphere, and laboratory experiments have determined that sulfur hexafluoride is produced from granite, a type of plutonic rock (Harnisch and Eisenhauer, 1998; Busenberg and Plummer, 2000; Deeds and others, 2008). Wells MW-197S1, MW-207S1, and MW-207S2 in the northern subarea are completed in locally derived alluvium eroded in part from Miocene deposits containing volcanic material. Water from these wells did not have detectable tritium and had carbon-14 activities ranging from 35 to 62 pmc, indicating that the wells contain older groundwater. The presence of sulfur hexafluoride in wells having older groundwater and completed in alluvium containing volcanic material indicates that sulfur hexafluoride in these wells may be derived from volcanic materials in the aquifer rather than from atmospheric sulfur hexafluoride from commercial production since the 1970s.

In Water Valley, locally derived alluvium contains material eroded from basalt, a type of volcanic rock. Groundwater sulfur hexafluoride concentrations in this area are less than the maximum concentration recorded in the atmosphere but higher than expected relative to tritium concentrations and carbon-14 activities. These patterns indicate that sulfur hexafluoride concentrations in this area also are being released from volcanic materials in the alluvium. For example, in water from well site MW-193, tritium was not detected, and carbon-14 activities decreased with depth from 61 pmc in the shallow well (MW-193S1) to 14 pmc in the deepest well (MW-193S3), with unadjusted groundwater ages of 4,100 and 16,250 ybp that predate industrial releases of sulfur hexafluoride to the atmosphere. Sulfur hexafluoride concentrations at this site increased with depth and with groundwater age, indicating that sulfur hexafluoride is accumulating with contact time between groundwater unconsolidated deposits. Similarly, the highest concentrations in the western subarea were in water from well MW-203D completed within partly consolidated Miocene deposits containing volcanic material.

The results of this study are consistent with previous work indicating that sulfur hexafluoride concentrations accumulate with groundwater age in the Mojave River Basin as a result of releases from weathered volcanic materials in the aquifer (Deeds and others, 2008, 2015). The application of sulfur hexafluoride as a tracer of groundwater age relies on equilibrium with atmospheric sulfur hexafluoride at the time of recharge and is complicated by the presence of unknown amounts of sulfur hexafluoride released from materials in the aquifer (Harnisch and Eisenhauer, 1998; Busenberg and Plummer, 2000). In Hinkley Valley, sulfur hexafluoride concentrations may be suitable for estimating the age of younger water in wells completed in alluvium that does not contain volcanic material; however, groundwater ages were not estimated as part of this study from sulfur hexafluoride data.

F.4.4. Summary of Groundwater-Age Data

Modern (post-1952) water that passed near the Hinkley compressor station after Cr(VI) releases began in 1952 may contain anthropogenic Cr(VI); however, not all modern water recharged from the Mojave River would have passed near the Hinkley compressor station and would contain anthropogenic Cr(VI). Groundwater age (time since recharge) was evaluated using a suite of radioactive and industrial gas tracers. Radioactive tracers associated with the atmospheric testing of nuclear weapons beginning in 1952 included tritium, its decay product helium-3, and carbon-14. Carbon-14 and terrigenic helium also are useful for the dating of older groundwater. Industrial gases used for dating modern groundwater included CFCs (CFC-11, CFC-12, and CFC-113) and sulfur hexafluoride. Each tracer has a different environmental history associated with its release to the atmosphere, its entry into the hydrologic cycle, and reactions that may (or may not) occur between groundwater and aquifer materials.

Tritium, tritium/helium-3, and carbon-14 were the most effective tracers of modern groundwater in this study. Tritium, measured as part of this study by helium ingrowth, has an LRL of 0.01 TU. The SRL for tritium was 0.05 TU. In comparison, tritium measurements commonly used in studies of groundwater age have an LRL of about 0.2 TU. Some samples having tritium concentrations near the SRL also had carbon-14 activities less than the estimated initial carbon-14 activity at the time of recharge (A_o) of 84 pmc; most samples having tritium concentrations greater than 0.1 TU had a carbon-14 activity greater than 87 pmc, consistent with post-1952 groundwater.

Streamflow in the Mojave River is intermittent, and tritium/helium-3 recharge dates were grouped into recharge cohorts corresponding to measured Mojave River streamflows and recharge between 1958 and 2011. Streamflow in 1993 produced the largest volume of recharge from the Mojave River, and 1993 was the most commonly measured recharge cohort. In general, groundwater ages were younger near recharge areas along the Mojave River with older groundwater ages farther downgradient and at depth. Groundwater within the Q4 2015 regulatory Cr(VI) plume was young and was recharged after Cr(VI) releases from the Hinkley compressor station. Water from several deeper wells, completed in the deep zone of the upper aquifer and within the footprint of the Q4 2015 regulatory Cr(VI) plume, was recharged before releases from the Hinkley compressor station. Water containing tritium and recharged in 1958 was present as far downgradient as well MW-174S1 in the southern part of Water Valley. Tritium-containing groundwater was not present on the downgradient side of the Mount General fault in the northern subarea. Tritium was present at only low concentrations in water from wells in the western subarea with the highest concentrations in water from well MW-121S recharged in 1980. Much of the tritium-containing groundwater within the aquifer, and presumably some groundwater containing anthropogenic Cr(VI) released from the Hinkley compressor station, was removed by groundwater pumping for agriculture.

Carbon-14 activities were similar to tritium and tritium/helium-3 age dates with higher carbon-14 activities exceeding or approaching 100 pmc in water from shallow wells within the Q4 2015 regulatory Cr(VI) plume. Carbon-14 activities consistent with post-1952 water were as high as 95 pmc in water from well MW-174S1 in the southern part of Water Valley. Older groundwater was present in deeper wells downgradient from the Q4 2015 regulatory Cr(VI) plume, and water from well MW-104D, completed in the deep zone of the upper aquifer 1 mi downgradient from the margin of the Q4 2015 regulatory Cr(VI) plume, was recharged almost 20,000 ybp. Some older groundwater that predates releases from the Hinkley compressor station had Cr(VI) concentrations greater than the 3.1 μg/L interim regulatory C(VI) background concentration. For example, water from well MW-154S1, completed in mudflat/playa deposits in the northern subarea, has a carbon-14 activity of 32 pmc with an unadjusted age of 9,400 ybp and a Cr(VI) concentration of 11 μg/L, and water from well MW-203D, completed in Miocene rock, has a carbon-14 activity of 14 pmc with an unadjusted age of 16,250 ybp and Cr(VI) concentrations ranging from 5.4 to 8.9 μg/L. Hexavalent chromium concentrations in water from wells completed in Mojave-type deposits with unadjusted ages as old as 4,190 ybp were as high as 3.6 μg/L; this value may represent an upper limit on Cr(VI) concentrations in groundwater within Mojave-type deposits that likely approximates background Cr(VI) concentrations for groundwater within Mojave-type aquifer materials. The distribution of older groundwater inferred from terrigenic helium, produced by decay of radioactive uranium and thorium within the aquifer deposits and the outgassing of mantle volatiles, was similar to the distribution of older groundwater estimated from carbon-14 activities.

Industrial gases, including CFCs and sulfur hexafluoride, were analyzed as part of this study to increase the range of modern groundwater dating. Chlorofluorocarbons were detected in water from all wells sampled in this study, including water from wells having no detectable tritium and low carbon-14 activities. The data indicate water from most wells in Hinkley and Water Valleys is affected to some degree by nonatmospheric sources of CFCs, limiting the use of CFCs for groundwater dating purposes. However, qualitatively, CFC data indicate younger groundwater in shallow wells near recharge sources along the Mojave River and older groundwater farther downgradient, with older groundwater in deeper wells. Concentrations of CFC-11 associated with treated wastewater in Mojave River recharge were used to define the footprint of 1983 water recharged from the Mojave River. The extent of 1983 water estimated from CFC-11 data generally was consistent with groundwater ages estimated from tritium/helium-3 data. Sulfur hexafluoride was released from volcanic rocks within and underlying aquifer deposits. Increased concentrations of sulfur hexafluoride were not associated with the Lockhart and Mount General faults.

F.5. Strontium Isotopes

Strontium isotopes provide information on rock, minerals, and geologic materials that water has contacted within an aquifer (McNutt and others, 1990; Banner, 1995; Katz and Bullen, 1996; McNutt, 1999; Dogramaci and Herczeg, 2002). In this study, strontium isotopes were measured in water from wells to evaluate the depositional provenance of aquifer materials (Miller and others, 2018, 2020). Interpretation of strontium isotope data involves understanding processes that control rock and mineral formation throughout geologic timescales.

The four naturally occurring stable isotopes of strontium have atomic masses of 84, 86, 87, and 88. These isotopes have geologic abundances of 0.56, 9.86, 7.0, and 82.58 percent, respectively (McNutt, 1999). Geologic materials have two sources of strontium-87: primordial strontium-87 formed with the creation of strontium-84, -86, and -88 and radiogenic strontium-87 formed by the decay of rubidium-87. The half-life for decay of rubidium-87 to strontium-87 is 4.88×10^{10} years, more than three times the generally accepted age of the universe. Strontium isotope data, expressed as the ratio of strontium-87 to strontium-86, are of interest for geologic studies (Faure and Powell, 1972; Bataille and Bowen, 2012). With available techniques, this ratio can be measured accurately to within 0.00001.

Strontium has a greater affinity for substitution within calcium-containing minerals, and rubidium has a greater affinity for substitution within potassium-containing minerals (Faure and Powell, 1972). As the primordial Earth cooled, differences in mineral substitution caused rubidium and strontium abundances to differ between the mantle and early continental crust (Faure and Powell, 1972; Veizer, 1989; Bataille and Bowen, 2012). The present-day mantle strontium-87/86 ratio, estimated to range from 0.702 to 0.706 (Faure and Powell, 1972), is a result of the primordial strontium-87/86 ratio of 0.699, estimated from the composition of chondritic meteorites (Wasserburg and others, 1969), plus strontium-87 additions from the decay of rubidium-87. Given this conceptual model, the earliest crustal rocks formed about 3 billion years ago would have a strontium-87/86 ratio of about 0.720. Crustal rocks formed later would have lower strontium-87/86 ratios. Subsequent melting of the continental crust would have further altered the strontium and rubidium abundances in crustal rock, altering the rubidium/strontium ratio and the strontium-87/86 ratio of those rocks, as rubidium-87 decayed to strontium-87 over geologic time. Collectively, these processes result not only in large-scale differences in the strontium-87/86 ratio of mantle and continental rocks but also in differences in the strontium-87/86 ratio at smaller scales between rocks and minerals and in alluvium eroded from different geologic materials.

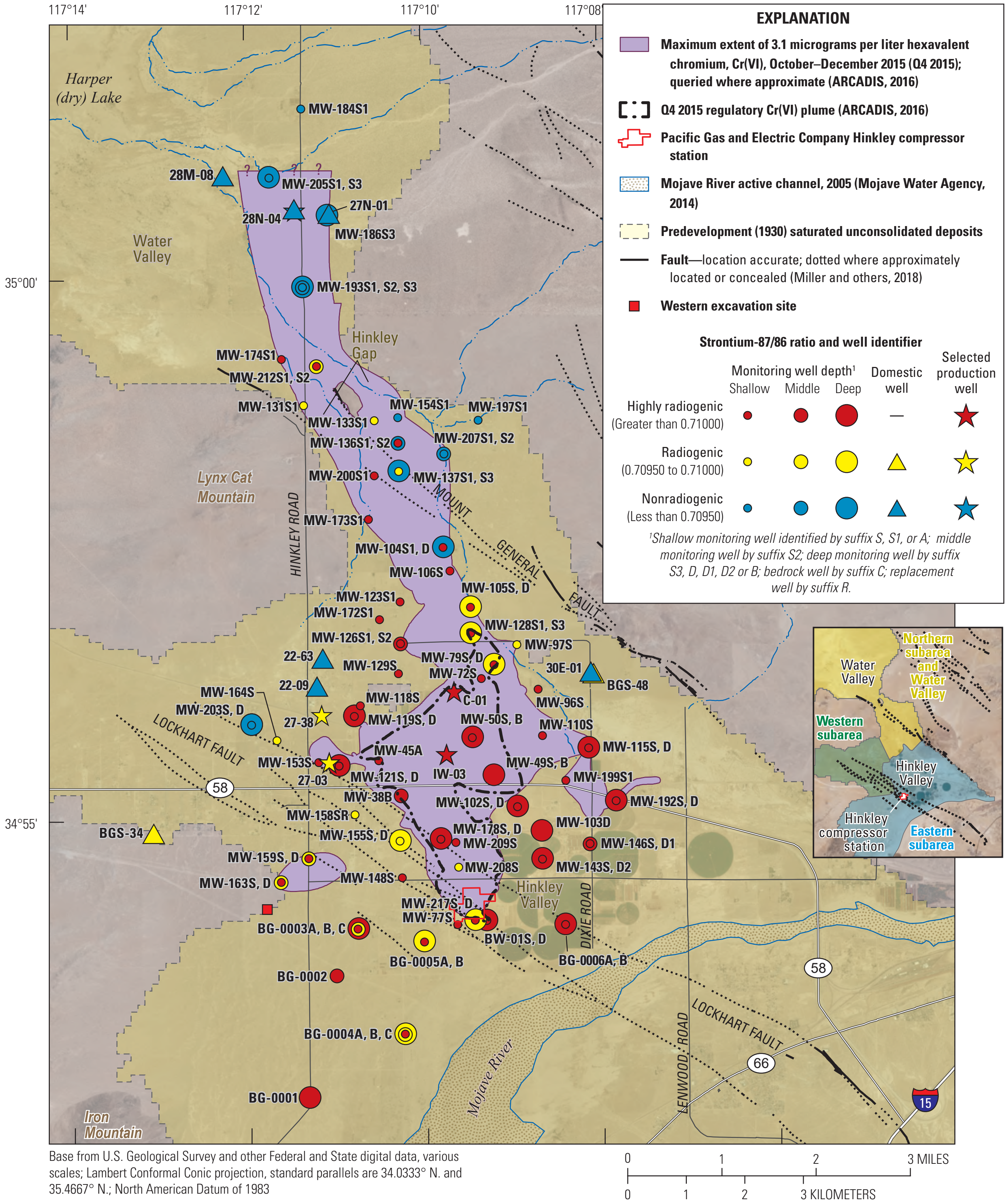
The strontium-87/86 ratio of modern seawater is 0.70910 (Spooner, 1976). Rocks, geologic materials, and water with strontium-87/86 ratios greater than 0.70910 have more strontium-87 from the decay of rubidium-87 than seawater; such strontium-87/86 ratios are often referred to as “radiogenic.” In contrast, strontium-87/86 ratios less than 0.70910 have less strontium-87 from the decay of rubidium-87 than seawater and are often referred to as “nonradiogenic.”

Felsic rocks in the San Bernardino Mountains have strontium-87/86 ratios of 0.710 or greater (DePaolo, 1981; Bataille and Bowen, 2012). In contrast, Miocene volcanic rocks in the Mojave Desert have low strontium-87/86 ratios, ranging from 0.7045 to 0.7095 (Glazner and O’Neil, 1989). The abundance of rubidium, and presumably the strontium-87/86 ratio of Mojave River alluvium, increases with increases in the fraction of felsic alluvium eroded from the San Bernardino Mountains. The fraction of felsic alluvium eroded from the San Bernardino Mountains increased, and the fraction of mafic alluvium eroded from the San Gabriel Mountains decreased, in Mojave-type deposits over the last 5 million years as a result of geologic movement along the San Andreas Fault near the headwaters of the Mojave River 40 mi southwest of the study area (Groover and Izbicki, 2019).

Differences in strontium-87/86 ratios in alluvium eroded from felsic rock in the San Bernardino Mountains, mafic rock from the San Gabriel Mountains, and alluvium eroded from Miocene rocks east of the study area can be used to support interpretations of the depositional provenance of alluvial materials composing aquifers within the study area. Strontium is an exchangeable cation similar to calcium, and strontium weathered from rock and minerals exchanges rapidly with strontium in groundwater. As a consequence, the strontium-87/86 ratio of water from wells is a surrogate for the strontium-87/86 ratio of rocks, minerals, and other geologic materials and commonly reflects the depositional provenance of unconsolidated deposits (Izbicki and others, 1994; Katz and Bullen, 1996; Johnson and DePaolo, 1997). Many wells in the study area are screened in aquifer materials having more than one depositional provenance. The strontium-87/86 ratio in water from wells reflects the dominant unit yielding water to the well, thereby simplifying hydrologic interpretations of subsurface geology.

F.5.1. Strontium Isotope Results

The strontium-87/86 ratios in water from wells sampled in Hinkley and Water Valleys ranged from 0.70744 to 0.71085, with a median ratio of 0.71011 (chapter E, appendix E.1, table E.1.1: U.S. Geological Survey, 2021). For the purposes of this professional paper, strontium-87/86 ratios less than 0.70950 were classified as “nonradiogenic,” strontium-87/86 ratios between 0.70950 and 0.71000 were radiogenic, and strontium-87/86 ratios greater than 0.71000 were classified as “highly radiogenic” (fig. F.21). Highly radiogenic ratios with values greater than 0.71000 were present in water from wells throughout Hinkley Valley as far downgradient as the southern part of Water Valley in wells MW-174S1 and MW-212S1. Nonradiogenic ratios with values less than 0.70950 were present in water from wells in the northern subarea downgradient from the Mount General fault and in Water Valley (fig. F.21). Nonradiogenic ratios also were present in water from well MW-203D, completed in partly consolidated Miocene deposits underlying Mojave-type deposits in the western subarea, and domestic wells 22-09 and 22-63, completed in bedrock aquifers underlying former residential areas in Hinkley Valley. Nonradiogenic ratios in well MW-203S may result from Miocene materials or water from deeper deposits at this site. For the purposes of this study, radiogenic and nonradiogenic strontium-87/86 ratios are discussed separately.



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 F.21. Strontium-87/86 ratios in water from wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

F.5.1.1. Radiogenic Strontium Isotopes

Highly radiogenic strontium-87/86 ratios, greater than 0.71000, were measured in water from shallow wells throughout the eastern, western, and northern subareas within Hinkley Valley and in the southern part of Water Valley (fig. F.21). Highly radiogenic strontium-87/86 ratios also were measured in water from deeper wells downgradient from the Lockhart fault that are completed within the lower zone of the upper aquifer within Hinkley Valley. Almost 80 percent of wells having highly radiogenic strontium-87/86 ratios were completed, at least in part, in sand or coarser textured Mojave-type deposits eroded from felsic rock in the San Bernardino Mountains identified by Miller and others (2018, 2020). Highly radiogenic strontium-87/86 ratios in water from wells MW-174S1 and MW-212S1 likely represent the northernmost extent of saturated deposits sourced from the Mojave River in the study area. Miller and others (2018, 2020) describe material sourced from the Mojave River in the overlying unsaturated zone farther downgradient, some of these unsaturated deposits may have been saturated under predevelopment conditions before water-level declines associated with agricultural pumping.

Ratios of strontium-87/86 decrease with depth in the eastern subarea upgradient from the Lockhart fault and in the western subarea because of progressively older Mojave River deposits at depth. Older Mojave River deposits have smaller fractions of highly radiogenic felsic alluvium eroded from the San Bernardino Mountains and greater fractions of less radiogenic mafic alluvium eroded from the San Gabriel Mountains than recent Mojave River deposits (chapter A, fig. A.5). Mudflat/playa deposits in the eastern subarea near the toe of alluvial fans eroded from Mount General also are highly radiogenic (fig. F.21), which is consistent with their Mojave-type provenance and felsic mineralogy (chapter C, fig. C.10). Highly radiogenic strontium-87/86 ratios, within material deposited by the Mojave River (Miller and others, 2018, 2020), were present in water from wells in a nearly continuous band along the west side of the northern subarea in Hinkley Valley as far north as wells MW-174S1 and MW-212S1 in the southern part of Water Valley (fig. F.21). Many of the coarse-textured Mojave River deposits within the predevelopment aquifer in the northern subarea are above the present-day water table (Miller and others 2018, 2020) and are no longer saturated as a result of pumping and water-level declines. Highly radiogenic strontium-87/86 ratio values in water from wells reflect groundwater within thin lenses of saturated, coarse-textured Mojave River deposits (commonly less than 10 ft thick) in the northern subarea and the southern part of Water Valley.

Median chromium concentrations in nonradiogenic and radiogenic aquifer materials were 28 and 31 milligrams per kilograms (mg/kg), respectively. Median chromium concentrations within these materials are significantly higher than the median chromium concentration of 19 mg/kg in highly radiogenic aquifer material within Hinkley and Water Valleys outside the regulatory Cr(VI) plume (fig. F.22*A*). These low-chromium, highly radiogenic aquifer materials were eroded from felsic materials within the San Bernardino Mountains.

In contrast to materials outside the Q4 2015 regulatory Cr(VI) plume, median chromium concentrations in highly radiogenic aquifer materials within the Q4 2015 regulatory Cr(VI) plume were 23 mg/kg. This concentration is slightly higher than Cr(VI) concentrations in similar materials outside the Q4 2015 regulatory Cr(VI) plume, indicating that chromium may have been added to aquifer material from Cr(VI) containing groundwater within the Q4 2015 regulatory Cr(VI) plume. Higher chromium concentrations on aquifer material within the Q4 2015 regulatory Cr(VI) plume are consistent with observations and measurements of chromium sorbed to aquifer material within the Q4 2015 regulatory Cr(VI) plume (chapter C, figs. C.21, C.22). The delta chromium-53 isotope data presented in section “F.6.1.1 Hexavalent Chromium and Chromium Isotope Compositions Within the Regulatory Hexavalent Chromium Plume,” later in this chapter are consistent with this interpretation.

Well MW-153S, in the western subarea, is completed in weathered hornblende diorite; water from well MW-153S is highly radiogenic and has a strontium-87/86 isotope ratio of 0.71032. Chromium concentrations in core material adjacent to the screened interval of MW-153S were as high as 405 mg/kg (Groover and Izbicki, 2018). Similarly, water from well MW-121D, overlying weathered bedrock in the western subarea, had a strontium-87/86 isotopic ratio of 0.71045, and chromium concentrations in core material were as high as 118 mg/kg (Groover and Izbicki, 2018). Although highly radiogenic strontium-87/86 isotope ratios are commonly indicative of felsic, low-chromium Mojave-type deposits, some local rocks, including hornblende diorite and aquifer materials eroded from those rocks in the western subarea, also have highly radiogenic strontium-87/86 ratios; those materials also have high chromium concentrations. Consequently, radiogenic and highly radiogenic strontium-87/86 isotopic ratios were not diagnostic of felsic, low-chromium, Mojave-type deposits (fig. F.22*A*) and were not included within the summative-scale analyses in chapter G within this professional paper.

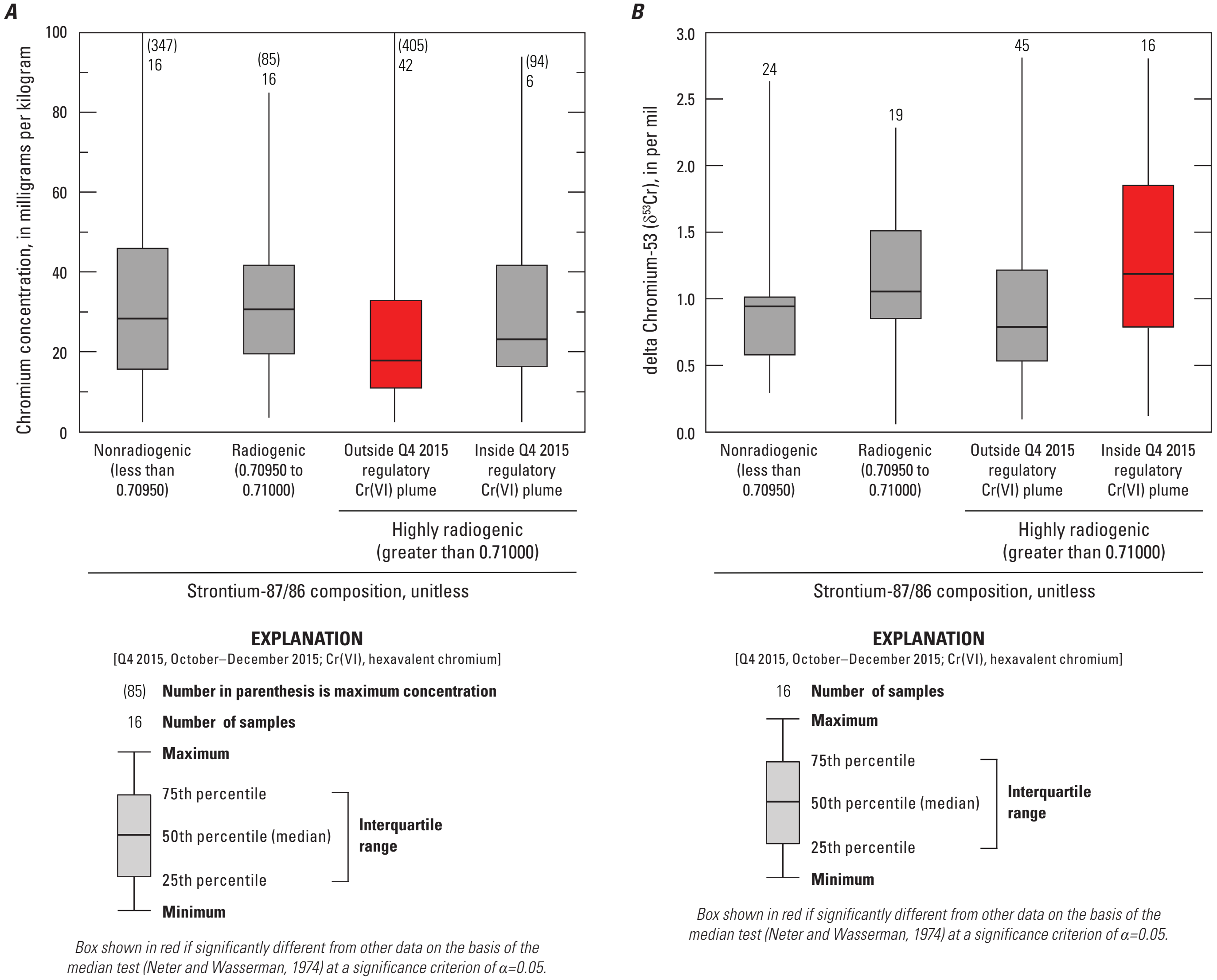


Figure F.22. *A*, Chromium concentrations and *B*, delta chromium-53 values measured in nonradiogenic, radiogenic, and highly radiogenic aquifer materials adjacent to the screened interval of sampled wells, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

F.5.1.2. Nonradiogenic Strontium Isotopes

Nonradiogenic strontium-87/86 ratios less than 0.70950 were present in water from wells completed in locally derived alluvium within Water Valley and the northern subarea of Hinkley Valley downgradient from the Mount General fault (fig. F.21). The lowest strontium-87/86 ratio was in water from well MW-186S3. Core material from this well contained basaltic fragments and had chromium concentrations as high as 155 mg/kg (fig. F.22*A*; Groover and Izbicki, 2018). Water from well MW-203D, completed in Miocene deposits underlying the western subarea, also had nonradiogenic strontium-87/86 ratios. Core material from well MW-203D contained weathered clasts having chromium concentrations as high as 347 mg/kg (Groover and Izbicki, 2018).

All wells having nonradiogenic strontium-87/86 ratios were outside the mapped regulatory Cr(VI) plume, and water from these wells had a median Cr(VI) concentration of 3.3 µg/L, which is greater than the interim Cr(VI) background concentration of 3.1 µg/L. Miocene materials in Hinkley and Water Valleys are isolated from surficial sources of recharge along the Mojave River by depth and their downgradient location within long groundwater-flow paths through the aquifer. As a consequence, water from wells completed in Miocene materials commonly has low carbon-14 activities and great age. The age of groundwater and long contact times with aquifer materials increase silicate weathering, creating alkaline groundwater pH values (table F.4) that contribute to desorption of Cr(VI) from aquifer materials.

Nonradiogenic strontium-87/86 ratios are diagnostic of certain locally derived non-Mojave-type deposits containing Miocene material. These materials have higher chromium concentrations and have weathered extensively, thus, potentially mobilizing chromium to groundwater.

F.5.2. Summary of Strontium Isotope Results

Highly radiogenic strontium-87/86 isotope ratios with values greater than 0.71000, consistent with material sourced from the Mojave River, were present in water from wells throughout Hinkley Valley as far downgradient as the southern part of Water Valley in wells MW-174S1 and MW-212S1. Similar highly radiogenic strontium-87/86 isotope ratios also were present in water from well MW-153S completed in weathered hornblende diorite associated with Iron Mountain along the western margin of Hinkley Valley. Although the Q4 2015 regulatory Cr(VI) plume lies within highly radiogenic Mojave-type deposits, radiogenic strontium-87/86 ratios were not diagnostic of these materials.

Nonradiogenic strontium-87/86 ratios less than 0.70950 were present in water from wells completed in locally derived alluvium within the northern subarea of Hinkley Valley downgradient from the Mount General fault and in Water Valley (fig. F.21). All wells having nonradiogenic strontium-87/86 ratios were outside the mapped regulatory Cr(VI) plume. Nonradiogenic strontium-87/86 ratios are diagnostic of locally derived deposits containing Miocene material that have higher chromium concentrations and have weathered extensively, thus, potentially mobilizing chromium to groundwater.

Although nonradiogenic strontium-87/86 ratios less than 0.70950 are diagnostic of chromium containing Miocene material, radiogenic strontium-87/86 ratios greater than 0.71000 are not diagnostic of felsic, low-chromium materials, and highly radiogenic ratios also occur within chromium-containing hornblende diorite rock. As a consequence, strontium-87/86 ratios were not used as part of the summative-scale analyses to calculate the extent of the Cr(VI) plume (chapter G). However, nonradiogenic strontium-87/86 ratios were used to confirm the natural source of Cr(VI) in water from some wells in the northern subarea downgradient from the Mount General Fault and Water Valley outside the summative-scale plume in support of the summative-scale results.

F.6. Chromium Isotopes

Chromium isotopes provide information on rock, minerals, and geologic material that water has contacted within an aquifer and information on processes controlling chromium concentrations in groundwater. Interpretation of chromium isotope data is often complex and involves understanding of mineral composition, rock/water interaction (including weathering, sorption, desorption, and secondary mineral formation), and aqueous geochemistry that includes mixing, complexation, and redox reactions that oxidize Cr(III) to Cr(VI) and reduce Cr(VI) to Cr(III) in natural settings and within groundwater plumes (chapter E, fig. E.1).

The four naturally occurring isotopes of chromium have atomic masses of 50, 52, 53, and 54 (Coplen and others, 2002). Chromium-52 and chromium-53, the two most abundant isotopes, have global abundances of 83.8 and 9.5 percent, respectively. Abundances of chromium-52 and chromium-53 isotopes are expressed in delta notation as per mil differences in the chromium-53/chromium-52 ratio within a sample relative to the chromium-53/chromium-52 ratio in the chromium isotope standard NIST979 (National Institute of Health, 2014). The global average delta chromium-53 composition of oceanic and continental basalts, ultramafic rocks, and granitic and sedimentary rocks that compose the Earth's crust is relatively homogeneous and near 0 per mil (Ellis and others, 2002; Schoenberg and others, 2008), and most chromium in industrial products has delta chromium-53 values near 0 per mil (Ellis and others, 2002). However, recent work has determined that some metamorphosed, ultramafic rocks and hydrothermal chromates may have delta chromium-53 values approaching 1 per mil (Schoenberg and others, 2008; Farkaš and others, 2013).

Changes in chromium isotope composition can occur as a result of fractionation during chemical reactions where one isotope (usually the lighter isotope) is preferentially incorporated into the product, leaving the heavier isotope in the remaining reactant. Weathering of chromium from primary minerals, oxidation of Cr(III) to Cr(VI), and speciation of aqueous forms of Cr(VI) between $HCrO_4^{1-}$ and CrO_4^{2-} (chapter E, fig. E.19) have not been determined to fractionate chromium in natural settings, although limited fractionation may occur as a result of sorption near the margins of Cr(VI) plumes (Ellis and others, 2004). Chromium in groundwater contains slightly more of the heavier isotope chromium-53 than rock as a result of reduction of Cr(VI) to Cr(III) that occurs on the surfaces of mineral grains or in groundwater after chromium has weathered from rock (Izbicki and others, 2008; Ščančar and Milačič, 2014). Values of delta chromium-53 as high as 5.1 per mil have been measured in native groundwater in the Mojave Desert as a result of this process (Izbicki and others, 2008).

Changes in chromium isotope composition occurring as a result of reductive fractionation can be calculated from the following:

$$(R_{samp}/R_o)=(C/C_o)\alpha-1 \qquad \text{(F.7)}$$

where

R_{samp} is the chromium-53/chromium-52 ratio in the sample water;
R_o is the initial chromium-53/chromium-52 ratio;
C is the chromium concentration in the sample water;
C_o is the initial chromium concentration; and
α is the chromium fractionation factor, 0.9965 (Ellis and others, 2002).

For convenience, the chromium fractionation factor, α, is often expressed using epsilon (ε) notation:

$$\varepsilon_{a-b}=(\alpha_{a-b}-1)\times 1{,}000 \qquad \text{(F.8)}$$

where

a is the reactant and
b is the product.

Laboratory-derived values for ε range from 3.4 to 4.5 (Ellis and others, 2002; Kitcher and others, 2004; Sikora and others, 2008). Laboratory-derived fractionation factors are measured during controlled conditions and commonly differ from apparent fractionation factors estimated from field data collected in environmental settings near Cr(VI) plumes. Several studies (Bullen, 2007; Berna and others, 2009; Izbicki and others, 2012) explained this difference through a combination of reductive fractionation and advective mixing of anthropogenic Cr(VI) in groundwater with native groundwater near plume margins. In contrast, Raddatz and others (2011) determined there was limited reduction of Cr(VI) in oxic groundwater and indicated that Cr(VI) concentrations near plume margins were controlled largely by mixing with native groundwater containing Cr(VI).

Because chromium isotope compositions for rock and industrial products are well defined and changes in chromium concentrations resulting from reduction of Cr(VI) to Cr(III) can be calculated from isotopic data, chromium isotopes have been used as a tool to determine the source of Cr(VI) in groundwater and to define the extent of anthropogenic Cr(VI) in areas having high natural background Cr(VI) concentrations (Ellis and others, 2002; Bullen, 2007; Izbicki and others, 2008). More appropriately, the delta chromium-53 values of groundwater can be used to understand the interaction between chemical processes, such as reductive fractionation of Cr(VI) to Cr(III), and physical processes, such as mixing of water containing anthropogenic and natural Cr(VI), in and near plume margins (Ellis and others, 2002, 2004; Bullen, 2007; Izbicki and others, 2008, 2012; Aragon, 2009; Berna and others, 2009).

F.6.1. Chromium Isotope Results and Discussion

The delta chromium-53 values of selected rock and other geologic materials in Hinkley and Water Valleys were analyzed to determine if initial rock compositions in the study area are similar to the global average composition of 0 per mil (table F.5). In addition to local chromium-containing rock (including hornblende and basalt) and alluvial material eroded from those rocks, chromium-containing metamorphic minerals (including fuchsite and actinolite) that were eroded from the San Gabriel Mountains and may be present within older Mojave River alluvium in Hinkley Valley (chapter C) also were analyzed.

The delta chromium-53 values of rock, selected minerals, and other geologic material sampled as part of this study ranged from −0.42 to 0.03 per mil (U.S. Geological Survey, 2021), with most materials having slightly negative delta chromium-53 values (table F.5). The most negative delta chromium-53 value was from a basalt outcrop in Water Valley (table F.5). Heavy minerals (primarily magnetite) within core material collected from mudflat/playa deposits at MW-192 had a delta chromium-53 value of −0.23 per mil, whereas more easily weathered actinolite and hornblende had values ranging from −0.11 to −0.02 per mil (table F.5). Given an overall precision for delta chromium-53 measurements of about 0.15 per mil (Izbicki and others, 2008), with the exception of basalt and magnetite, most delta chromium-53 values were not analytically different from the expected delta chromium-53 value of 0 per mil. Positive delta chromium-53 values as high as +1 per mil reported for mafic geologic materials in other studies (Schoenberg and others, 2008; Farkaš and others, 2013) were not measured as part of this study (table F.5).

The delta chromium-53 values in water from wells sampled in Hinkley and Water Valleys ranged from −0.13 to 2.8 per mil (chapter E, appendix E.1, table E.1.1), with considerable spatial variability across the study area (fig. F.23). The delta chromium-53 value was near 0 per mil in water from well MW-208S, within the Q4 2015 regulatory Cr(VI) plume less than 0.6 mi downgradient from the Hinkley compressor station, which had a Cr(VI) concentration of 2,500 µg/L—the highest concentration measured as part of this study. In general, delta chromium-53 values were commonly more positive (containing more of the heavier chromium-53 isotope) in water from wells near the Mojave River and from wells penetrating bedrock in the western subarea, with less positive values farther downgradient in the northern subarea and Water Valley (fig. F.23). The delta chromium-53 values were as heavy as 2.8 per mil in water from domestic well BGS-34 completed in bedrock underlying the western subarea, which had a Cr(VI) concentration of 2.3 µg/L. However, delta chromium-53 values also were as heavy as 2.8 per mil in water from well MW-50S within the Q4 2015 regulatory Cr(VI) plume, which had a Cr(VI) concentration of 16 µg/L. The range in delta chromium-53 values for wells having older groundwater (table F.4) was similar to the overall range in delta chromium-53 values.

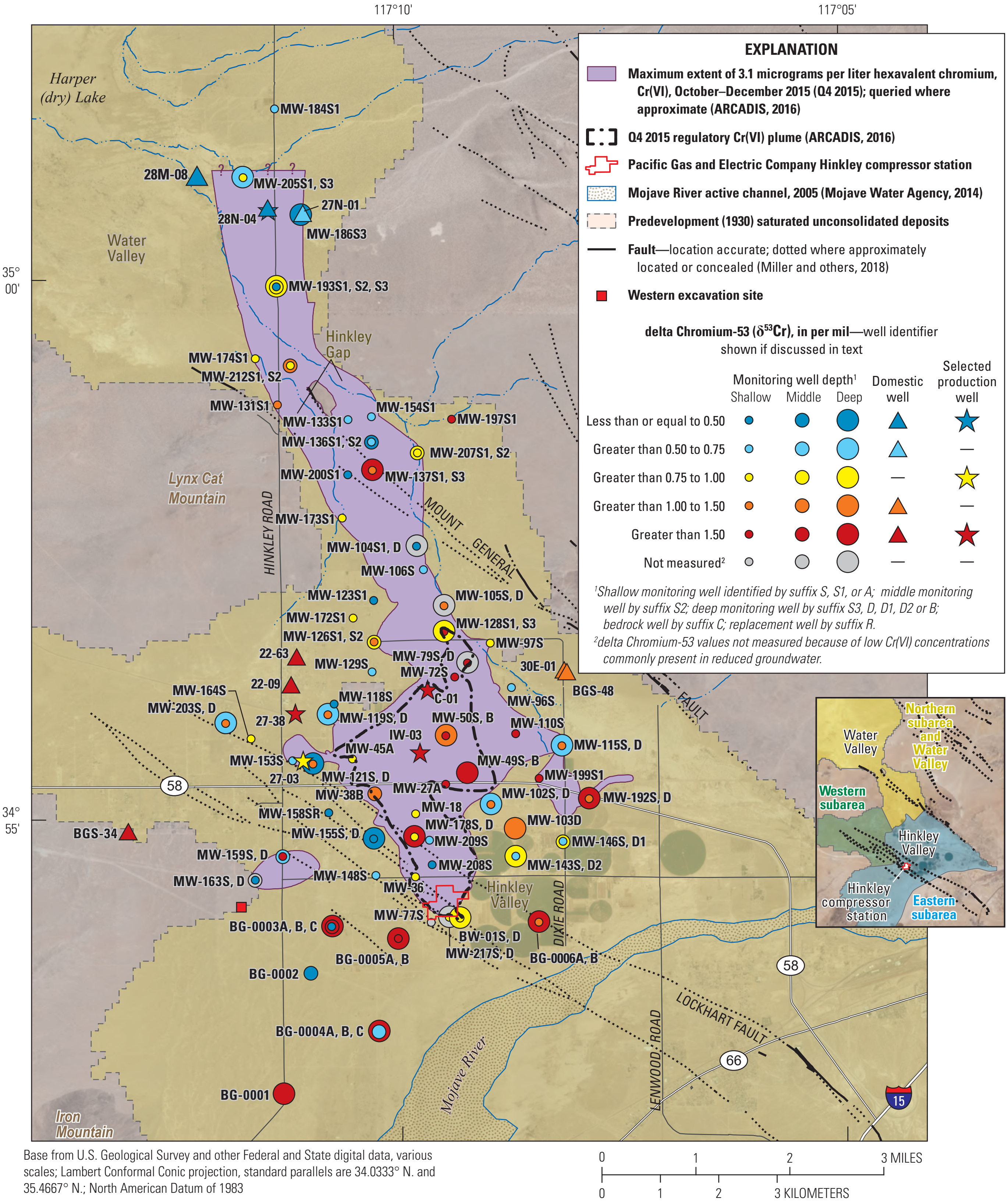
Table F.5. Chromium concentrations, chromium-53 to chromium-52 isotope ratios, and delta chromium-53 values of selected solid materials, western Mojave Desert, including Hinkley and Water Valleys, California.

[Latitude and longitude in degrees, minutes, seconds, dd°mm'ss.ss" or ddd°mm'ss.ss", respectively. Samples digested in 22.6 M hydrofluoric acid and 15.8 M nitric acid (where M denotes molarity) at 115 degrees Celsius before analyses. **Abbreviations**: ^{53}Cr, chromium-53; ^{52}Cr, chromium-52; δ, delta, used to denote differences in the isotopic ratio of the sample relative to differences in a standard; per mil, parts per thousand (‰) difference; —, no data; combusted, combustion at 500 degrees Celsius; <, less than; >, greater than; µm, micrometer]

Material or site	Location			Sample depth, in feet below land surface	Chromium, in milligrams per kilogram[1]		Sample fraction[2]	Sample processing	^{53}Cr/^{52}Cr ratio, unitless	δ^{53}Cr, in per mil	Standard deviation of δ^{53}Cr values, in per mil
	Area	Latitude	Longitude		Minimum	Maximum					
Fuchsite (chromium-mica)	San Gabriel Mountains	34°20'40.44"	117°37'3.02"	0	6,090	8,620	Bulk	—	0.113443	−0.10	0.02
							Bulk	—	0.113445	−0.08	0.02
Actinolite	San Gabriel Mountains	34°20'32.90"	117°37'12.66"	0	920	4,010	Bulk	—	0.113452	−0.02	0.02
							Bulk	—	0.113442	−0.11	0.01
							Bulk	—	0.113448	−0.06	0.01
Hornblende	Iron Mountain	34°51'11.30"	117°13'24.88"	0	170	306	Bulk	—	0.113444	−0.09	0.05
							Bulk	—	0.113445	−0.08	0.01
Metabasalt	Iron Mountain	34°54'40.13"	117°13'29.25"	0	271	507	Bulk	Combusted	0.113435	−0.17	0.01
Basalt	Water Valley	35°04'47.35"	117°09'44.82"	0	177	216	Bulk	Combusted	0.113406	−0.42	0.02
MW-154	Northern subarea, Hinkley Valley	34°58'42"	117°10'17"	72 to 77	57	60	Bulk	—	0.113448	−0.06	0.03
							Bulk	Combusted	0.113443	−0.09	0.02
MW-163	Western subarea, Hinkley Valley	34°54'25"	117°11'38"	106 to 110	57	61	Bulk	Combusted	0.113435	−0.17	0.02
					555		Heavy mineral fraction	—	0.113457	0.03	0.02
MW-192	Eastern subarea, Hinkley Valley	34°55'09"	117°07'52"	62 to 67	639		Heavy mineral fraction	—	0.113428	−0.23	0.01
Mafic alluvium	Sheep Creek fan	34°29'23.69"	117°3'709.71"	0	88	118	Bulk	—	0.113450	−0.04	0.01
							Bulk	—	0.113447	−0.06	0.03
							Bulk	Combusted	0.113439	−0.13	0.02
							Bulk	Combusted	0.113437	−0.15	0.02
							Bulk	Combusted	0.113436	−0.16	0.02
							<250 µm	Combusted	0.113445	−0.08	0.02
							>250 µm	Combusted	0.113432	−0.19	0.03

[1] Chromium concentration data by portable (handheld) x-ray fluorescence are from Groover and Izbicki (2018). Chromium concentration data for heavy mineral fractions (minerals having a specific gravity greater than 3.32) by portable (handheld) x-ray fluorescence are from Morrison and others (2018).

[2] Sample fraction categories include (1) bulk sample, which means the entire sample was digested and analyzed; (2) heavy mineral fraction, which means the sample was sorted by density using methylene iodide and only minerals having a specific gravity greater than 3.2 were digested and analyzed; (3) >250 µm, which means the sample was sorted by particle size and only particles having a particle size diameter greater than 250 µm were digested and analyzed; and (4) <250 µm, which means the sample was sorted by particle size and only particles having a particle size diameter less than 250 µm were digested and analyzed.



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 F.23. The delta chromium-53 isotopic composition in water from sampled wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

F.6.1.1. Hexavalent Chromium and Chromium Isotope Compositions Within the Regulatory Hexavalent Chromium Plume

Concentrations of Cr(VI) in water from 21 wells sampled within the footprint of the Q4 2015 regulatory Cr(VI) plume between March 2015 and November 2017 ranged from 0.1 to 2,500 µg/L, with delta chromium-53 values ranging from 0.13 to 2.8 per mil (fig. F.24*B*; chapter E, appendix E.1, table E.1.1). The delta chromium-53 values of groundwater within the mapped Q4 2015 regulatory Cr(VI) plume differed spatially. Values of delta chromium-53 near 0 per mil were associated with higher Cr(VI) concentrations near the Hinkley compressor station, and higher, more positive delta chromium-53 values were present downgradient within the Q4 2015 regulatory Cr(VI) plume (fig. F.23).

The Q4 2015 regulatory Cr(VI) plume lies within felsic, low-chromium, highly radiogenic aquifer materials (fig. F.22*B*) deposited by the Mojave River. The median delta chromium-53 value within the Q4 2015 regulatory Cr(VI) plume of 1.2 per mil is significantly higher than the median delta chromium-53 value of 0.79 per mil in similar highly radiogenic materials outside the Q4 2015 regulatory Cr(VI) plume (fig. F.22*B*) as a result of reductive fractionation of anthropogenic Cr(VI) released from the Hinkley compressor station to Cr(III) within the plume.

The apparent fractionation factor (ε_{app}) estimated from environmental data describes the combined effect of reductive fractionation and other processes on changes in the isotopic composition of a constituent as the ratio of the heavy and light isotope in the product divided by the ratio in the reactant (Coplen and others, 1999). The apparent Cr(VI) fractionation factor estimated from delta chromium-53 and Cr(VI) data within the Q4 2015 regulatory Cr(VI) plume was ε_{app}=0.28. This value is similar to the apparent fractionation factor of ε_{app}=0.3 identified for the Hinkley site (Bullen 2007; Izbicki and others, 2012) and within the range of ε_{app}=0.1 to 0.4 estimated for a similar site at Topock, Calif., about 300 mi to the east of Hinkley Valley (Izbicki and others, 2012; not shown on figures).

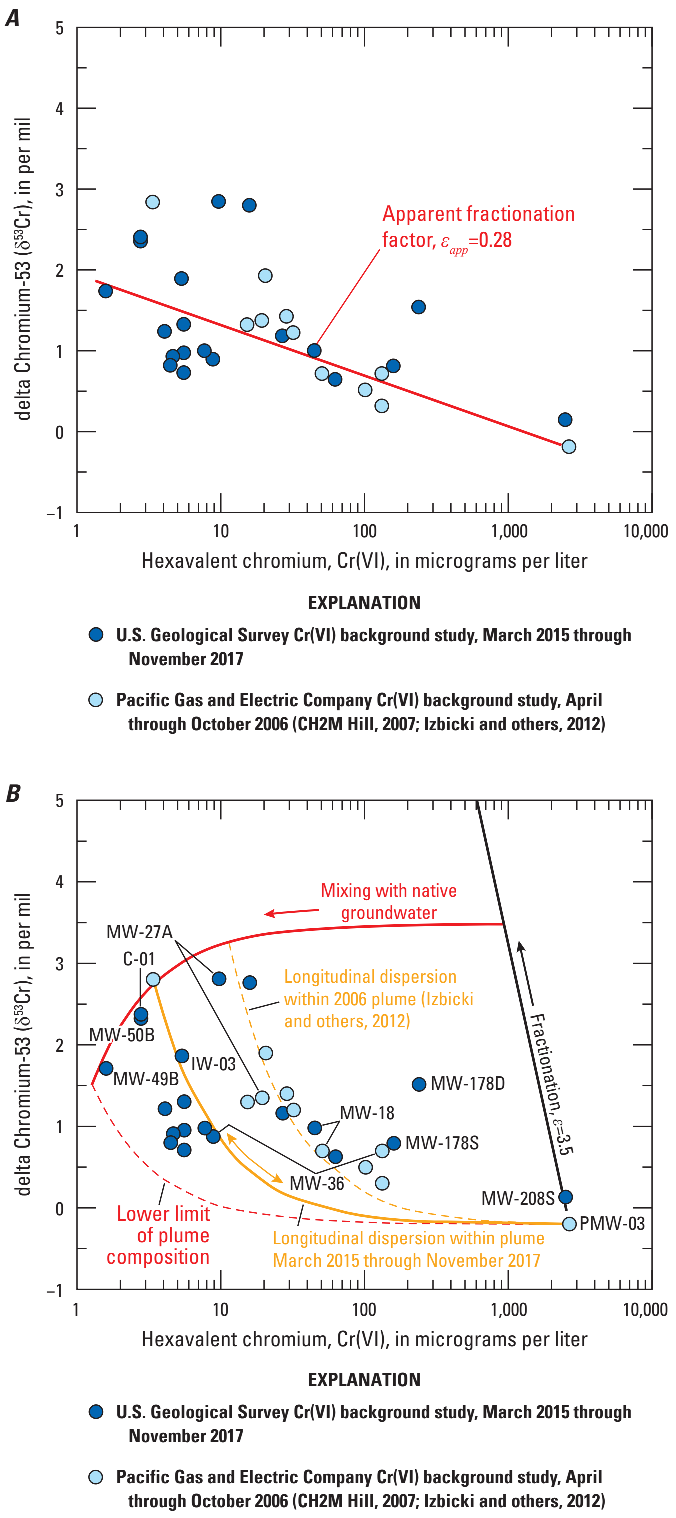


Figure F.24. The delta chromium-53 isotopic composition as a function of hexavalent chromium concentration interpreted using *A*, apparent fractionation factor and *B*, laboratory-derived fractionation factors, mixing with native groundwater, and longitudinal dispersion within the mapped summative-scale plume, Hinkley Valley, western Mojave Desert, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

For most isotopic systems, apparent fractionation factors differ from fractionation factors (ε) describing chemical and microbiological processes estimated under controlled laboratory conditions. To understand these differences, Cr(VI) concentrations and delta chromium-53 values of water from wells within the regulatory Cr(VI) plume were examined with respect to (1) reduction of Cr(VI) to Cr(III), calculated using the laboratory-derived fractionation factor ε; (2) mixing with native groundwater; and (3) longitudinal dispersion within the plume (fig. F.24*B*). Calculations were made following the approach described by Bullen (2007) and Izbicki and others (2012), using a laboratory-derived fractionation factor of ε=3.5 (fig. F.24*B*; Ellis and others, 2002; Berna and others, 2009; Izbicki and others, 2012). When interpreted in this manner, Cr(VI) and delta chromium-53 data describe chemical processes, mixing with native groundwater associated with groundwater flow, and mixing within the plume associated with longitudinal dispersion as groundwater moves downgradient. All three processes likely occurred simultaneously within groundwater as a result of Cr(VI) releases from the Hinkley compressor station.

Within the Q4 2015 regulatory Cr(VI) plume, water from well MW-208S had a Cr(VI) concentration of 2,500 µg/L and a delta chromium-53 value of 0.13 per mil (fig. F.24*B*). Well PMW-03, within the boundary of the Hinkley compressor station (sampled before this study by Izbicki and others [2012]), had a Cr(VI) concentration of 2,760 µg/L and a delta chromium-53 value of −0.23 per mil. Wells MW-208S and PMW-03 are the only sampled wells within the Q4 2015 regulatory Cr(VI) plume having delta chromium-53 values near 0 per mil that reflect Cr(VI) and delta chromium-53 values expected for the initial Cr(VI) release.

Hexavalent chromium is a strong oxidant and would have reacted with naturally occurring reductants within the aquifer, including organic material and ferrous iron (Fe^{2+}) oxides on the surfaces of mineral grains, as it moved with groundwater downgradient from the Hinkley compressor station (Bullen, 2007). As these reactions proceeded, Cr(VI) would have been reduced to Cr(III) and removed from groundwater; consequently, Cr(VI) concentrations in groundwater would have decreased, and the delta chromium-53 value of the remaining Cr(VI) in groundwater would have increased (fractionated) to progressively more positive (heavier) values.

As the leading edge of the Cr(VI) plume moved downgradient from the release location within the Hinkley compressor station, the remaining fractionated Cr(VI) would have mixed with native groundwater. The calculated mixing line (fig. F.24*B*), fit to measured data, defines the upper envelope of delta chromium-53 values and Cr(VI) concentrations within the Cr(VI) plume. On the basis of these data, fractionated Cr(VI) downgradient from the Hinkley compressor station would have reached a maximum delta chromium-53 value of about 3.5 per mil, with a corresponding Cr(VI) concentration of about 900 µg/L (fig. F.24*B*). Once naturally occurring reductants reacted with Cr(VI), they would have been consumed and would no longer be present within the aquifer to react with additional Cr(VI). As releases from the Hinkley compressor station continued, Cr(VI) would no longer encounter natural reductants within aquifer material as groundwater flowed downgradient within the plume, and unfractionated Cr(VI) from later releases would mix as a result of longitudinal dispersion with fractionated Cr(VI) from earlier releases that had mixed with native groundwater (fig. F.24*B*).

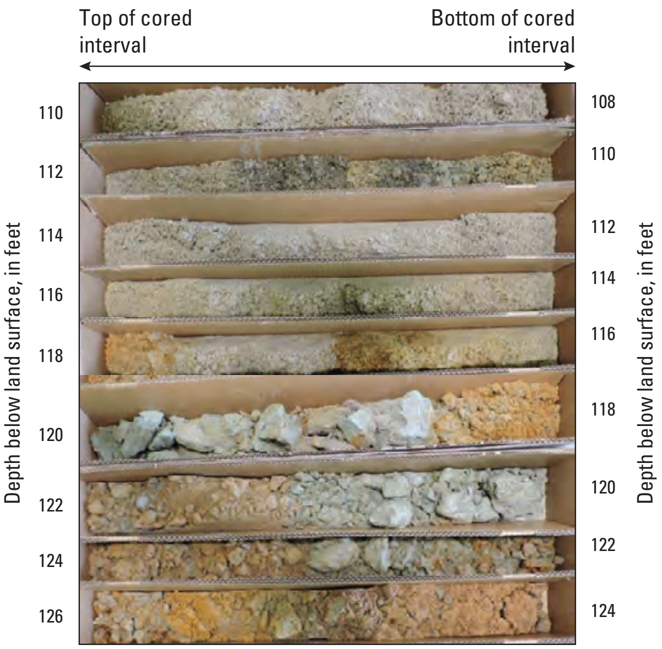
Samples collected between March 2015 and November 2017 within the Q4 2015 regulatory Cr(VI) plume define a wide range of Cr(VI) concentrations and delta chromium-53 values (fig. F.24*B*). Most samples indicate a combination of Cr(VI) reduction and longitudinal dispersion, with greater mixing of native water and water containing anthropogenic Cr(VI) than was reported in samples collected as part of the previous Cr(VI) background study (CH2M Hill, 2007). The Cr(VI) plume is a complex environment, and Cr(VI) concentrations within the Cr(VI) plume are locally controlled by geology, groundwater pumping (including agricultural pumping and pumping for plume management purposes), land application of Cr(VI) with subsequent irrigation return, and in situ reduction of Cr(VI) (chapter A).

Wells MW-18, MW-27A, and MW-36 within the Q4 2015 regulatory Cr(VI) plume were sampled and analyzed for Cr(VI) and delta chromium-53 as part of the previous PG&E Cr(VI) background study (CH2M Hill, 2007); these wells were resampled and analyzed as part of this study. Changes in Cr(VI) concentrations and delta chromium-53 values in water from wells MW-27A and MW-18 that occurred since 2006 can be described by longitudinal dispersive processes within the plume, whereas changes in Cr(VI) concentrations and delta chromium-53 values in water from well MW-36 seem to be described by a more complex combination of reductive fractionation and mixing with native groundwater (fig. F.24*B*). Most Cr(VI) samples within the Q4 2015 regulatory Cr(VI) plume seem to be more affected by mixing with native groundwater than data collected within the 2006 plume (fig. F.24*B*; CH2M Hill, 2007). This increase in mixing with native groundwater may have resulted from groundwater-management activities since 2006, especially pumping which may enhance mixing with native groundwater, used to manage anthropogenic Cr(VI) concentrations within the Cr(VI) plume.

Within the Q4 2015 regulatory Cr(VI) plume, wells MW-208 and PMW-03 reflect the initial composition of Cr(VI) released from the Hinkley compressor station and have reacted only slightly with aquifer material or native groundwater. Water from wells MW-178S and MW-178D has reacted with aquifer materials but has mixed less with native groundwater than water from most other sampled wells (fig. F.24*B*). These wells are on the downgradient side of the Lockhart fault, which impedes movement of groundwater in this area and presumably limits mixing of water from wells MW-178S and MW-178D in the Cr(VI) plume with native groundwater. In 2006, well MW-36, within strands of the Lockhart fault, had a Cr(VI) concentration and delta chromium-53 value similar to water from well MW-178S and at that time also seemed to have mixed only slightly with native groundwater.

In contrast to wells near the Lockhart fault, a high fraction of mixing with native groundwater is present in water from wells MW-49B and MW-50B near the center of Hinkley Valley (fig. F.24*B*). It is possible that high concentrations of Cr(VI) released from the Hinkley compressor station have not been continuously present through time upgradient from these wells. Groundwater-flow paths change through time in response to pumping, recharge, and other factors, and Cr(VI) that entered this area during initial releases from the Hinkley compressor station may have been displaced by recharge water from the Mojave River containing low concentrations of Cr(VI). A high fraction of mixing with native groundwater also was present in water from production wells C-01 and IW-03 (fig. F.24*B*) used to pump groundwater for land application of Cr(VI) within the Q4 2015 Cr(VI) regulatory plume. Pumping from long-screened production wells may enhance mixing of native groundwater with water containing anthropogenic Cr(VI); similar mixing does not occur in samples collected from short-screened monitoring wells.

At the concentrations of concern for management purposes near the regulatory Cr(VI) plume margins, Cr(VI) and delta chromium-53 data have little independent predictive value for identification of anthropogenic Cr(VI) in water from wells. However, delta chromium-53 values indicate Cr(VI) within the plume is not conservative, and large amounts of Cr(VI) have reacted with aquifer materials and were removed from groundwater as it flowed downgradient from the Hinkley compressor station. Consistent with reactions between anthropogenic Cr(VI) in groundwater and aquifer material apparent in Cr(VI) and delta chromium-53 data, abundant chromium-containing oxides and other surface coatings were observed in core material collected within the Cr(VI) plume downgradient from the Hinkley compressor station (fig. F.25). These coatings are similar to material observed at other sites where anthropogenic Cr(VI) was released into groundwater (Sedlazeck and others, 2017). The chemical composition of oxide coatings on mineral grains that compose aquifer materials within the Q4 2015 regulatory Cr(VI) plume, is discussed in chapter C within this professional paper.



Photograph by Krishangi Groover, U.S. Geological Survey

Figure F.25. Chromium-containing oxides and other surface coatings on the surfaces of mineral grains within alluvium collected from well EX-48, downgradient from the Pacific Gas and Electric Company natural gas compressor station, Hinkley Valley, western Mojave Desert, California. (Photograph by Krishangi Groover, U.S. Geological Survey, March 2017.)

F.6.1.2. Hexavalent Chromium and Chromium Isotope Compositions Outside the Regulatory Hexavalent Chromium Plume

In the eastern and western subareas, natural chromium within water from wells was characterized on the basis of reductive fractionation of Cr(VI) to Cr(III) sourced from local alluvium, Mojave-type deposits, and weathered hornblende diorite. Fractionation trend lines calculated from these respective source materials, assuming a laboratory-derived value of $\varepsilon=3.5$, bound the range of most measured Cr(VI) and delta chromium-53 values in water from wells outside the Q4 2015 regulatory Cr(VI) plume (figs. F.26*A*, *B*). Native groundwater has mixed with water from mudflat/playa deposits, containing high concentrations of fractionated chromium, to produce high concentrations of Cr(VI) measured in water from wells in the northern subarea of Hinkley Valley and Water Valley.

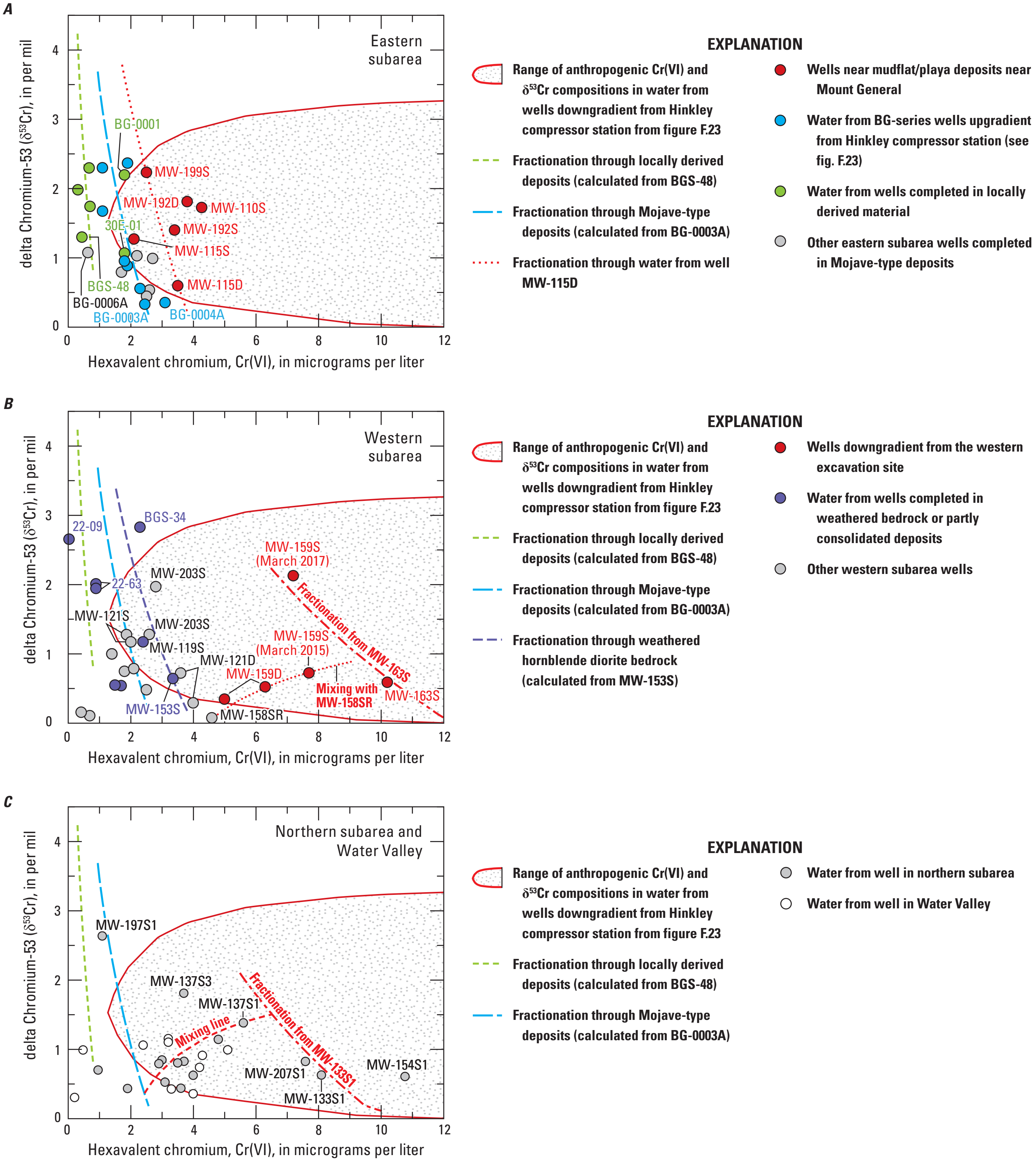


Figure F.26. The delta chromium-53 isotopic composition as a function of hexavalent chromium concentration in the *A*, eastern, *B*, western, and *C*, northern subareas (including Water Valley) for water from wells in Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

For the purposes of this discussion, the initial chemical and isotopic composition of chromium sourced from local alluvium was characterized by water from well BGS-48, and the initial composition of chromium sourced from weathered hornblende diorite was characterized by water from well MW-153S. Reductive fractionation of Cr(VI) sourced from Mojave-type deposits was characterized by the composition of water from well BG-0003A; the fractionation trend line calculated from BG-0003A lies between the fractionation trend lines calculated for the local alluvium and hornblende diorite end members (figs. F.26*A*, *B*). Although instructive for understanding the origin of natural Cr(VI) in water from some wells and identification of potential chromium end members, this approach is not diagnostic of natural Cr(VI) in water from wells.

F.6.1.2.1. Eastern Subarea

Hexavalent chromium concentrations and delta chromium-53 values in water from most wells in local alluvium and Mojave-type deposits in the eastern subarea outside the Q4 2015 regulatory Cr(VI) plume are outside the range of anthropogenic compositions expected within the Q4 2015 regulatory Cr(VI) plume (fig. F.26*A*). In general, most of these Cr(VI) concentrations and delta chromium-53 values fall near compositions expected from the reductive fractionation of Cr(VI) along respective fractionation lines through local alluvium (BGS-48) and Mojave-type (BG-0003A) end members (fig. F.26*A*).

In contrast to water from most wells in the eastern subarea, Cr(VI) concentrations and delta chromium-53 values in water from six wells (MW-110S, MW-115S, MW-115D, MW-192S, MW-192D, and MW-199S1) in the eastern subarea outside the mapped regulatory Cr(VI) plume near Mount General were within the range of anthropogenic compositions within the Q4 2015 regulatory Cr(VI) plume (fig. F.26*A*). Samples collected from these six wells as part of this study between March 2015 and November 2017, had Cr(VI) concentrations ranging from 2.1 to 3.8 µg/L (chapter E, appendix E.1, table E.1.1). Regulatory Cr(VI) concentrations in water from wells MW-110S, MW-115S, MW-115D, MW-192S, MW-192D, and MW-199S1 have been as high as 7.6, 4.8, 4.1, 4.4, 5.0, and 3.7 µg/L, respectively (Pacific Gas and Electric Company data, accessed January 12, 2018, at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/).

The eastern subarea near Mount General contains mudflat/playa deposits interfingered within aquifer deposits at depth (Miller and others 2018, 2020), although only well MW-115S is completed within those deposits (Groover and Izbicki, 2018). Mudflat/playa deposits in the eastern subarea are felsic and contain low concentrations of chromium (chapter C; fig. C.11); most of that chromium remains within resistive magnetite mineral grains, and although highly oxidative manganese-IV oxides are present, pore water Cr(VI) concentrations within these deposits do not exceed 3.3 µg/L (chapter E, table E.6) and do not appear to be a source of high Cr(VI) concentrations to water in nearby wells. With the exception of well MW-115D, water from these wells contains measurable tritium and was recharged within the timeframe of releases from the Hinkley compressor station.

If mixing with younger post-1952 water is not considered, reductive fractionation of Cr(VI) in older (pre-1952) water from well MW-115D that predates Cr(VI) releases from the Hinkley compressor station may explain Cr(VI) concentrations in water from wells MW-199S1 and MW-192S (fig. F.26*A*) but does not explain Cr(VI) concentrations in water from wells MW-110S and MW-192D. If mixing with younger post-1952 water is considered, reductive fractionation of water from well MW-115D does not explain Cr(VI) and delta chromium-53 compositions in water from wells MW-115S, MW-199S1, and MW-192S. Although hexavalent chromium concentrations and delta chromium-53 values in water from wells MW-110S, MW-192S, MW-192D, and MW-199S1 are not diagnostic of anthropogenic Cr(VI), Cr(VI) concentrations in water from these wells were previously identified as unusual on the basis of their Cr(VI) concentrations at the measured pH (chapter E, fig. E.18*B*).

F.6.1.2.2. Western Subarea

Hexavalent chromium concentrations and delta chromium-53 values in water from about one-half of sampled wells in the western subarea outside the Q4 2015 regulatory Cr(VI) plume are within the range expected for anthropogenic compositions within the Cr(VI) plume (fig. F.26*B*). This includes wells completed entirely or partly within weathered bedrock underlying the western subarea.

Water from well MW-153S, completed in weathered hornblende diorite, plots within the range expected for anthropogenic compositions. Core material adjacent to the screened interval of well MW-153S had a chromium concentration of 405 mg/kg (Groover and Izbicki, 2018), the highest measured chromium concentration adjacent to the screened interval of any sampled well. Water from wells MW-121D and MW-119S, completed in unconsolidated Mojave-type deposits overlying weathered hornblende diorite, has Cr(VI) concentrations and delta chromium-53 values along the fractionation trend line through MW-153S (fig. F.26*B*). Water from these wells was not previously identified as unusual on the basis of its Cr(VI) concentration at the measured pH (chapter E, fig. E.18*B*). Water from other wells completed in weathered bedrock elsewhere in the western subarea has Cr(VI) concentrations and delta chromium-53 values outside the range of anthropogenic compositions (fig. F.26*B*).

In contrast to water from most other wells in the western subarea, Cr(VI) concentrations and delta chromium-53 values in water from three wells (MW-159S, MW-159D, and MW-163S) downgradient from the western excavation site are not traceable through reductive fractionation of chromium sourced from local materials (fig. F.26*B*). The Cr(VI) concentrations in water from these wells, sampled as part of this study, ranged from 5.3 to 10 µg/L (fig. F.26*B*), and regulatory Cr(VI) concentrations in water from wells MW-159S, MW-159D, and MW-163S have been as high as 6.7, 6.3, and 10 µg/L, respectively (Pacific Gas and Electric Company data, accessed January 12, 2018, at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/). The Cr(VI) concentration and chromium-53 composition of water from these three wells are within ranges expected for anthropogenic Cr(VI). The Cr(VI) concentrations and delta chromium-53 values in water from wells downgradient from the western excavation site are consistent with a combination of reductive fractionation of water from well MW-163S (closest to the western excavation site) and mixing with water from well MW-158SR (downgradient from the western excavation site). The data are consistent with a similar Cr(VI) source in water from these three wells, possibly from the western excavation site.

F.6.1.2.3. Northern Subarea

Hexavalent chromium concentrations and delta chromium-53 values in water from wells in the northern subarea and Water Valley are largely within the expected range of anthropogenic compositions within the Q4 2015 regulatory Cr(VI) plume. Hexavalent chromium concentrations and delta chromium-53 values in the northern subarea and Water Valley are less related to fractionation of chromium sourced from local rock and alluvium than elsewhere in the study area. Instead, Cr(VI) concentrations and delta chromium-53 values in the northern subarea are consistent with mixing and fractionation of chromium within water from mudflat/playa deposits, characterized by older water from well MW-133S1 having a carbon-14 activity of 72 pmc (table F.4) that predates releases from the Hinkley compressor station.

Similar to mudflat/playa deposits in the eastern subarea, deposits in the northern subarea contain highly oxidative manganese-IV oxides that facilitate oxidation of Cr(III) to Cr(VI). However, chromium concentrations in mudflat/playa deposits in the northern subarea are higher and contain Miocene materials (chapter C, fig. C.10) that have weathered more extensively than geologically younger, felsic, mudflat/playa deposits in the eastern subarea.

Hexavalent chromium concentrations in water from most wells in the northern subarea and Water Valley were not previously identified as unusual on the basis of their Cr(VI) concentrations at the measured pH. However, Cr(VI) concentrations in water from wells MW-133S1 and MW-154S1 sampled as part of this study were 8.6 and 9.8 µg/L, and regulatory concentrations in water from these wells have been as high as 9.8 and 20 µg/L, respectively (Pacific Gas and Electric Company data, accessed January 12, 2018, at https://www.waterboards.ca.gov/lahontan/water_issues/projects/pge/). Water samples from wells MW-133S1 and MW-154S1 were identified as unusual on the basis of their Cr(VI) concentrations at the measured pH (chapter E, fig. E.18*B*).

F.6.1.3. Reductive Fractionation of Hexavalent Chromium in Oxic Conditions

Differences in Cr(VI) concentrations and delta chromium-53 values within the Q4 2015 regulatory Cr(VI) plume can be attributed to fractionation, mixing with native groundwater, and longitudinal dispersion within the plume (fig. F.24*B*). Differences in Cr(VI) concentrations and delta chromium-53 values outside the Q4 2015 regulatory C(VI) plume can be attributed to variations in the composition of chromium-containing source materials, reductive fractionation of Cr(VI) from those source materials, and mixing of Cr(VI) from different sources (figs. F.26*A*, *B*, *C*). Within Hinkley and Water Valleys, reductive fractionation of chromium isotopes would occur during oxic conditions. Raddatz and others (2011) determined reduction of Cr(VI) in oxic groundwater was limited. However, organic material and reduced ferrous iron sorbed to the surfaces of mineral grains that compose the aquifer may serve as natural reductants, even during oxic conditions (Fendorf and others, 2000).

Hexavalent chromium concentrations and delta chromium-53 values in water from selected wells completed within Mojave-type deposits in the eastern subarea upgradient from the Hinkley compressor station and installed as part of this study (BG-0002, BG-0003A, BG-0004A, BG-0005A, and BG-0006A) were evaluated to estimate fractionation of chromium isotopes during reduction of Cr(VI) to Cr(III) under oxic conditions. Data from these wells represent changes that occur along short groundwater-flow paths in parts of the aquifer that (1) have comparatively uniform geology, (2) are relatively unaffected by irrigation and septic return water, and (3) are upgradient from and not affected by anthropogenic Cr(VI) releases from the Hinkley compressor station. Geologic material encountered at these wells includes recent and older Mojave-type deposits. These materials do not contain large amounts of organic carbon. but older Mojave-type deposits may contain abundant Fe^{2+} oxides that may serve as natural reductants within aquifer material.

Water from the selected BG wells was alkaline, with pH values ranging from 7.7 to 8.1. The probability of Cr(VI) concentrations in water at their measured pH values was greater than 30 percent, consistent with natural Cr(VI) (chapter E, fig. E.18*B*) and not indicative of anthropogenic Cr(VI). Dissolved-oxygen concentrations in water from these wells ranged from 1.3 to 8.4 mg/L (fig. F.27*A*). The initial dissolved-oxygen concentrations in water from these wells were calculated from recharge temperatures and excess air concentrations (fig. F.5*A*). Calculated initial dissolved-oxygen concentrations compared favorably to dissolved-argon concentrations measured in water from wells, with an R^2 value of 0.97 (fig. F.5*A*). Argon, a noble gas, is nonreactive and has a Henry's law constant (unitless) of 3.4×10^{-2} (Ozima and Podosek, 2002) that is similar to the Henry's law constant for oxygen of 3.2×10^{-2} (Sander, 2015).

The amount of dissolved oxygen consumed since groundwater recharge was calculated as the difference between the initial dissolved-oxygen concentration and the measured dissolved-oxygen concentration (figs. F.27*A*, *B*). Concentrations of Cr(VI) in water from the selected wells were higher in water from wells having higher dissolved-oxygen concentrations (fig. F.27*A*) and decreased with consumption of dissolved oxygen (fig. F.27*B*), whereas delta chromium-53 values increased with the consumption of dissolved oxygen (R^2=0.60; fig. F.26*C*), consistent with reductive fractionation of Cr(VI). More reduction was measured in water from well BG-0005A than other wells. The chromium in water from well BG-0005A was previously identified as different from chromium in the other BG wells (fig. F.26*A*), and core material adjacent to the screened interval of well BG-0005A contains more abundant chromium-containing actinolite eroded from the San Gabriel Mountains (chapter C, fig. C.9*A*) than other sampled wells. If BG-0005A is removed from the least-squares regression analysis of Cr(VI) concentrations and delta chromium-53 values (fig. F.27*C*), the R^2 value increases from 0.60 to 0.95. Excluding BG-0005A, the apparent fractionation factor calculated from these data (ε_{app}=1.3) approaches the laboratory fractionation factor (ε=3.5) used in this study. The data indicate that reductive fractionation of Cr(VI) to Cr(III) can occur in oxic groundwater in the presence of natural reductants within aquifer materials, and reductive fractionation does not need suboxic or reducing conditions to proceed.

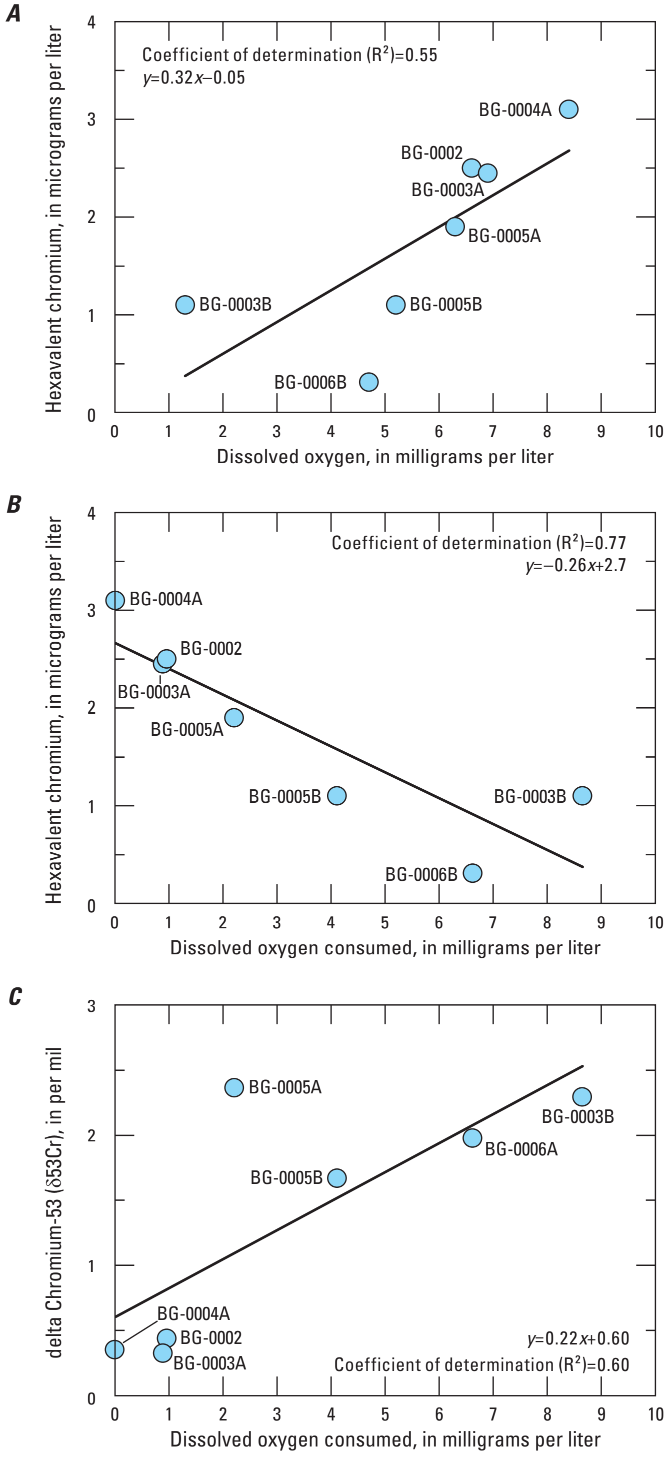


Figure F.27. Hexavalent chromium as a function of *A*, dissolved oxygen and *B*, dissolved oxygen consumed since recharge, and *C*, delta chromium-53 as a function of dissolved oxygen consumed since recharge, for selected wells near recharge areas along the Mojave River, Hinkley Valley, western Mojave Desert, California, May 2016 (R^2, coefficient of determination). Data are available in chapter E (appendix E.1, table E.1.1) and U.S. Geological Survey (2021).

F.6.2. Summary of Chromium Isotope Results

Hexavalent chromium is highly reactive, and reduction of Cr(VI) to Cr(III) occurs in the presence of natural reductants, such as organic material and Fe^{2+} oxide coatings on the surfaces of mineral grains, causing shifts in delta chromium-53 values even in oxic groundwater. Reductive fractionation of chromium under oxic conditions was identified in Mojave-type deposits with an apparent fractionation factor (ε_{app}=1.3) that approaches the laboratory fractionation factor (ε=3.5) used in this study. Anthropogenic Cr(VI) released from the Hinkley compressor station did not move conservatively with groundwater under oxic conditions present within the aquifer. Instead, anthropogenic Cr(VI) reacted with aquifer materials and was removed from groundwater as it flowed downgradient from the Hinkley compressor station. This chromium remains within the aquifer adsorbed to mineral surfaces.

The range in delta chromium-53 values within the Q4 2015 regulatory Cr(VI) plume extends from near 0 per mil, consistent with initial releases of anthropogenic Cr(VI), to as high as 2.8 per mil, consistent with fractionation during reduction of Cr(VI) to Cr(III). The lowest delta chromium-53 values are in water from wells near the Hinkley compressor station having the highest Cr(VI) concentrations, and higher delta chromium-53 values are present in water from wells having lower Cr(VI) concentrations farther downgradient. Despite their anthropogenic source and initial delta chromium-53 values near 0 per mil, some of the highest delta chromium-53 values measured as part of this study were within the Q4 2015 regulatory Cr(VI) plume.

Hexavalent chromium concentrations and delta chromium-53 values within the Q4 2015 regulatory Cr(VI) plume can be calculated assuming laboratory-derived fractionation factors, mixing with native groundwater, and longitudinal dispersion within the Cr(VI) plume. An understanding of these processes facilitates interpretation of the hydrologic history of selected samples within the Q4 2015 regulatory Cr(VI) plume. For example, water from wells near the Lockhart fault showed less mixing with native groundwater; water from wells MW-49 and MW-50B showed a high fraction of mixing with native groundwater with subsequent mixing with recharge water from the Mojave River, rather than longitudinal dispersion within the Cr(VI) plume; and water from production wells C-01 and IW-03, used to pump groundwater for land application of Cr(VI) within the Q4 2015 regulatory Cr(VI) plume, showed a high fraction of mixing of Cr(VI) in water within the Q4 2015 regulatory Cr(VI) plume with native groundwater.

At Cr(VI) concentrations of concern for management purposes near the regulatory Cr(VI) plume margins, Cr(VI) and delta chromium-53 values have little independent predictive value for identification of anthropogenic Cr(VI) in water from wells. However, process-oriented interpretation of delta chromium-53 data with respect to fractionation of selected end members can identify Cr(VI) consistent with natural chromium sourced from aquifer materials in Hinkley and Water Valleys. Compositional end members described include locally derived alluvium, Mojave-type deposits, and weathered hornblende diorite bedrock. Although not diagnostic of anthropogenic Cr(VI), some wells in the eastern and western subareas outside the Q4 2015 regulatory Cr(VI) plume have compositions within the range of anthropogenic Cr(VI) concentrations and delta chromium-53 values. In some cases, these concentrations and values may originate from natural materials represented by compositional end members of Mojave-type deposits, locally derived materials, and weathered bedrock. Hexavalent chromium concentrations and delta chromium-53 values in water from wells within the northern subarea and Water Valley have a different geochemical history that includes mixing with chromium-containing water from underlying mudflat/playa deposits.

Hexavalent chromium concentrations and delta chromium-53 values were not predictive of anthropogenic Cr(VI) and likely could not have been interpreted without the large amount of ancillary data collected as part of this study. Hexavalent chromium concentrations and delta chromium-53 values in water from some wells are outside the range of anthropogenic compositions measured within the Q4 2015 regulatory Cr(VI) plume and indicative of natural Cr(VI). However, the composition of water from wells MW-110S and MW-192D in the eastern subarea, within the range of anthropogenic Cr(VI) concentrations and delta chromium-53 values, could not be explained by fractionation of Cr(VI) from representative end members in the eastern subarea, such as water from well MW-115D that predates Cr(VI) releases from the Hinkley compressor station. Similarly, chromium-containing source materials that would explain the composition of water from wells MW-163S, MW-159S, and MW-159D downgradient from the western excavation site were not identified (chapter C), but Cr(VI) and delta chromium-53 data indicate that the water from these wells seems to be related to a single source upgradient from MW-163S.

Because of their complexity and lack of diagnostic specificity, delta chromium-53 values were not used as part of the summative-scale analyses to calculate the extent of the Cr(VI) plume (chapter G). However, delta chromium-53 values were used to confirm processes used to explain Cr(VI) concentrations in water from some wells near the margins of the summative-scale plume.

F.7. Conclusions

Hexavalent chromium, Cr(VI), was discharged in cooling wastewater to unlined surface ponds from 1952 to 1964 at the Pacific Gas and Electric Company (PG&E) Hinkley compressor station 80 miles northeast of Los Angeles, California, in the Mojave Desert. Chromium-containing wastewater seeped into groundwater in the underlying unconsolidated aquifer. A background Cr(VI) concentration of 3.1 micrograms per liter was estimated for uncontaminated groundwater by a 2007 PG&E study. This value was adopted as the interim regulatory Cr(VI) background concentration by the Lahontan Regional Water Quality Control Board to map the Cr(VI) plume extent for regulatory purposes. In response to limitations of the 2007 study's methodology, and to an increase in the mapped extent of Cr(VI) concentrations greater than 3.1 micrograms per liter between 2008 and 2011, the Lahontan Regional Water Quality Control Board agreed that the 2007 PG&E background Cr(VI) concentration study be updated. The U.S. Geological Survey was requested by the Lahontan Regional Water Quality Control Board to complete an updated background study of Cr(VI) concentrations in Hinkley and Water Valleys.

Multiple environmental and isotopic tracers were used to evaluate the source, movement, and age of groundwater, as well as chemical reactions and environmental processes occurring in groundwater, in and near the mapped October–December 2015 (Q4 2015) regulatory Cr(VI) plume. A suite of environmental tracer data from more than 100 sampled wells was used to evaluate the extent of groundwater and anthropogenic Cr(VI) movement downgradient from the Hinkley compressor station.

The stable isotopes of oxygen and hydrogen in water, delta oxygen-18 and delta deuterium, respectively, are tracers of the source of groundwater. Consistent with previous studies, delta oxygen-18 and delta deuterium data indicated most groundwater in Hinkley and Water Valleys was recharged as infiltration of Mojave River streamflow. Most Mojave River streamflow originated from precipitation near Cajon Pass, a low-altitude gap between the San Bernardino and San Gabriel Mountains 40 miles southwest of Hinkley Valley, rather than as infiltration of runoff from local precipitation in the desert. Departure of delta oxygen-18 and delta deuterium values from the meteoric water line along an evaporative trend line indicated water from wells in the eastern subarea of Hinkley Valley was partly evaporated and affected by irrigation return. Although Mojave River water was present throughout Hinkley and Water Valleys, highly evaporated irrigation return water was not widely present farther downgradient than well MW-104S1, about 1 mile downgradient from the Q4 2015 regulatory Cr(VI) plume.

Agricultural pumping has decreased groundwater levels as much as 60 feet since 1952. Groundwater pumping for agricultural purposes created a local pumping depression beginning in the early 1950s that persisted until groundwater-level declines and subsequent adjudication restricted agricultural pumping within Hinkley Valley in the early 1990s. While present, the pumping depression limited groundwater movement downgradient from the eastern subarea into the northern subarea of Hinkley Valley.

The delta oxygen-18 and delta deuterium isotope data indicated small amounts of locally recharged water, not from the Mojave River, in deeper wells and in wells near the margins of the aquifer in the western subarea, the northern subarea, and parts of Water Valley. This water would not contain anthropogenic Cr(VI) from the Hinkley compressor station. Although groundwater containing anthropogenic Cr(VI) passed near the Hinkley compressor station and would have been recharged from the Mojave River, not all water recharged from the Mojave River would have passed near the Hinkley compressor station and contain anthropogenic Cr(VI) released from that source.

Dissolved gases, including the noble gases neon and argon and nitrogen gas, can be used to evaluate conditions and processes that occurred at the water table during recharge, including recharge temperature and entrapment of excess air. Nitrogen gas data also were used to evaluate the potential for denitrification in the aquifer. Neon, argon, and nitrogen gas data indicated warmer recharge temperatures and less excess air in water from wells farther downgradient from the Mojave River in the northern subarea of Hinkley Valley and in Water Valley compared to wells closer to the river. Differences in recharge temperature and excess air in water from wells reflect changes in groundwater-recharge processes along the Mojave River since the onset of agricultural pumping and water-level declines beginning in the early 1950s. Groundwater recharge from the river before agricultural development likely occurred as a result of infiltration of warmer, sustained streamflows through a comparatively thin unsaturated zone underlying the river.

After agricultural development and subsequent water-level declines, excess air data indicated that infiltration and recharge were more rapid and occurred through a thicker unsaturated zone. Winter streamflows that contribute groundwater recharge needed to be of sufficient magnitude to flow from the mountain front to reach Hinkley Valley despite losing water through infiltration across largely dry stream reaches. These winter streamflows were larger and less frequent than streamflows that reached the valley before agricultural development. Recharge temperature and excess air data estimated from dissolved noble gas and nitrogen gas data were used in calculations of groundwater age.

Groundwater age (time since recharge) was evaluated using a suite of radioactive and industrial gas tracers. Radioactive tracers associated with the atmospheric testing of nuclear weapons beginning in 1952 included tritium, its decay product helium-3, and carbon-14. Industrial gases included chlorofluorocarbons (trichlorofluoromethane [CFC-11], dichlorodifluoromethane [CFC-12], and trichlorotrifluoroethane [CFC-113]) and sulfur hexafluoride. Each tracer has a different environmental history associated with its release to the atmosphere, its entry into the hydrologic cycle, and reactions that may (or may not) occur between groundwater and aquifer materials.

As a result of agricultural pumping, some groundwater containing tritium, and presumably anthropogenic Cr(VI), has been removed from the aquifer. Modern (post-1952) water that passed near the Hinkley compressor station after Cr(VI) releases began in 1952 may contain anthropogenic Cr(VI); however, not all modern water recharged from the Mojave River would have passed near the Hinkley compressor station and contain anthropogenic Cr(VI) released from that source.

The timing of atmospheric tritium and carbon-14 releases from the testing of nuclear testing, beginning in 1952 and reaching a maximum in 1963, coincides with Cr(VI) releases from the Hinkley compressor station between 1952 and 1964. However, with the exception of small flows in 1958, the Mojave River was largely dry between 1952 and 1969—the period spanning Cr(VI) releases from the Hinkley compressor station. Large streamflows in the Mojave River that would have recharged water containing tritium and carbon-14 associated with atmospheric nuclear weapons testing did not occur until 1969. As a consequence, Cr(VI) was initially released from the Hinkley compressor station into groundwater that did not contain tritium and carbon-14 associated with atmospheric nuclear weapons testing, and anthropogenic Cr(VI) would have moved through the aquifer underlying Hinkley Valley in advance of tritium-containing groundwater. By 1969, when large streamflows and groundwater recharge from the Mojave River occurred, tritium in precipitation had decreased from its maximum concentration, whereas carbon-14 activities remained elevated in comparison to tritium. Because of the timing of atmospheric releases and groundwater recharge, carbon-14 activity within groundwater may be a more sensitive tracer of modern- (post-1952) groundwater than tritium in Hinkley and Water Valleys, particularly for parts of the aquifer at the edge of the modern water extent, containing small fractions of modern water.

Tritium concentrations in water from wells ranged from less than the study reporting level of 0.05 to 1.9 tritium units. Tritium was detected in 51 percent of sampled wells and is a robust tracer of modern water, with the highest concentrations in water from wells in the eastern subarea near the Mojave River. In general, tritium was detected more frequently, and at higher concentrations, in water from shallower wells than from deeper wells at the same location. Higher tritium concentrations in water from shallower wells is consistent with more rapid groundwater movement in more permeable deposits that compose the shallow zone of the upper aquifer than in deeper units. Tritium was detected in samples from wells throughout much of the eastern subarea of Hinkley Valley and all wells in the Q4 2015 regulatory Cr(VI) plume. Low concentrations of tritium, less than 0.1 tritium units, were detected in water from wells in the western subarea downgradient from the Lockhart fault but were generally absent upgradient from the fault. Tritium also was detected in water from wells downgradient from the regulatory Cr(VI) plume in most sampled wells in the northern subarea upgradient from the Mount General fault. Water from wells as far downgradient as MW-174S1 and MW-212S1 in Water Valley as far as 7 miles downgradient from the Mojave River contained detectable tritium.

Tritium detections were less abundant, and tritium concentrations were lower, in aquifers underlying Hinkley Valley than initially expected given the large amount of recharge from the Mojave River in recent years. Lower than expected tritium detections and concentrations likely were partly caused by agricultural pumping that resulted in water-level declines as great as 60 feet in some areas and removed groundwater containing tritium [and presumably anthropogenic Cr(VI)] from aquifers underlying Hinkley and Water Valleys. Unlike specific conductance data, major-ion data (chapter E), delta oxygen-18 data, and delta deuterium data, tritium data indicate some water moved downgradient from agricultural pumping depressions in the eastern subarea into the northern subarea in Hinkley Valley as far as the southern part of Water Valley 7 miles downgradient from the Mojave River. Tritium was not detected in water from most wells completed in Water Valley or near the margins of the aquifer, including wells completed in locally derived alluvium in the eastern subarea near Mount General or weathered bedrock in the western subarea.

Tritium/helium-3 recharge cohorts (representing water recharged from the Mojave River when streamflow was known to occur) ranged from 1958 for water from shallower wells farther downgradient in the northern subarea and Water Valley to 2011 for water from shallower wells near the Mojave River. Groundwater age increased with distance downgradient from the Mojave River and with depth. Water recharged in 1958 was present in deeper wells near the margin of the Q4 2015 regulatory Cr(VI) plume, and tritium was not detected in deeper wells farther downgradient. The most commonly measured recharge cohort in water from wells was 1993. Streamflow in 1993 produced the largest volume of recharge from the Mojave River, and agricultural pumping in Hinkley Valley was beginning to decline at that time. The 2011 recharge cohort was the most commonly measured cohort in shallow wells near the Mojave River. Downgradient from the Mojave River, water in shallow wells containing irrigation return assigned to the 2011 cohort may have been affected by helium loss to the atmosphere when pumped to the surface for irrigation. The loss of helium during irrigation effectively reset the tritium/helium-3 age clock and created the appearance of younger water.

Carbon-14 activities in water from wells ranged from 8.9 to 127-percent modern carbon. Activities greater than 100-percent modern carbon indicate post-1952 water affected by the atmospheric testing of nuclear weapons. The distribution of carbon-14 activities was similar to the distribution of tritium, with higher activities near the Mojave River, lower activities farther downgradient, and the lowest activities in deeper wells and wells near the margins of the aquifer. The lowest carbon-14 activities represent groundwater ages (unadjusted for reactions with aquifer materials) of almost 20,000 years before present (ybp). Carbon-14 activities were inversely correlated with terrigenic helium (expressed as a percentage of total helium), and both are tracers of older groundwater with groundwater age increasing as carbon-14 activities decreased and terrigenic helium percentages increased. Terrigenic helium was not elevated near the Lockhart or Mount General faults, demonstrating the relative inactivity of these faults.

On the basis of carbon-14 data, modern groundwater was present in water from wells as far downgradient as MW-174S1 and MW-212S1 and S2 in Water Valley, and the spatial distribution of carbon-14 was similar to the distribution of modern water estimated on the basis of tritium data. Water from 11 sampled wells had unadjusted carbon-14 ages greater than 10,000 ybp, and water from 24 wells had carbon-14 ages greater than 5,000 ybp. Older groundwater was present in water from deeper wells in the northern subarea and Water Valley, in water from wells in locally derived alluvial fan deposits along the flanks of Mount General, and in water from wells within strands of the Lockhart fault. Although water from shallow wells upgradient from the Lockhart fault did not generally contain measurable tritium, carbon-14 activities indicate that this water has a relatively recent near modern (post-1952).

Near the leading edge of the Q4 2015 regulatory Cr(VI) plume, large differences in groundwater age were present at depth within the deep zone of the upper aquifer, possibly as a result of agricultural pumping and pumping to reverse hydraulic gradients for containment of the Cr(VI) plume. Hexavalent chromium concentrations in older groundwater were as high as 11 micrograms per liter but did not exceed 3.6 micrograms per liter in older water from wells completed in “Mojave-type deposits”; this value may represent an upper limit on Cr(VI) concentrations in groundwater within Mojave-type deposits that likely approximates background Cr(VI) concentrations within those deposits in the study area.

Industrial gas data, including chlorofluorocarbons (trichlorofluoromethane [CFC-11], dichlorodifluoromethane [CFC-12], and trichlorotrifluoroethane [CFC-113]) and sulfur hexafluoride, were collected to extend groundwater-age estimates from tritium/helium-3 data further back in time and to provide an additional constraint on the tritium/helium-3 and carbon-14 age of water from wells. Anthropogenic releases of some industrial gases to the atmosphere, including releases of CFC-12, predate atmospheric testing of nuclear weapons beginning in 1952. The distributions of chlorofluorocarbons and sulfur hexafluoride were qualitatively similar to the distributions of tritium and carbon-14, with higher concentrations in shallower wells near the Mojave River and lower concentrations farther downgradient and in water from deeper wells. However, industrial gas data were not generally suitable for groundwater-age dating because of uncertainty caused by addition of these compounds from nonatmospheric inputs.

Chlorofluorocarbon and sulfur hexafluoride concentrations in water from some wells were higher than concentrations expected solely from atmospheric inputs as a result of contributions from domestic (septic), treated municipal wastewater, industrial, or other sources. In some areas, sulfur hexafluoride concentrations increased with increasing groundwater age because of release of sulfur hexafluoride from volcanic materials within the aquifer. Concentrations of CFC-11 higher than concentrations expected from atmospheric inputs were present in water from wells in much of the eastern subarea, including part of the mapped Q4 2015 regulatory Cr(VI) plume extent. Higher than expected CFC-11 concentrations were attributed to treated municipal wastewater discharges to the Mojave River from an upstream regional wastewater treatment plant beginning in 1983. The extent of 1983 water estimated from CFC-11 data is consistent with groundwater-age data estimated from tritium/helium-3 data.

Strontium and chromium isotopes are affected by reactions between aquifer materials and water. These isotopes provide information on rock, minerals, and geologic material that water has contacted in an aquifer and on processes controlling concentrations of these elements in groundwater. Strontium-87/86 ratios and delta chromium-53 isotope values were used to trace interactions of groundwater with aquifer materials and evaluate processes occurring in the regulatory Cr(VI) plume.

Strontium-87/86 ratios in water from sampled wells ranged from 0.70744 to 0.71085. Highly radiogenic strontium-87/86 ratios greater than 0.71000 were present in water from wells completed in coarse-textured Mojave-type deposits throughout the eastern, western, and northern subareas in Hinkley Valley and in the southern part of Water Valley as far downgradient as well MW-174S1. These materials commonly have low chromium concentrations. However, highly radiogenic strontium-87/86 ratios also were present in water from wells completed in weathered bedrock underlying unconsolidated deposits in the western subarea near Iron Mountain. Consequently, highly radiogenic strontium-87/86 ratios were not diagnostic of coarse-textured, low-chromium Mojave-type deposits. In contrast, nonradiogenic strontium-87/86 ratios less than 0.70950, present in the northern subarea downgradient from the Mount General fault and in Water Valley, were diagnostic of chromium-containing unconsolidated deposits partly eroded from Miocene deposits to the east of the study area and from basalts in Water Valley.

Values for delta chromium-53 ranged from near 0 to 2.8 per mil. The extent of reductive fractionation, mixing with native groundwater, and mixing from longitudinal dispersion within the Q4 2015 regulatory Cr(VI) plume can be estimated on the basis of the delta chromium-53 isotope composition of groundwater within the plume. These data were used to evaluate the interaction between chemical processes and physical processes within groundwater containing native and anthropogenic Cr(VI). Reductive fractionation of Cr(VI) to trivalent chromium and its subsequent removal from groundwater in the presence of natural reductants under oxic conditions was identified in Mojave-type deposits, with an apparent fractionation factor (ε_{app}=1.3) that approaches the laboratory fractionation factor (ε=3.5) used in this study. Groundwater delta chromium-53 values indicated Cr(VI) was not conservative within the plume, and large amounts of Cr(VI) were removed by reduction to trivalent chromium during the initial release and remain stored on aquifer material downgradient from the Hinkley compressor station. Most wells completed in local alluvial fan material, Mojave-type deposits, and weathered bedrock in the eastern and western subareas had Cr(VI) concentrations and delta chromium-53 values outside the expected range of anthropogenic Cr(VI) and delta chromium-53.

Hexavalent chromium concentrations and delta chromium-53 values in most wells outside the plume are consistent with fractionation of natural materials represented by compositional end members of locally derived alluvial materials, Mojave-type deposits, or weathered bedrock. Natural end members were not identified for some wells in the eastern subarea associated with mudflat/playa deposits near Mount General, and for wells in the western subarea downgradient from the western excavation site. Hexavalent chromium concentrations and delta chromium-53 values of water from wells in the northern subarea and Water Valley indicate a different geochemical history for Cr(VI) than other areas within Hinkley Valley, which included mixing with chromium-containing water from underlying mudflat/playa deposits. Hexavalent chromium concentrations and delta chromium-53 values in water from wells within the ranges expected for anthropogenic concentrations were not diagnostic of anthropogenic Cr(VI) at the concentrations of interest in this study.

The stable isotopes of oxygen and hydrogen, delta oxygen-18 and delta deuterium, respectively, and tritium/helium-3 and carbon-14 groundwater-age data were used in the summative-scale analyses developed to identify natural and anthropogenic Cr(VI) in Hinkley and Water Valleys (chapter G). Although questions in the summative-scale analyses were not specifically based on noble gas data, age-dating information from industrial gases, or strontium-87/86 ratio and delta chromium-53 data, these data were used to support the summative-scale analyses.

F.8. References Cited

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Appendix F.1. Dissolved Atmospheric and Industrial Gas Data

This appendix contains one table with dissolved atmospheric and industrial gas concentrations in water from sampled wells in Hinkley and Water Valleys in California (table F.1.1; available for download at https://doi.org/10.3133/pp1885). Dissolved atmospheric gas data are provided for argon, nitrogen (dinitrogen), and methane. Dissolved-argon and nitrogen gas data were used to evaluate recharge temperature and excess air in groundwater for interpretation of tritium/helium-3 groundwater ages and to understand geochemical processes that occur within groundwater, including nitrogen reduction, and reductive fractionation of hexavalent chromium under oxic conditions. Dissolved industrial gas data are provided for trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), and sulfur hexafluoride. Dissolved industrial gas data were measured at concentrations suitable for groundwater-age dating purposes. All data are available online (U.S. Geological Survey, 2021). Replicate data for quality assurance purposes are provided within the table.

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Appendix F.2. Calculated Physical and Groundwater Age Values

This appendix contains one table with selected isotope and dissolved gas data and calculated physical and groundwater-age values for water from wells in Hinkley and Water Valleys in California (table F.2.1; available for download at https://doi.org/10.3133/pp1885). Isotope data are provided for carbon-14 and tritium; dissolved atmospheric gas data are provided for argon, neon, and nitrogen. The carbon-14 data were used to calculate groundwater ages that are unadjusted for reactions with aquifer materials. The dissolved gas data were input into the computer program Dissolved Gas Modeling and Environmental Tracer Analysis (DGMETA; Jurgens and others, 2020) that was used to calculate groundwater recharge temperature, excess air, and excess nitrogen concentrations in groundwater. The tritium data were used with helium concentration and helium isotope data (chapter E, appendix E.1, table E.1.1) to calculate tritium/helium-3 groundwater ages, assign recharge cohorts (time of recharge estimated from flow in the Mojave River at Barstow, California, station number 10262500), and calculate the fraction of modern (post-1952) water in a sample according to an approach developed by Schlosser and others (1989). Measured data and laboratory precision data are available online at https://doi.org/10.5066/F7P55KJN (U.S. Geological Survey, 2021).

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