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

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The Pacific Gas and Electric Company (PG&E) Hinkley compressor station (fig. 1), in the Mojave Desert, 80 miles northeast of Los Angeles, California, is used to compress natural gas as it is transported through a pipeline from Texas to California. Between 1952 and 1964, cooling water was treated with a compound containing hexavalent chromium, Cr(VI), to prevent corrosion of machinery within the compressor station. Cooling wastewater containing Cr(VI) was discharged to unlined ponds and released into groundwater. Since 1964, cooling-water management practices have been used that do not contribute chromium to groundwater.

A 2007 PG&E-funded study estimated the natural Cr(VI) background concentration in Hinkley Valley to be 3.1 micrograms per liter (µg/L; CH2M Hill, 2007); this value was adopted as the interim Cr(VI) background concentration for regulatory purposes by the Lahontan Regional Water Quality Control Board (RWQCB) in 2007. The Lahontan RWQCB requested that the 2007 background Cr(VI) concentration study be updated by the U.S. Geological Survey (USGS) to (1) address limitations with the 2007 study methodology (Lahontan Regional Water Quality Control Board, 2011) and (2) include increases in the mapped extent of Cr(VI) concentrations greater than 3.1 µg/L and increases in the regulatory Cr(VI) plume extent between 2008 and 2012. The purpose of the updated study was to estimate Cr(VI) background concentrations in unconsolidated deposits that compose the upper aquifer underlying Hinkley and Water Valleys (Izbicki and Groover, 2016).

Rock and aquifer deposits within Hinkley Valley have chromium concentrations commonly less than 25 milligrams per kilogram (Izbicki and others, 2023). These concentrations are typical of the region and less than the average bulk continental crustal concentration for chromium of 185 mg/kg (Reimann and de Caritat, 1998). With the exception of hornblende diorite that crops out in Iron Mountain along the western margin of Hinkley Valley, chromium-containing rocks in the area are either (1) not consistently high in chromium; (2) have limited areal extent; or (3) in the case of basalt, are present only in Water Valley. More than 90 percent of the chromium in aquifer deposits is contained within unweathered mineral grains and is comparatively unavailable to groundwater. Consequently, natural Cr(VI) in water from wells within Hinkley and Water Valleys is related to factors other than chromium abundance, including (1) mineralogy and weathering rates of chromium-containing minerals; (2) accumulation of chromium weathered from chromium-containing minerals within iron- and manganese-oxide surface coatings on mineral grains and subsequent oxidation of accumulated trivalent chromium, Cr(III), to Cr(VI) in the presence of manganese oxides; (3) texture of aquifer deposits, with finer-textured deposits having greater surface area and more abundant iron- and manganese oxide coatings; and (4) pH-dependent desorption of Cr(VI) from iron- and manganese oxide surface coatings on mineral grains into groundwater under appropriate aqueous geochemical conditions. Once oxidized to Cr(VI), desorption of Cr(VI) from sorption sites on the surfaces of mineral grains increases with increasing pH. During timespans of several thousand years, pH increases with groundwater age (time since recharge) as silicate minerals that compose aquifers weather, and natural Cr(VI) concentrations may increase in older groundwater within Hinkley and Water Valleys as long as that older water remains oxic (contains dissolved oxygen).

Figure 1. Pacific Gas and Electric Company (PG&E) compressor station, Hinkley, California, March 2009. (Photograph by Steven Perry, ARCADIS, Inc., courtesy of PG&E).

The extent of anthropogenic (human-made) Cr(VI) released from the Hinkley compressor station was estimated using a summative-scale analysis of geologic, hydrologic (including groundwater source and age), and geochemical data collected from more than 100 wells between March 2015 and November 2017 (Izbicki and others, 2023). Sampled wells were selected by the USGS with input from a Technical Working Group (TWG) consisting of local community members, the Independent Review Panel (IRP) Manager, the Lahontan RWQCB, PG&E, and PG&E consultants (fig. 2). The summative scale developed from data collected as part of this study consisted of eight questions requiring binary (yes or no) answers for each sampled well (table 1). The questions were intended to provide (1) a transparent framework for data interpretation in which all stakeholders participated; (2) unbiased interpretation of data traceable to numerical measurements; (3) a framework in which geologic, hydrologic, and geochemical data could be interpreted collectively; and (4) a framework to consolidate different types of data into simple, easy-to-understand illustrations.

A score of -1 was assigned for answers to questions within the summative scale that were consistent with natural Cr(VI); a score of +1 was assigned for answers consistent with anthropogenic Cr(VI). Scores for each question in the summative scale were summed to create a single score for each sampled well. Possible scores ranged from –8 for wells having all answers consistent with natural Cr(VI), to +8 for wells having all answers consistent with anthropogenic Cr(VI). Data were not available to score every question within the scale for every sampled well. Consequently, summative-scale scores were evaluated as the percent of the total possible score for each well, with possible scores ranging from –100 to +100 percent for natural and anthropogenic Cr(VI), respectively. When data from each well were scored using the questions and metrics

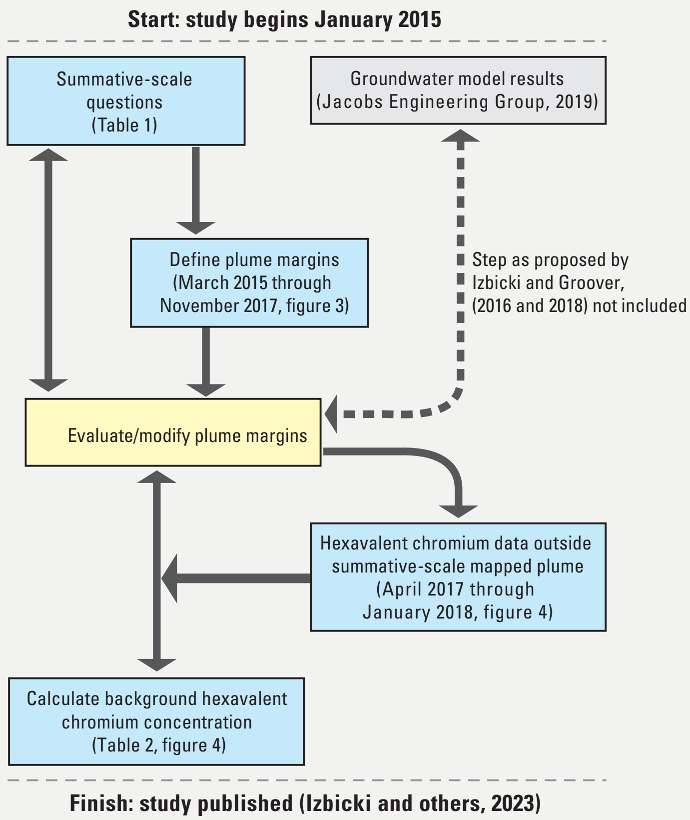

Figure 2. Data collection, summative-scale analyses and interpretation, background calculation, and report preparation for U.S. Geological Survey background hexavalent chromium, Cr(VI), study, Hinkley and Water Valleys, western Mojave Desert, California. Data are modified from Izbicki and others (2023).

within the summative scale, all stakeholders would score each well the same way and would draw the same summative-scale Cr(VI) plume extent.

The summative-scale scores were used to draw the boundary of the summative-scale Cr(VI) plume around the lowest magnitude positive-percentage score that produced a contiguous plume extent (percentage scores greater than 50 percent). The summative-scale Cr(VI) plume extent of 5.5 square miles (mi^2; fig. 3) was larger than the 2.2 mi^2 extent of the October–December 2015 (Q4 2015) regulatory Cr(VI) plume (ARCADIS, 2016) but smaller than the 8.3 mi^2 maximum mapped extent of Cr(VI) concentrations greater than the interim regulatory Cr(VI) background concentration of 3.1 µg/L (fig. 3). The summative-scale Cr(VI) plume is within unconsolidated "Mojave-type" aquifer deposits transported to the area by the Mojave River that are composed of low-chromium alluvium and near shore lake (beach) deposits (Miller and others, 2020). Most groundwater within the summative-scale Cr(VI) plume was neutral to slightly alkaline (regulatory pH values less than 7.2; ARCADIS, 2016), contained tritium (a radioactive isotope of hydrogen having a half-life of 12.3 years), and was recharged from the Mojave River after 1952 (Izbicki and others, 2023).

The summative-scale Cr(VI) plume is within the area covered by the PG&E monitoring-well network. Although the summative-scale Cr(VI) plume includes wells identified as containing anthropogenic Cr(VI), the summative-scale Cr(VI) plume may include wells that have Cr(VI) concentrations below regulatory concern and does not define the Cr(VI) plume extent for regulatory purposes. Hexavalent chromium concentrations in water from wells outside the summative-scale Cr(VI) plume extent were used to calculate background Cr(VI) concentrations that can be used to update the regulatory Cr(VI) plume extent.

The selected study design (fig. 2; Izbicki and Groover, 2016, 2018) compared the summative-scale Cr(VI) plume extent with particle-track simulations calculated using an updated groundwater-flow model of Hinkley Valley prepared by PG&E consultants (Jacobs Engineering Group, Inc., 2019). Differences among measured groundwater-age data, Cr(VI) regulatory data, and particle simulations (Izbicki and others, 2023) were not reconciled within the timeframe of this study; consequently, the updated groundwater-flow model was not used to iteratively evaluate and refine the summative-scale Cr(VI) plume extent.

Outside the summative-scale Cr(VI) plume extent, naturally occurring Cr(VI) concentrations greater than the interim Cr(VI) regulatory background concentration of 3.1 µg/L were identified in water from wells completed in (1) fine-textured materials, including mudflat/playa deposits; (2) materials having visually abundant iron- and manganese-oxide surface coatings; (3) weathered hornblende diorite bedrock in the western subarea; and (4) weathered Miocene (5.3 to 23 million years old) materials underlying the western subarea, parts of the northern subarea downgradient from the Mount General fault, and Water Valley (fig. 3). Naturally occurring Cr(VI) concentrations in groundwater within these materials differ but can exceed 10 µg/L in areas where older, oxic (contains dissolved oxygen) groundwater is strongly alkaline with pH values greater than 8.0.

Hexavalent chromium concentrations as high as 10 µg/L (Izbicki and others, 2023) were measured in water from wells downgradient from the "western excavation site" (fig. 3). The western excavation site, on property owned by PG&E, was used as an illegal disposal site by unknown parties. The western excavation site has a different hydrologic history from the Hinkley compressor station and is managed separately for regulatory purposes. Chemical and mineralogic data did not indicate high natural abundance, unusual mineralogy, unusual sorptive properties, or unusual aqueous geochemistry for chromium within unconsolidated deposits that would contribute to natural high Cr(VI) concentrations in water from wells downgradient from the western excavation site (Izbicki and others, 2023). Although Cr(VI) releases have not been confirmed at the western excavation site, Cr(VI) concentrations in water from downgradient wells were not used for the calculation of background Cr(VI) values.

Background Cr(VI) concentrations near the margins of the Cr(VI) plume can be used for regulatory purposes including updating the regulatory Cr(VI) plume extent, plume management, and establishment of cleanup goals. Background Cr(VI) concentrations were calculated using the computer program ProUCL 5.1 (Singh and Maichle, 2015) as the upper 95-percent tolerance level, UTL_{95}. The UTL_{95} is the value below which 95 percent of measured concentrations are expected to fall 95 percent of the time. The UTL_{95} controls for false positive and false negative results (statistical errors) in estimates of background.

Hexavalent chromium data from 81 wells completed in undifferentiated, unconsolidated deposits outside the summative-scale Cr(VI) plume, collected quarterly between April 2017 and March 2018, were used to calculate an overall UTL_{95} value of 3.8 µg/L. The overall UTL_{95} value is similar to the maximum Cr(VI) concentration of older groundwater in contact with Mojave-type deposits of 3.6 µg/L (Izbicki and others, 2023). For regulatory purposes, including plume management near the summative-scale Cr(VI) plume margin, UTL_{95} values of 2.8, 3.8, and 4.8 µg/L were calculated for the eastern and western subareas and the northern subarea upgradient from the Mount General fault, respectively (table 2). A separate UTL_{95} value of 5.8 µg/L was calculated for wells near mudflat/playa deposits in the eastern subarea near Mount General. A UTL_{95} value of 2.3 µg/L was calculated for Cr(VI) concentrations that may have been present in Mojave-type deposits within the updated regulatory Cr(VI) plume if Cr(VI) had not been released from the Hinkley compressor station. This value is lower than values elsewhere in Hinkley Valley because of

Table 1. Summative-scale questions used to determine the extent of natural and anthropogenic (human-made) hexavalent chromium, Cr(VI), Hinkley and Water Valleys, western Mojave Desert, California. Data are modified from Izbicki and others (2023).

[Items in the scale are formulated as questions requiring a binary, yes or no, answer. Based on the answers to each question, a score of –1 is consistent with a natural source and a score of 1 is consistent with an anthropogenic source. **Abbreviations:** USGS, U.S. Geological Survey; PG&E, Pacific Gas and Electric Company; mg/kg, milligrams per kilogram; GAMA, Groundwater Ambient Monitoring Assessment Project]

Question	Data source	Chapter where data are discussed	Answer and score	
			Yes	No
1. Are geologic materials at the well screen fine textured (predominately silt or finer)?	USGS lithologic descriptions of core material (PG&E lithologic descriptions from well logs or drillers logs used if core material was not available)	Chapters B, C and E	−1	1
2. Do geologic materials at the well screen contain more than 85 mg/kg chromium?	Portable (handheld) X-ray fluorescence (HXRF) measurements of core material	Chapter B	−1	1
3. Do geologic materials at the well screen contain more than 970 mg/kg manganese?	Portable (handheld) X-ray fluorescence (HXRF) measurements of core material	Chapter B	−1	1
4. Are Cr(VI) concentrations trended upward, downward or no trend with time?	Regulatory Cr(VI) data collected between July 2012 and June 2017, interpreted using the Mann-Kendall test for trend (Helsel and others, 2020)	Chapter D	1	−1
5. Is there an excess of Cr(VI) with respect to pH, with the probability of natural Cr(VI) occurrence at the measured pH less than 30 percent?	pH-dependent sorption evaluated on the basis of pH and Cr(VI) concentrations in California-wide GAMA data	Chapter E	1	−1
6. Is there an excess of Cr(VI) with respect to other trace elements?	Principal component analyses (PCA; Helsel and others, 2020) of Cr(VI), arsenic, vanadium, uranium, iron, and manganese.	Chapter E	1	−1
7. Was the water recharged from the Mojave River?	delta oxygen-18, δ18O, and delta deuterium, δD, data	Chapter F	1	−1
8. Does the water contain measurable modern, post-1952, water (with measurable tritium) and a carbon-14 activity greater than 84 percent modern carbon?	Tritium, helium-3, and carbon-14 data.	Chapter F	1	−1

coarser textured, low-chromium deposits and proximity to recharge areas along the Mojave River that results in younger, less alkaline (near-neutral pH) groundwater compared to wells farther downgradient. The value may be a suitable cleanup metric for wells within the updated regulatory Cr(VI) plume. The UTL_{95} values calculated for undifferentiated deposits in the northern subarea downgradient from the Mount General fault and in Water Valley were 9.0 and 6.1 µg/L, respectively. These values define background Cr(VI) concentrations in areas farther downgradient from the plume margins (fig. 4).

Hexavalent chromium concentrations in water from more than 70 domestic wells sampled in Hinkley and Water Valleys between January 27 and 31, 2016, did not exceed 4.0 µg/L (Izbicki and Groover, 2018). Hexavalent chromium concentrations in water from domestic wells were within background ranges expected for native (uncontaminated) groundwater within the various subareas in Hinkley Valley. However, domestic wells in former residential areas within the community of Hinkley having Cr(VI) concentrations as high as 8.6 µg/L had been destroyed by PG&E based on guidance from the Lahontan RWQCB and were not available for sample collection. Water from 47 percent of sampled domestic wells had arsenic, uranium, or nitrate concentrations above drinking water limits (maximum contaminant levels, MCLs) for these constituents.

Remediation of anthropogenic Cr(VI) within groundwater downgradient from the Hinkley compressor station is accomplished using a number of techniques, including bioremediation using ethanol as a reductant injected within a volume of aquifer known as the in situ reactive zone (IRZ). Laboratory-microcosm studies showed that soluble Cr(VI) was rapidly reduced to Cr(III) with additions of ethanol. Reduced Cr(III) was sorbed and then sequestered into crystalline iron and manganese oxides on the surfaces of mineral grains within the microcosms during a period of several months. Sequestration of chromium with manganese oxides facilitated reoxidation of Cr(III) back to Cr(VI) within 14 days after oxic conditions were established within laboratory microcosms. The amount of reoxidation of Cr(III) to Cr(VI) increased with manganese (Mn) concentration, and as much as 20 percent of the added Cr was oxidized to Cr(VI) in microcosms prepared as part of this study. Although much of the reoxidized Cr(VI) remained sorbed to mineral grains, aqueous Cr(VI) was present within the microcosms. Microcosm studies are not directly analogous to reactions that occur within aquifers; however, maintenance of anoxic (does not contain oxygen) conditions within the IRZ could ensure future sequestration of chromium within treated aquifer materials as Cr(III).

Results of the USGS Cr(VI) background study are presented by Izbicki and others (2023). Hexavalent chromium background concentrations can be used for regulatory purposes to define and manage the Cr(VI) plume margins, identify unusual Cr(VI) concentrations outside the Cr(VI) plume margins, and establish cleanup goals within the updated regulatory Cr(VI) plume. The Lahontan RWQCB has the sole authority to establish and update Cr(VI) background concentrations for regulatory purposes.

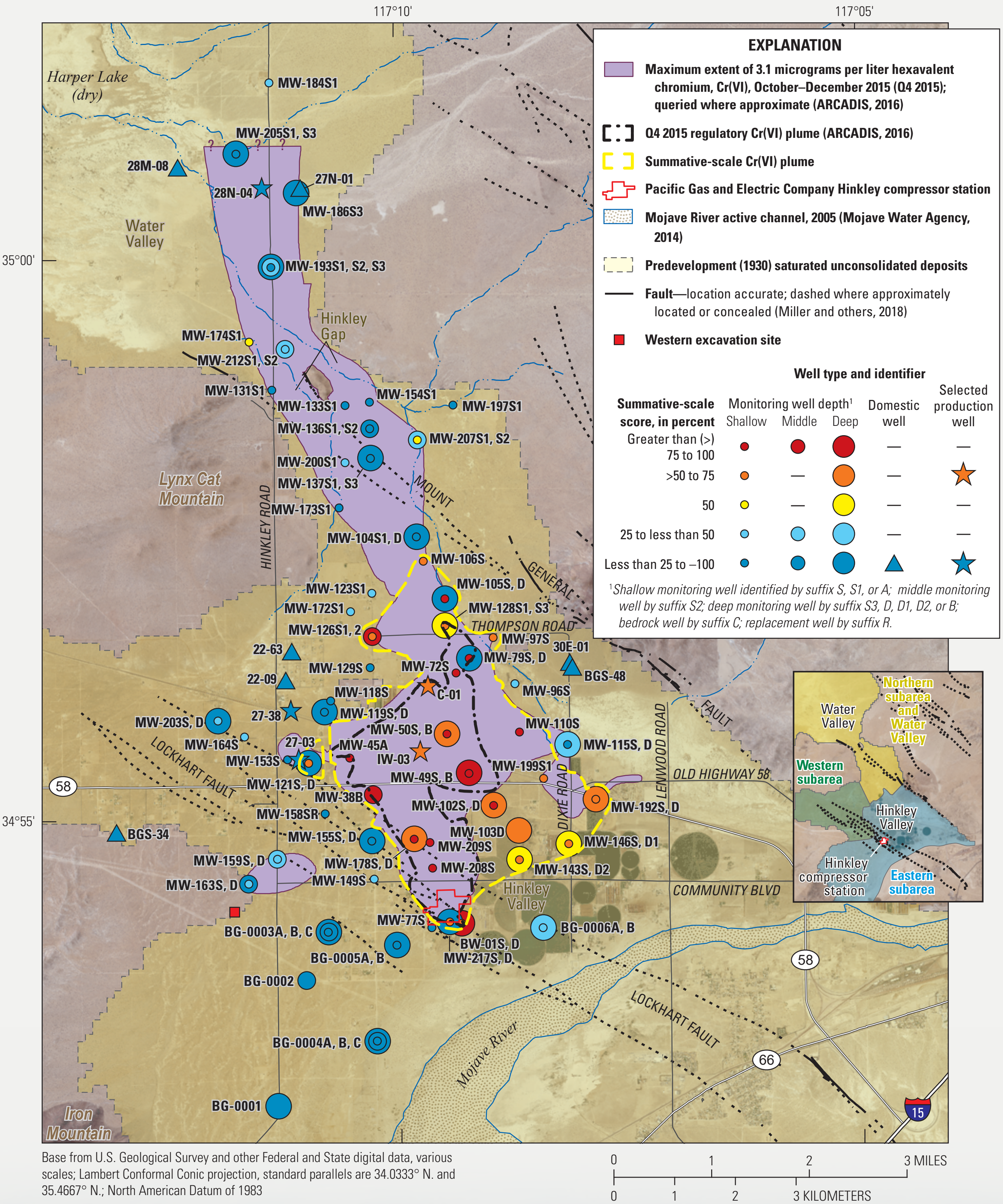

Figure 3. Summative-scale scores and summative-scale hexavalent chromium plume extent, Hinkley and Water Valleys, western Mojave Desert, California, March 2015 through November 2017. Summative-scale scores were calculated from data available in Izbicki and others (2023) chapter E (appendix E.1, table E.1.1), Groover and Izbicki (2018), and U.S. Geological Survey (2021). Selected data and scores are available in Izbicki and others (2023) chapter G (appendix G.1, table G.1.1).

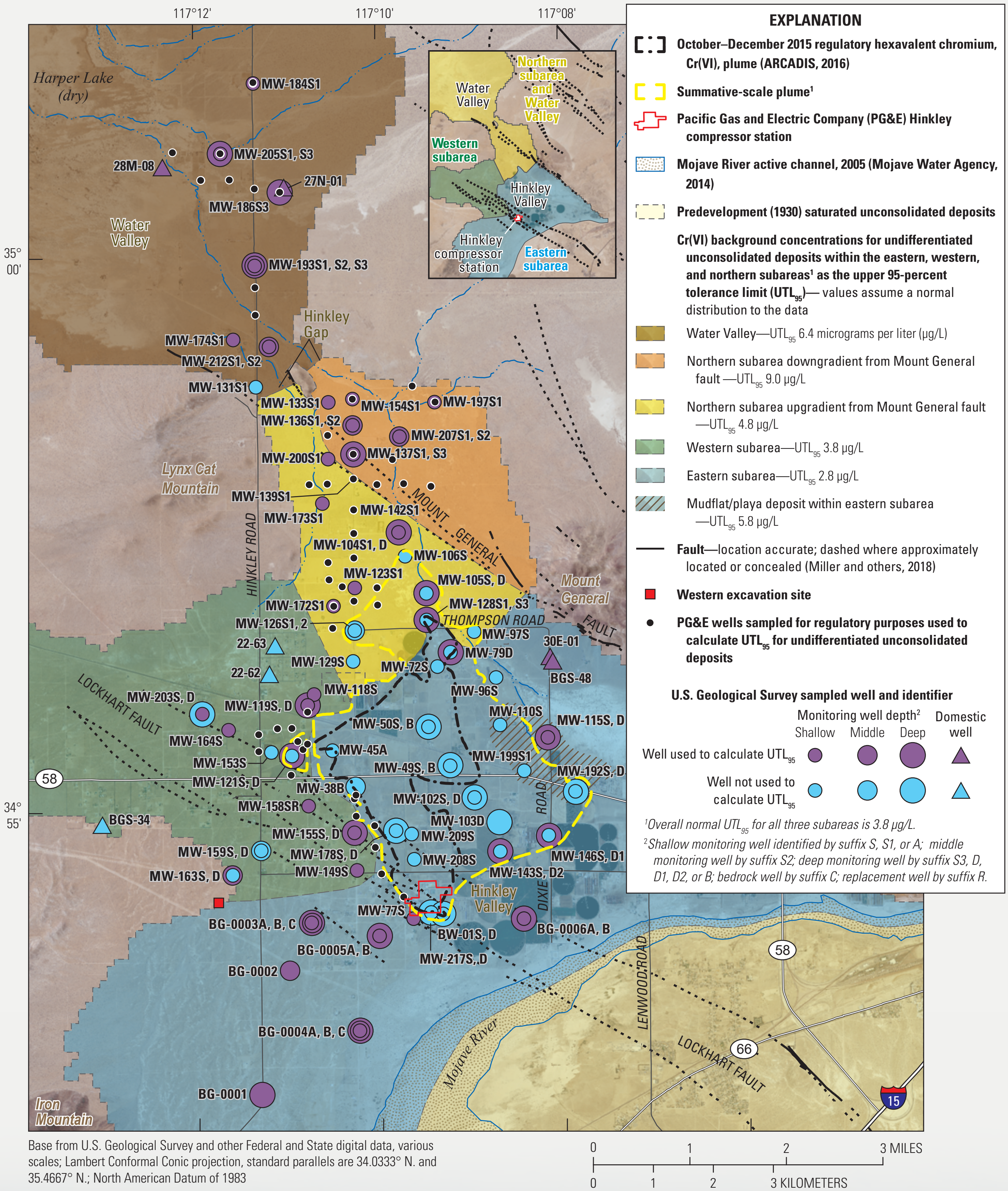

Figure 4. Background hexavalent chromium, Cr(VI), concentrations within Hinkley and Water Valleys, western Mojave Desert, California, April 2017 through March 2018. Data are modified from Izbicki and others (2023).

Table 2: Background hexavalent chromium, Cr(VI), conentrations for plume management within Hinkley Valley, western Mojave Desert, California, April 2017 through March 2018. Locations of subareas identified in table 2 are shown in figure 4.

[Background Cr(VI) concentrations calculated as the upper 95-percent tolerance limit, UTL_{95}, using the computer program ProUCL 5.1 (Singh and Maichle, 2015). The number of wells is the number of wells used in the calculation. **Abbreviation:** µg/L, micrograms per liter]

Number of wells	UTL_{95}, in µg/L	Maximum Cr(VI), in µg/L	Modeled distribution
Eastern subarea[1]			
24	2.8	3.6	normal
Western subarea			
27	3.8	3.8	normal
Northern subarea (upgradient of Mount General fault)[2]			
30	4.8	4.0	normal
Overall (eastern and western subareas and the northern subarea upgradient of the Mount General fault)			
81	3.8	4.0	normal

[1]A separate UTL_{95} value of 5.8 µg/L calculated for mudflat/playa deposits and older groundwater near Mount General. An additional UTL_{95} value of 2.3 µg/L calculated for the Cr(VI) plume extent after regulatory updates.

[2]Separate UTL_{95} values of 9.0 and 6.1 µg/L were calculated for the northern subarea downgradient from the Mount General fault and for Water Valley, respectively.

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