



# Cr(VI) occurrence and geochemistry in water from public-supply wells in California



John A. Izbicki<sup>a,\*</sup>, Michael T. Wright<sup>a</sup>, Whitney A. Seymour<sup>a</sup>, R. Blaine McCleskey<sup>a</sup>,  
Miranda S. Fram<sup>a</sup>, Kenneth Belitz<sup>a</sup>, Bradley K. Esser<sup>b</sup>

<sup>a</sup> US Geological Survey, United States

<sup>b</sup> Lawrence Livermore National Laboratory, United States

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## ABSTRACT

Hexavalent chromium, Cr(VI), in 918 wells sampled throughout California between 2004 and 2012 by the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP) ranged from less than the study reporting limit of 1 microgram per liter ( $\mu\text{g/L}$ ) to 32  $\mu\text{g/L}$ . Statewide, Cr(VI) was reported in 31 percent of wells and equaled or exceeded the recently established (2014) California Maximum Contaminant Level (MCL) for Cr(VI) of 10  $\mu\text{g/L}$  in 4 percent of wells. Cr(VI) data collected for regulatory purposes overestimated Cr(VI) occurrence compared to spatially-distributed GAMA-PBP data. Ninety percent of chromium was present as Cr(VI), which was detected more frequently and at higher concentrations in alkaline ( $\text{pH} \geq 8$ ), oxic water; and more frequently in agricultural and urban land uses compared to native land uses. Chemical, isotopic (tritium and carbon-14), and noble-gas data show high Cr(VI) in water from wells in alluvial aquifers in the southern California deserts result from long groundwater-residence times and geochemical reactions such as silicate weathering that increase pH, while oxic conditions persist. High Cr(VI) in water from wells in alluvial aquifers along the west-side of the Central Valley results from high-chromium in source rock eroded to form those aquifers, and areal recharge processes (including irrigation return) that can mobilize chromium from the unsaturated zone. Cr(VI) co-occurred with oxyanions having similar chemistry, including vanadium, selenium, and uranium. Cr(VI) was positively correlated with nitrate, consistent with increased concentrations in areas of agricultural land use and mobilization of chromium from the unsaturated zone by irrigation return.

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## 1. Introduction

Chromium is the 21st most abundant element in the earth's crust (Emsley, 2001), with an average concentration between 100 and 180 milligrams per kilogram (mg/kg) (Nriagu and Niebor, 1988; Reimann and Caritat, 1998; Hitchon et al., 1999). Chromium concentrations are higher in basaltic and ultramafic rocks which have average concentrations of about 200 and 2400 mg/kg, respectively (Nriagu and Niebor, 1988; Reimann and Caritat, 1998), than in granitic rocks which have an average concentration of 10 mg/kg (Reimann and de Caritat, 1998). However, even granitic rocks have sufficient chromium to yield high Cr(VI) concentrations in groundwater under the proper geochemical conditions (Izbicki et al., 2008a).

Natural occurrence of chromium in alkaline, oxic groundwater as hexavalent chromium, Cr(VI), has been reported since the mid-1970s (Robertson, 1975, 1991), and is commonly associated with the presence of ultramafic rocks and serpentinites in ophiolite complexes (Oze et al., 2007). These rocks are relatively common along the western coast of North America (Oze et al., 2004a, 2004b) with serpentine exposed over approximately 2860 square kilometers ( $\text{km}^2$ ) in California (Kruckeberg, 1984). These rocks may potentially impact groundwater geochemistry over a greater area through erosion, transport, and weathering (Morrison et al., 2009; Smith et al., 2014). In California, naturally-occurring Cr(VI) in water from wells has been reported in the Mojave Desert (Ball and Izbicki, 2004; Izbicki et al., 2008a, 2012), the west-side of the Central Valley (Chung et al., 2001; Dawson et al., 2008; Morrison et al., 2009, 2015; Mills et al., 2011; Manning et al., 2015), and the Coast Ranges (Gonzalez et al., 2005; Steinpress, 2005) (Fig. 1). Reported concentrations in these areas can exceed the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) for total

\* Corresponding author.

E-mail address: [jaizbick@usgs.gov](mailto:jaizbick@usgs.gov) (J.A. Izbicki).

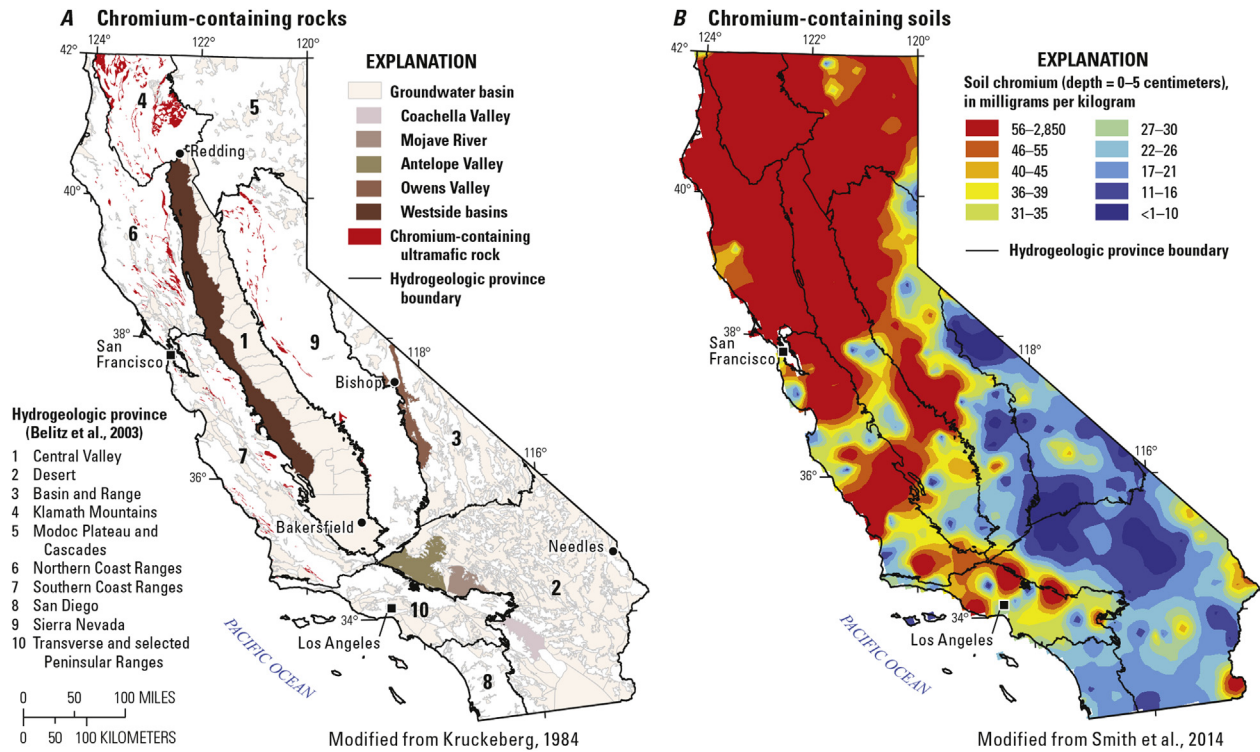


Fig. 1. Areal extent of chromium-containing rocks and soils in California.

chromium of 100 micrograms per liter ( $\mu\text{g/L}$ ) (US Environmental Protection Agency, 2009).

In addition to naturally-occurring sources, chromium has a wide range of industrial uses (Nriagu and Niebor, 1988), and Cr(VI) is a common industrial contaminant. Prior to widespread reports of naturally-occurring Cr(VI), chromium in groundwater was presumed to be associated primarily with anthropogenic contamination (Hem, 1959). Chromium (VI) is highly soluble and mobile in alkaline, oxic groundwater; and contamination can migrate for kilometers with only limited attenuation (Perlmutter et al., 1963; Blowes, 2002; Izbicki et al., 2012). The wide-spread industrial use of chromium and the multiplicity of sources in urban areas can combine to create regional-scale contamination, such as contamination observed in alluvial aquifers underlying parts of the Los Angeles metropolitan area (U.S. Environmental Protection Agency, 2008; California State Water Resources Control Board, 2014a).

Chromium (VI) is a carcinogen if inhaled (Daugherty, 1992; ATSDR, 2012), and may be a carcinogen if ingested (Sedman et al., 2006; Beaumont et al., 2008). Concern over chronic exposure to low-levels of Cr(VI) in drinking water prompted establishment of a California MCL for Cr(VI) of 10  $\mu\text{g/L}$  (California State Water Resources Control Board, 2014b). The purpose of this paper is to identify areas in California where groundwater used for public drinking water supply have concentrations greater than the California MCL and to identify geologic, hydrologic, geochemical, and other factors that contribute to the occurrence of Cr(VI). This study was done as part of the California State Water Resources Control Board Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP).

### 1.1. Geochemistry of chromium

The most common chromium-containing mineral, chromite ( $\text{FeCr}_2\text{O}_4$ ), is highly resistant to weathering. Chromium also is commonly substituted within minerals such as amphiboles,

garnets, micas, pyroxenes and spinels (Reimann and Caritat, 1998; Motzer, 2005). These minerals are more easily weathered than chromite and, where present, may contribute considerable chromium to the environment (Morrison et al., 2009; Rajapaksha et al., 2013).

In most minerals, chromium is present in the +3 oxidation state (Nriagu and Niebor, 1988). Cr(III), an essential micronutrient for humans, is strongly sorbed to mineral surfaces and sparingly soluble under acidic conditions (Kotas and Stasicka, 2000) (Fig. 2). Oxidation of Cr(III) to Cr(VI) occurs in the presence of Mn oxides (Schroeder and Lee, 1975; Eary and Rai, 1987; Guha et al., 2000). Although Cr(VI) is strongly sorbed by Fe oxides at acidic and near neutral pH, it is not strongly sorbed in alkaline or high-ionic strength water (Rai and Zachara, 1984). Under these conditions, Cr(VI) may desorb and enter solution most commonly as the oxyanion  $\text{CrO}_4^{2-}$  (Fig. 2), or as neutral complexes with calcium and magnesium ( $\text{CaCrO}_4^0$  and  $\text{MgCrO}_4^0$ , respectively) (Lelli, 2014). Microbially-mediated reduction of Cr(VI) to Cr(III) occurs in the presence of organic material and other reducing agents (Rai and Zachara, 1984). In some cases, reduction of Cr(VI) to Cr(III) also can occur abiotically (Beller et al., 2014). Depending on pH, the reduced chromium may be rapidly sorbed and removed from solution (Mayer and Schick, 1981; Rai and Zachara, 1984; Charlet and Manceau, 1992).

In simplified conceptual models of the natural-occurrence of chromium in groundwater (Kotas and Stasicka, 2000; Izbicki et al., 2008a; Scancar and Milacic, 2014), the abundance of Cr(III) and Cr(VI) on the surfaces of mineral grains and in solution is determined by: 1) the concentration of chromium in primary minerals, 2) the weathering rates of those minerals, 3) the abundance and reactivity of manganese oxides that convert Cr(III) to Cr(VI), and 4) the abundance and reactivity of reductants that allow microbially-mediated or abiotic reduction of Cr(VI) to Cr(III). In general, the rate of reduction of Cr(VI) to Cr(III) is at least an order of magnitude greater than the rate of oxidation of Cr(III) to Cr(VI) (Scancar and

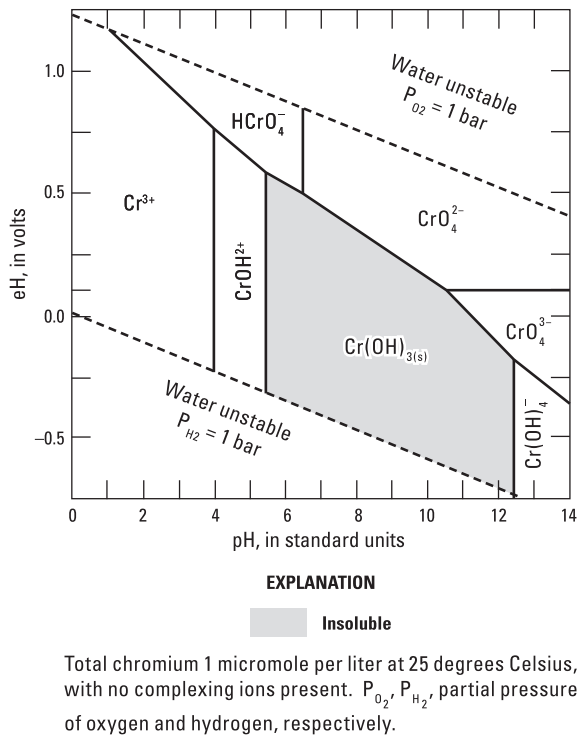


Fig. 2. Aqueous forms of chromium.

Milacic, 2014), so that little Cr(VI) is present on aquifer materials in most settings. However, in settings having an abundance of easily weathered chromium-containing minerals and reactive Mn oxides, Cr(VI) may occur naturally in large concentrations (Morrison et al., 2009; Mills et al., 2011). In alkaline soils and unsaturated deposits, Cr(VI) on the surfaces of mineral grains can desorb and enter solution where it can be mobilized by natural or artificial recharge (Izbicki et al., 2008b, 2008c; Mills, 2011). In saturated deposits, if the pH of groundwater increases along groundwater flowpaths, as a result of silicate weathering or other processes, Cr(VI) can accumulate in alkaline groundwater over long time periods as long as oxic conditions persist (Izbicki et al., 2008a).

## 1.2. Hydrogeologic setting

For the GAMA-PBP, Belitz et al. (2003) divided California into 10 hydrogeologic provinces (Fig. 1). (For the purposes of this paper, these provinces were combined into 8 provinces as discussed in the "Methods" section.) Each hydrogeologic province represents a large area having similar hydrologic, geologic, and climatic conditions. The provinces having the largest areal extent are the Desert (including the Basin and Range), Coast Ranges (combined Northern and Southern Coast Ranges), Sierra Nevada, and Central Valley provinces; while the Desert and Central Valley provinces have the largest areal extent of groundwater basins. The largest numbers of public-supply wells, and the largest population dependent on groundwater as a source of supply, are in the Central Valley, Transverse and Selected Peninsular Ranges, and Coast Ranges provinces (Belitz et al., 2015; Table 1).

Ultramafic and serpentine rock containing chromium occurs in the Klamath Mountains, Coast Ranges, and in the foothills along the west-slope of the Sierra Nevada (Fig. 1A) (Kruckenberg, 1984; Oze et al., 2004; Morrison et al., 2009). These rocks have eroded to form alluvial deposits that compose aquifers in the Coast Ranges, and the west-side of the Central Valley provinces. Although

ultramafic and serpentine rock also are along the east-side of the Central Valley, alluvium in the east-side is dominated by alluvium eroded from granitic rock in the higher altitudes of the Sierra Nevada. Chromium-containing mafic rocks also occur to a lesser extent along the western margin of the Desert hydrogeologic province (Izbicki et al., 2008a). The combination of erosion, transport, and weathering of chromium-containing rock has resulted in high-chromium concentrations in soils in northern California and parts of southern California (Smith et al., 2014) (Fig. 1B). In contrast, chromium concentrations in soils within most of the Desert (including the Basin and Range), and San Diego hydrogeologic provinces are low.

The lowest groundwater recharge rates are in the Desert, including parts of the Basin and Range hydrogeologic provinces. Under present-day climatic conditions precipitation in these areas is less than 150 millimeters per year, and groundwater throughout much of the area was recharged many thousands of years ago (Kulongoski et al., 2003, 2005; Izbicki, 2007). Alluvial materials that compose groundwater basins within these areas are often comparatively non-reactive, and in some areas dissolved oxygen may persist in groundwater for many thousands of years (Izbicki et al., 2004; Izbicki and Michel, 2004). Older groundwater also is present in deeper aquifers elsewhere in California, but materials that compose these aquifers are more reactive and dissolved oxygen may not be present in older groundwater (Izbicki, 1996; Izbicki and Martin, 1997; Izbicki et al., 2003).

## 2. Methods

### 2.1. Data sources and field procedures

Between 2004 and 2012, the GAMA-PBP assessed nearly the entire groundwater resource used for public drinking-water supply in California (Belitz et al., 2015). Areas of the state that contain public-wells were divided into 87 areas, which were subsequently grouped into 35 study units to facilitate sample collection and data interpretation. Each study unit consisted of an alluvial groundwater basin, subbasin, or group of groundwater basins (California Department of Water Resources, 2003) or a hard-rock area outside of defined groundwater basins (Belitz et al., 2003). Detailed descriptions of the study units, and well selection criteria are given in U.S. Geological Survey series reports published for each of the 35 study units (U.S. Geological Survey, 2015).

To ensure a statistically representative spatial distribution of wells sampled as part of the GAMA-PBP, the study units within the GAMA-PBP were divided into equal-area grids (Scott, 1990). State-wide, the median grid-cell size was 25 km<sup>2</sup>, with a median of 20 cells per study unit (Belitz et al., 2015). The objective was to sample one public-supply well (or other well representative of the groundwater resource used for public supply) per grid cell (grid wells). Additional non-grid wells were sampled to provide additional data for the purpose of understanding specific groundwater quality issues. These non-grid wells included wells screened at depths shallower or deeper than the screen depth intervals of public-supply wells.

More than 2400 wells were sampled as part of the GAMA-PBP (Belitz et al., 2015). Samples from 918 of these wells are discussed in this paper for Cr(VI). Because not all GAMA-PBP wells were sampled for Cr(VI), Cr(VI) data have a less rigorous statewide spatial distribution than most other GAMA-PBP data. For example, water from wells within the Klamath Mountains and Modoc Plateau and Cascades provinces was not analyzed for Cr(VI). In addition, wells in some study units within other hydrogeologic provinces were not analyzed for Cr(VI). As a consequence, data from several hydrogeologic provinces (Northern and Southern Coast Ranges; and

**Table 1**  
Hydrogeologic provinces, population, and public-supply wells sampled for hexavalent chromium, Cr(VI), in California as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004 to 2012. [Area, number of groundwater basins, and number of public-supply wells from Belitz et al. (2003). Population from U.S. Census data, 2000. Hydrologic province in italics if data combined from two provinces. km<sup>2</sup> is square kilometers; –, data from province combined into larger province for purposes of this study.]

Hydrogeologic province	Area, in km <sup>2</sup>	Number of groundwater basins	Area of groundwater basins, in km <sup>2</sup>	Population	Number of public-supply wells		Number of public-supply wells sampled for Cr(VI)	
					Inside basins	Outside basins	Inside basins	Outside basins
Central Valley	53,000	36	53,000	53,07,000	5360	0	254	0
<i>Desert</i>	<i>1,17,000</i>	<i>141</i>	<i>72,000</i>	<i>12,80,000</i>	<i>1500</i>	<i>80</i>	<i>205</i>	<i>0</i>
Desert	81,000	96	56,000	12,16,000	1240	60	–	–
Basin and range	36,000	45	16,000	64,000	260	20	–	–
Klamath Mountains	23,000	7	300	75,000	20	110	0	0
Modoc Plateau and Cascades	39,000	53	21,000	1,12,000	240	40	0	0
<i>Coast Ranges</i>	<i>80,000</i>	<i>153</i>	<i>19,000</i>	<i>80,22,000</i>	<i>2510</i>	<i>760</i>	<i>128</i>	<i>8</i>
Northern Coast Ranges	38,000	79	6000	14,23,000	770	280	–	–
Southern Coast Ranges	42,000	74	13,000	65,99,000	1740	480	–	–
San Diego Drainages	10,000	25	1000	34,30,000	180	120	37	13
Sierra Nevada	66,000	22	2000	7,15,000	330	1170	36	96
Transverse and Selected Peninsular Ranges	22,000	33	8000	1,48,99,000	2720	800	108	33

Numbers of samples does not include 343 samples collected and analyzed for Cr(VI) that were later determined to have been contaminated.

Desert and Basin and Ranges hydrologic provinces) were combined to ensure sufficient Cr(VI) data for analyses.

Samples were collected by U.S. Geological Survey field personnel according to U.S. Geological Survey protocols (U.S. Geological Survey, variously dated). Field parameters (temperature, dissolved oxygen, pH, alkalinity, and specific conductance) were measured at the time of collection, and samples were preserved in the field as required for specific analyses (Appendix A).

Samples for Cr(VI) analyses were processed in the field using exchange resins to remove Cr(III) (Ball and McCleskey, 2003a, 2003b). After processing, a filtered sample containing Cr(VI) and Cr(III) and the field processed sample containing only Cr(VI) were acidified to pH less than 2.0 using hydrochloric acid and shipped to the U.S. Geological Survey National Research Laboratory in Boulder, Colo. for analyses of chromium ([http://wwwbr.cr.usgs.gov/projects/GWC\\_chemtherm/](http://wwwbr.cr.usgs.gov/projects/GWC_chemtherm/), accessed November 4, 2014). Cr(III) was determined by difference between the two samples. Field speciation of Cr(VI) allowed for longer holding-times than the 24-h holding time provided by U.S. Environmental Protection Agency (1991) method 218.6 for Cr(VI) preservation and analyses. Most other samples were analyzed at the NWQL in Denver Colo. according to U.S. Geological Survey procedures (<http://nwql.usgs.gov/rpt.shtml?pubs>, accessed November 4, 2014).

Data collected by the GAMA-PBP are available through the U.S. Geological Survey's National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>), and the California State Water Resources Control Board's GeoTracker GAMA ([http://www.waterboards.ca.gov/gama/geotracker\\_gama.shtml](http://www.waterboards.ca.gov/gama/geotracker_gama.shtml)) on-line databases.

Additional data from 1480 public-supply wells within the California State Water Resources Control Board (SWRCB) Division of Drinking Water (DDW) database also were compiled and interpreted as part of this study. Public-supply wells sampled as part of the GAMA-PBP are included in the DDW data. Cr(VI) data for samples collected between 2004 and 2012 (the same time period over which GAMA-PBP samples were collected) were retrieved. For the purposes of this paper, if a well had more than one sample during that time period, the data from the sampling date closest to the date that the GAMA-PBP samples in the same study unit were collected was selected. DDW data were collected by well owners for drinking water compliance purposes and were analyzed by a

number of different laboratories certified by the State of California for analyses of Cr(VI). Field parameters were not typically measured, and samples were not generally preserved or filtered in the field. The DDW database does not include data for dissolved oxygen, tritium, or noble gases; thus, only the GAMA-PBP data were used for evaluation of relations between Cr(VI) and explanatory factors. The DDW data for Cr(VI) are not evenly distributed across the state because during the time period of this study, Cr(VI) was classified as an unregulated chemical and data were collected by only a subset of public-supply systems statewide. DDW data are publicly available from the SWRCB's on-line groundwater information system ([http://www.waterboards.ca.gov/gama/geotracker\\_gama.shtml](http://www.waterboards.ca.gov/gama/geotracker_gama.shtml)).

## 2.2. Quality assurance and statistical methods

Data from equipment and field blanks were used for quality assurance and to establish study reporting levels (SRL) for Cr(VI) and trace elements (Olsen et al., 2010; Davis et al., 2014) (Table S1). Least-squares regression analysis of 91 replicate sample pairs having Cr(VI) concentrations ranging from <1 to 28 µg/L, showed data compared favorably with a R<sup>2</sup> of 0.98 and mean square error of 0.30 µg/L. The average difference between replicate pairs was 4 percent, and in most cases the replicate sample values were identical. As part of this study 1261 samples were collected and analyzed for Cr(VI). Contamination, traced to corroded metal parts in a field pipette used to preserve samples with hydrochloric acid, was identified in 17 of 112 field blank samples collected between September 2004 and December 2005; and resulted in the removal of 343 samples, for a total of 918 samples analyzed for Cr(VI) discussed in this paper. The pipette was replaced with a pipette that did not contain metal parts and contamination issues ceased (Appendix A). Contamination contributed to the less rigorous statewide spatial distribution of Cr(VI) data compared to most other GAMA-PBP data.

Most Cr(VI) data were less than the SRL for this study. Non-parametric descriptive statistics such as medians (and even upper 25-percent quartiles) and associated statistical tests, such as the Median or Wilcoxon rank-sum test (Neter and Wasserman, 1974), are not meaningful for data having a high-occurrence of less than values. As a consequence, differences in Cr(VI) occurrence were

evaluated on the basis of the two-sample Kolmogorov–Smirnov test (Taylor and Emerson, 2011) (Appendix A). Co-occurrence of Cr(VI) and other trace elements was evaluated using Kendall's Tau correlation coefficients (Kendall, 1938) and Principle Component Analyses (PCA) (Kshirsagar, 1972; Gnanadesikan, 1977).

### 3. Results and discussion

#### 3.1. Cr(VI) occurrence

Cr(VI) concentrations in 918 public-supply wells sampled by the GAMA-PBP between 2004 and 2012 ranged from less than the study reporting limit (SRL) of 1 µg/L to 32 µg/L (Fig. 3A). Statewide, Cr(VI) concentrations exceeded the SRL of 1 µg/L in 31 percent of sampled wells, and exceeded the California MCL of 10 µg/L in 4 percent of sampled wells (Fig. 3A). Almost all dissolved chromium, approximately 90 ± 1 percent, was present as Cr(VI) (Fig. 4).

Cr(VI) concentrations in more than 1480 public-supply wells within the DDW database sampled between July 2000 and September 2011 exceeded 1 µg/L in 67 percent of the wells and exceeded the California MCL in 25 percent of wells, with a maximum Cr(VI) concentration of 69 µg/L (Fig. 3B). Similar to the GAMA-PBP data, most Cr(VI) concentrations in excess of the MCL occurred in the Desert and the west-side of the Central Valley. High concentrations also were present in the Transverse and selected Peninsular Ranges near Los Angeles, the eastern part of the San Diego hydrogeologic province, and in areas within the southern part of the Central Valley, and the Northern and Southern Coast Ranges hydrogeologic provinces which were not sampled for Cr(VI) as part of the GAMA-PBP. DDW data show no Cr(VI) concentrations in excess of the California MCL in either the Klamath Mountains or Modoc Plateau and Cascades hydrogeologic provinces (Fig. 3B), despite the presence of chromium-containing rock and soil in those areas (Fig. 1).

Comparison between GAMA-PBP and DDW data using least-

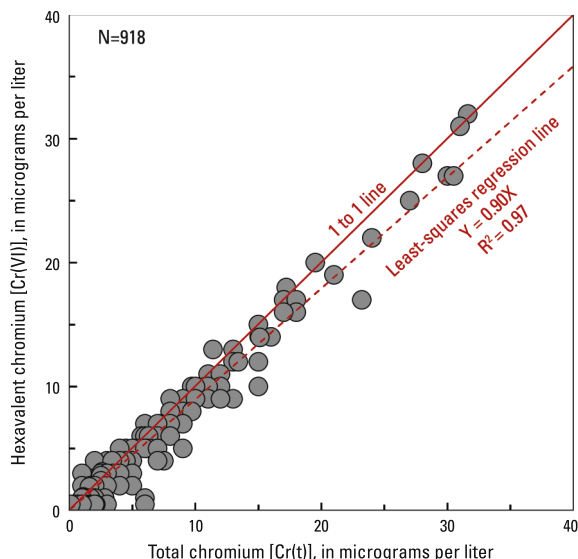


Fig. 4. Hexavalent chromium, Cr(VI), as a function of total chromium, Cr(t), in water from public-supply wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.

squares regression for the same wells sampled less than 3 years apart was good with an  $R^2$  of 0.91 and a Cr(VI) excess of 8 percent in the DDW data (not shown in figures). Some of the Cr(VI) excess in the DDW data may occur because Cr(VI) samples analyzed as part of the GAMA-PBP were filtered and Cr(VI) was separated from Cr(t) in the field; whereas, Cr(VI) samples in the DDW database were not filtered or consistently preserved in the field to prevent changes in Cr(VI) and Cr(III) concentrations. In contrast, a similar comparison between GAMA-PBP and DDW data for samples collected at the same well more than 3 years apart was poor, with an  $R^2$  of 0.58 and

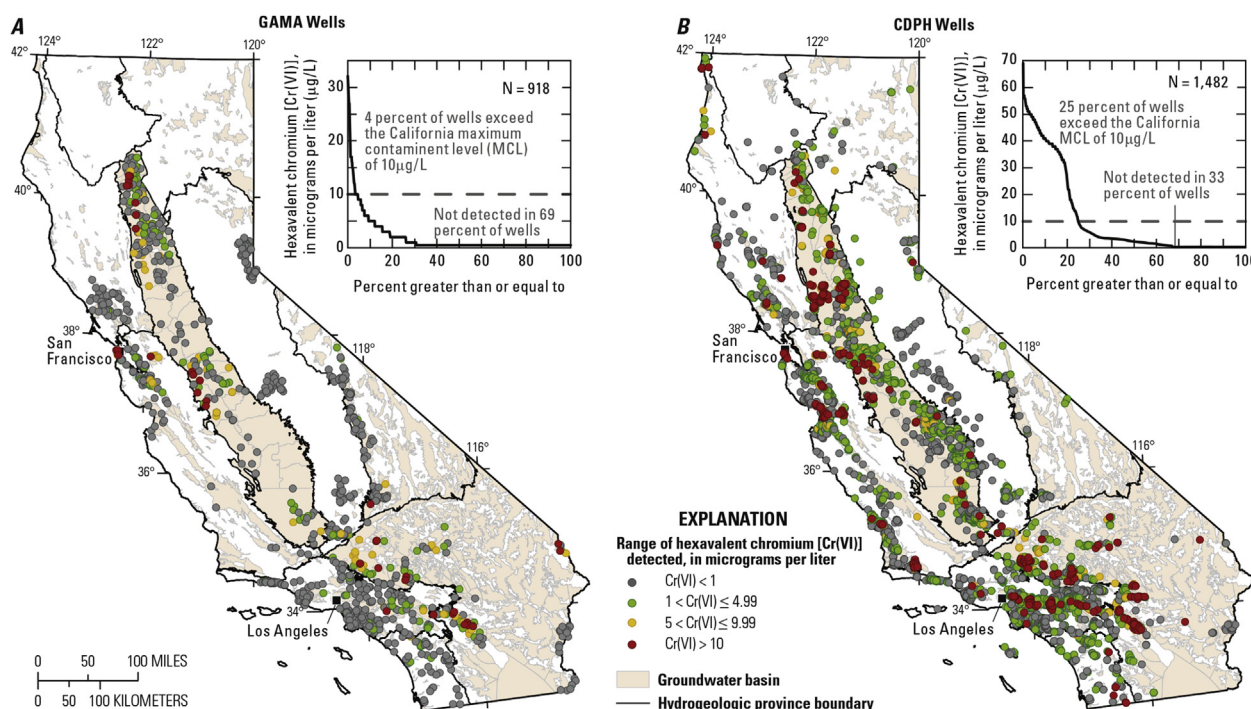


Fig. 3. Hexavalent chromium, Cr(VI), concentrations in water from public-supply wells in California: A) sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012, and B) from the California State Water Resources Control Board (SWRCB) Division of Drinking Water (DDW) databases, 2000–2011.

a Cr(VI) excess of 30 percent in the DDW data. This difference may result from changing sample collection, preservation, and laboratory methods in the longer period of record represented by the DDW data, or because of trends in Cr(VI) concentrations with time in water from some sampled wells.

DDW data were collected for public-health and regulatory purposes. The higher frequency of Cr(VI) detection and concentrations in excess of the California MCL in the DDW data compared to the GAMA-PBP data, especially in urban areas, may result from clustering of analyses in water from wells in areas known to have natural or anthropogenic Cr(VI) occurrence (Belitz et al., 2003, 2015). This clustering creates a spatial bias towards high values. Although Cr(VI) data were less rigorously distributed statewide than most constituents analyzed as part of the GAMA-PBP, they are from representative spatial distributions within individual study units, and are not subject to the same bias associated with sample collection for public-health and regulatory purposes that may over represent areas of known natural or anthropogenic contamination.

In both the GAMA-PBP and DDW data, Cr(VI) concentrations in excess of the California MCL occurred more frequently in the Desert and the west-side of the Central Valley hydrogeologic provinces than in other areas of California, with a few high concentrations in the Coast Ranges and the Transverse and Selected Peninsular Ranges provinces (Fig. 3). The effect of pH, redox, land use, and well construction on Cr(VI) concentrations are discussed to facilitate understanding of differences in Cr(VI) occurrence within different hydrogeologic provinces within California.

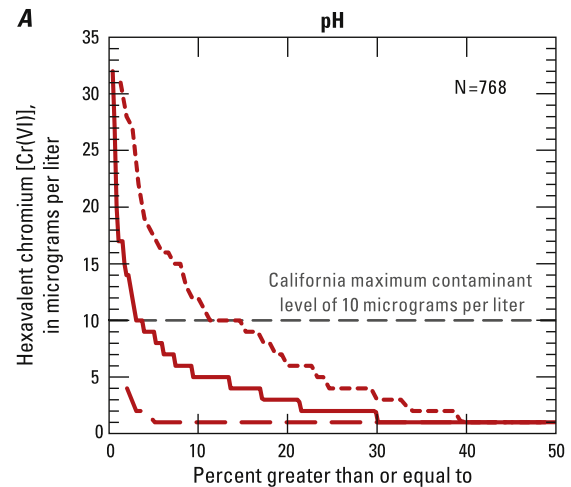
### 3.1.1. Occurrence with pH and redox

Differences in Cr(VI) occurrence with pH data were evaluated by grouping the data into three categories: 1) pH greater than or equal to 8, 2) pH greater than or equal to 7 but less than 8, and 3) pH less than 7. The divisions between the groups were not arbitrary and were established by adjusting the threshold values between the groups at 0.1 unit intervals to maximize the difference in Kendall's Tau correlation coefficients between Cr(VI) and pH within the groups. This approach resulted in statistically significant (although weak) correlation coefficients for pH greater than or equal to 8 of  $-0.173$ , for pH greater than or equal to 7 but less than 8 of  $0.184$ , and no significant correlation for pH less than 7.

Despite the negative correlation, Cr(VI) was detected more frequently and at higher concentrations in alkaline water having pH greater than or equal to 8 (Fig. 5); with Cr(VI) present at concentrations greater than the SRL in 45.3 percent of sampled wells and greater than the California MCL in 15 percent of sampled wells. In water from wells having pH greater than or equal to 7 but less than 8, Cr(VI) was present at concentrations greater than the SRL in 39 percent of sampled wells and greater than the California MCL in 4 percent of sampled wells. In water from wells having a pH less than 7, Cr(VI) was present at concentrations greater than the SRL in 8 percent of sampled wells and did not exceed the California MCL in any sampled wells.

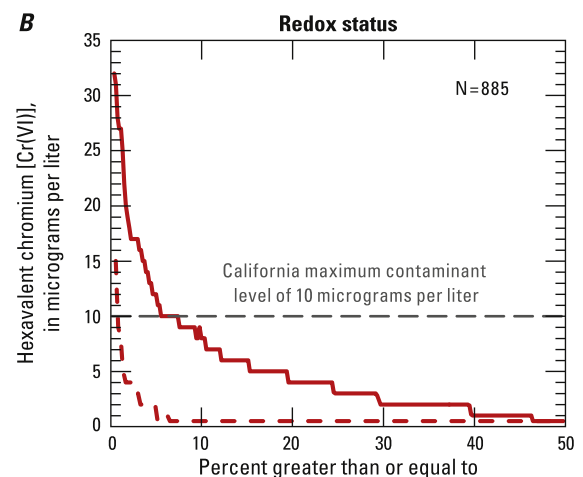
The negative correlation between Cr(VI) and pH in water having pH greater than or equal to 8 may result in part from decreases in dissolved oxygen concentrations and increased presence of reduced conditions in older, more alkaline groundwater. If only oxic water from wells is considered there is no significant correlation between Cr(VI) and pH greater than or equal to 8.0. The data are consistent with a threshold pH near 7.5 (Rai and Zachara, 1984; Izbicki et al., 2008), above which desorption of Cr(VI) from the surfaces of mineral grain occurs and most Cr(VI) is present in solution.

Differences in Cr(VI) occurrence by redox status were evaluated by grouping data into two categories, oxic, and reduced. Oxic water had dissolved oxygen concentrations greater than  $0.5$  mg/L.



EXPLANATION				
pH category	number of samples (N)	$D_{n,n'}$ at $\alpha=0.05$	$D_{n,n'}$	
— · — ·	greater than or equal to 8.0	170	0.107	0.139
—	7.0 to 7.99	503	—	—
· · ·	less than 7.0	95	0.152	0.291

Test statistics shown for comparisons between pH less than 7.0 and 7.0 to 7.99, and for pH 7.0 to 7.99 and greater than or equal to 8.0. Comparison between pH less than 7.0 and greater than or equal to 8.0 not shown. Data shown in red if Cr(VI) distributions are statistically different on the basis of the two-sample Kolmogorov-Smirnov test at a confidence criterion of  $\alpha=0.05$ : where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}^*$  at  $\alpha=0.05$  (Taylor and Emerson, 2011)



EXPLANATION				
Redox category	number of samples (N)	$D_{n,n'}$ at $\alpha=0.05$	$D_{n,n'}$	
—	Oxic	518	0.093	0.323
· · ·	Reduced	367	0.093	0.323

Data shown in red if Cr(VI) distributions are statistically different on the basis of the two-sample Kolmogorov-Smirnov test at a confidence criterion of  $\alpha=0.05$ : where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}^*$  at  $\alpha=0.05$  (Taylor and Emerson, 2011)

Fig. 5. Hexavalent chromium, Cr(VI), as a function of A) pH, and B) redox status, in water from public-supply wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.

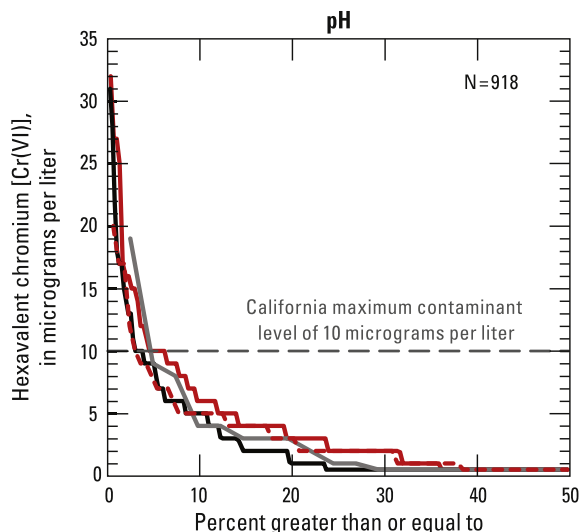
Reduced water had dissolved oxygen concentrations less than 0.5 mg/L. In the absence of dissolved oxygen data, nitrate (less than 0.5 mg/L as N), manganese (greater than or equal to 0.05 mg/L), or iron concentrations (greater than or equal to 0.1 mg/L) were used to characterize reduced water (McMahon and Chapelle, 2008). A similar approach was used to characterize the redox status of water from wells for analysis of the occurrence of vanadium in California (Wright and Belitz, 2010; Wright et al., 2014).

Statewide, Cr(VI) was detected more frequently and at higher concentrations in oxic water; with Cr(VI) present at concentrations greater than the SRL in 46.4 percent of sampled wells and greater than the MCL in 7.4 percent of sampled wells. In reduced water, Cr(VI) was detected at concentrations greater than the SRL in only 4.9 percent of sampled wells and water from only one well exceeded the MCL of 10 µg/L (Fig. 5B). In 10 of 14 samples in reduced water having reportable Cr(VI) concentrations, nitrate was present at concentrations ranging from 0.7 to 12.7 mg/L as N. In some studies, reduction of Cr(VI) to Cr(III) is reported to increase when nitrate is present (Han et al., 2010); however, other studies (Izbicki, 2008; Izbicki et al., 2008b; Chovanec et al., 2012) show nitrate interferes with microbially mediated reduction of Cr(VI) to Cr(III). Inhibition of Cr(VI) reduction may occur in some settings because many of the same microorganisms that reduce Cr(VI) also reduce nitrate (Chovanec et al., 2012), and these microorganisms may preferentially utilize nitrate, which is commonly present at higher concentrations than Cr(VI).

3.1.2. Occurrence with land use and well construction

Land use within a 500-m radius around wells is a useful predictor of water quality within wells in California (Johnson and Belitz, 2009). Examination of Cr(VI) occurrence in wells showed a statistically significant difference (Kolmogorov–Smirnov two-sample test at a confidence criterion of  $\alpha = 0.05$ ) between Cr(VI) concentrations in water from wells in natural (undeveloped) land compared to agricultural, and urban land uses (Fig. 6). Cr(VI) occurrence at concentrations greater than the SRL was greater in water from wells in both agricultural and urban land uses (38 and 36 percent, respectively), compared to natural land use (23 percent). However, Cr(VI) occurrence at concentrations in excess of the MCL appears to be greater only in urban land uses (6 percent) compared to natural and agricultural land uses (4 and 3 percent, respectively). There was no statistically significant difference in Cr(VI) occurrence between natural and mixed land uses, possibly because of the smaller number of sampled wells within the mixed land use category. Similar relations were observed between land use and Cr(t) occurrence by Ayotte et al. (2011). The results suggest that although Cr(VI) may be primarily naturally occurring, low-level region-scale contamination may increase Cr(VI) occurrence in public-supply wells in urban areas (U.S. Environmental Protection Agency, 2008; California State Water Resources Control Board, 2014a), and processes that alter the hydrology or geochemistry may increase the occurrence of Cr(VI) in agricultural and urban areas.

Sampled well depths ranged from 4.5 to more than 650 m below land surface, with a median depth of 122 m below land surface. Additional well-construction data available as part of the GAMA-PBP included top of shallowest opening (screened or perforated interval), and bottom of deepest opening. When only oxic waters are considered, well depth, top of perforated interval, and bottom of perforated interval were significantly positively correlated with Cr(VI) concentrations (Kendall's Tau correlation coefficients of 0.156, 0.070, and 0.078, respectively). For the same samples, pH was similarly positively correlated with well depth, top and bottom of perforated interval (Kendall's Tau correlation coefficients of 0.231, 0.189, and 0.201, respectively). These data suggest that in areas



Land use	number of samples (N)	EXPLANATION	
		$D_{n,n'}$ at $\alpha=0.05$	$D_{n,n'}$
Natural	401	—	—
Mixed	40	0.226	0.073
Agricultural	168	0.125	0.148
Urban	309	0.103	0.125

Data shown in red if Cr(VI) distributions are statistically different from natural Cr(VI) distribution on the basis of the Kolmogorov–Smirnov D statistic at a confidence criterion of  $\alpha=0.05$ : where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}$  at  $\alpha=0.05$  (Taylor and Emerson, 2011).

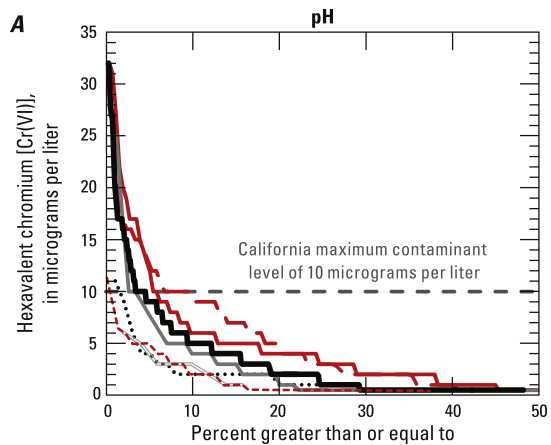
Fig. 6. Hexavalent chromium, Cr(VI), as a function of land use in water from public-supply wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment–Priority Basin Project (GAMA-PBP), 2004–2012.

where groundwater is oxic, Cr(VI) concentrations may increase with well depth, and with the depth of top and bottom of perforations, consistent with increases in pH in deeper groundwater and subsequent desorption of Cr(VI) from aquifer materials. In areas where aquifer materials are more reactive, and groundwater is reducing, Cr(VI) may not be present at depth if dissolved oxygen has been consumed.

3.1.3. Occurrence by hydrogeologic province

Cr(VI) occurrence was greater than statewide occurrence in the Desert and Central Valley hydrogeologic provinces with concentrations exceeding the SRL in 40.3 and 45.1 percent of samples and concentrations exceeding the California MCL in 9.7 and 5.9 percent of sampled wells, respectively (Fig. 7A).

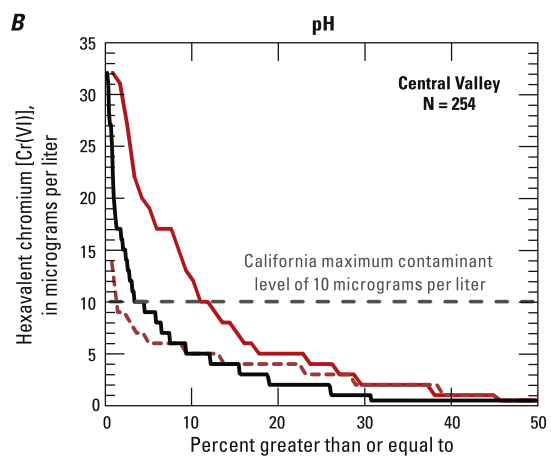
Cr(VI) concentrations greater than the California MCL were found in water from wells throughout the Desert (including Basin and Range) hydrogeologic province. However, Cr(VI) concentrations were highest in alluvial aquifers within the Antelope Valley and Coachella Valley study units (Fig. 1) where concentrations exceeded the SRL in 94 and 74 percent of sampled wells, and exceeded the California MCL in 26 and 20 percent of sampled wells, respectively. The chromium-containing Pelona Schist and related schists (Jacobson et al., 2000) that crop out in these areas (not shown on Fig. 1) may be a source of chromium (Izbicki et al., 2008a). Oxic, alkaline groundwater (with dissolved oxygen concentrations greater than 0.5 mg/L in 95 and 83 percent of sampled wells, and median pH's of 8 and 7.8, respectively), coupled with low



#### EXPLANATION

Hydrologic province	number of samples (N)	$D_{n,n'}$ at $\alpha=0.05$	$D_{n,n'}$
Central Valley	254	0.093	0.143
Desert	205	0.105	0.105
Coast Ranges	136	0.125	0.090
Transverse Ranges	143	0.122	0.083
San Diego	50	0.198	0.131
Sierra Nevada	132	0.127	0.142

Data shown in red if Cr(VI) distribution is statistically different from statewide Cr(VI) distribution on the basis of the two-sample Kolmogorov-Smirnov test at a confidence criterion of  $\alpha=0.05$ : where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}$  at  $\alpha=0.05$  (Taylor and Emerson, 2011)



#### EXPLANATION

Central Valley Hydrologic Province	Number of samples (N)	$D_{n,n'}$ at $\alpha=0.05$	$D_{n,n'}$
East-side	137	0.125	0.156
West-side	117	0.145	0.291

Data shown in red if Cr(VI) distribution is statistically different from statewide Cr(VI) distribution on the basis of the two-sample Kolmogorov-Smirnov test at a confidence criterion of  $\alpha=0.05$ : where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}$  at  $\alpha=0.05$  (Taylor and Emerson, 2011)

groundwater recharge rates and long flowpaths through aquifers within the Antelope and Coachella Valley study units, enable chromium weathered from chromium-containing minerals, and oxidized to Cr(VI), to enter and remain in solution. In contrast to other areas in the Desert, Cr(VI) concentrations did not exceed the California MCL for any wells sampled in the Owens Valley study unit and Cr(VI) was present at concentrations greater than the SRL in only 7 percent of sampled wells. The absence of identifiable chromium-containing source rock and more neutral groundwater (median pH 7.4), coupled with higher groundwater recharge rates from the adjacent Sierra Nevada, and shorter groundwater flowpaths may have combined to limit Cr(VI) concentrations in the Owens Valley study unit.

In contrast to the Central Valley as a whole, Cr(VI) was present at concentrations greater than the SRL in 49 percent of sampled wells, and greater than the California MCL in 11 percent of water from wells in study units along the west-side of the Central Valley (Fig. 7B). High Cr(VI) concentrations in the west-side of the Central Valley have been associated with chromium-containing rock that crop out along the valley margin (Fig. 1) (Morrison et al., 2009; Mills et al., 2011; Manning et al., 2015). Water from sampled wells in the west-side of the Central Valley was oxidic with a median dissolved oxygen concentration of 3.1 mg/L, and slightly alkaline with a median pH of 7.6. Concentrations in excess of the California MCL were present in water from only one well along the east-side of the Central valley province, although Cr(VI) occurs more frequently in public-supply wells at concentrations up to 4  $\mu\text{g/L}$  than statewide (Fig. 7B). Cr(VI) concentrations on the east-side of the valley exceeded the SRL in 45 percent of sampled wells. This was greater than the statewide exceedance of 31 percent, and similar to the Cr(VI) exceedance of the SRL on the west-side of the valley (Fig. 7B).

Cr(VI) concentrations were not statistically different from the statewide occurrence in the Coast Ranges, Transverse and selected Peninsular Ranges, and San Diego Drainages hydrogeologic provinces (as determined by the Kolmogorov-Smirnov two-sample test at a confidence criterion of  $\alpha = 0.05$ ) (Fig. 7). The Coast Ranges province has large areas of chromium-containing rock (Fig. 1), but Cr(VI) concentrations exceed the California MCL in only 3 percent of sampled wells with detections above the SRL in only 18 percent of sampled wells. Cr(VI) concentrations in the Coast Ranges may be limited by the comparatively large percentage of wells in this area having reduced groundwater (about 65 percent) compared to other parts of the state (Table 2). Water from only one well exceeded the MCL in the Transverse Range province and no wells exceeded the California MCL in the San Diego provinces, although Cr(VI) concentrations were greater than the SRL in 18 to 16 percent of sampled wells in these areas (Table 2). Comparison with DDW data (Fig. 3) shows a number of wells in urban areas near Los Angeles that have Cr(VI) concentrations greater than the California MCL. These wells may have been preferentially sampled and included within the DDW database.

Cr(VI) concentrations in the Sierra Nevada hydrogeologic province were statistically different from statewide concentrations and plot below the statewide distribution (Fig. 7A). The Sierra Nevada has fewer defined groundwater basins than other hydrogeologic provinces within California (Table 1), and about two-thirds of the wells sampled by the GAMA-PBP were in fractured-rock, rather than alluvial aquifers. No areas of known chromium-containing rock (Fig. 1A) were sampled as part of the GAMA-PBP. However DDW data show a number of wells having Cr(VI) greater than 1  $\mu\text{g/L}$  in areas where chromium-containing rock occurs (Fig. 3B), although Cr(VI) concentrations greater than the California MCL were not present. In areas of chromium-containing rock in the Sierra Nevada, such as the Western Metamorphic Belt, water from wells commonly has reduced conditions (Fram and Belitz, 2014),

**Fig. 7.** Hexavalent chromium, Cr(VI), as a function of A) hydrogeologic province and B) the east-side and west-side of the Central Valley hydrogeologic province in water from public-supply wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.



**Table 2**

Summary of well-construction, hexavalent chromium (Cr(VI)), redox, and pH data by hydrogeologic province for public-supply wells sampled for hexavalent chromium, Cr(VI), in California as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004 to 2012. [ $>$ , greater than or equal to;  $<$ , less than].

Hydrogeologic province	Number of analyses	Top of perforations	Bottom of perforations	Median well depth, in meters	Cr(VI)			Redox status		pH		
					Percent detections, $>1$ mg/L	Median	Percent $>10$ mg/L	Percent oxic	Percent reducing	Percent $>8$	Percent $<8$ and $>7$	Percent $<7$
Statewide	918	52.7	121.9	121.9	29.8	$<1$	4.5	68	32	20	67	13
Desert, including Basin and Range	205	61.0	121.9	121.9	40.3	$<1$	9.7	79	21	30	61	9
Central Valley	254	48.8	88.4	86.9	45.1	$<1$	5.9	65	35	21	72	7
Northern and Southern Coastal Ranges	136	67.1	134.1	130.1	17.6	$<1$	2.9	37	63	18	72	10
Transverse and selected Peninsular Ranges	141	73.2	168.6	167.6	17.6	$<1$	0.7	66	34	4	75	21
San Diego Drainages	50	29.6	142.6	134.1	15.6	$<1$	0	70	30	22	65	13
Sierra Nevada	132	32.6	114.6	111.6	15.8	$<1$	0	79	14	26	42	32
<i>Klamath Mountains</i>	–	21.0	54.3	37.2	22	0	95	5	8	38	54	–
<i>Modoc Plateau and Cascades</i>	–	47.2	82.6	98.5	47	0	96	4	12	49	39	–

Water from wells in the Klamath Mountains and Modoc Plateau and Cascades were not analyzed for Cr(VI) as part of the GAMA-PBP. Data in *italics* are for 39 and 90 wells analyzed for Cr(t) as part of the GAMA Program by Mathany and Belitz (2014) and Sheldon et al. (2013), respectively.

which would limit Cr(VI) occurrence. In most other areas, groundwater flowpaths are commonly short, limiting the potential interactions between groundwater and aquifer material. However, even in areas with oxic conditions, long residence times, and pH values greater than 8 Cr(VI) concentrations are low (Fram and Belitz, 2014).

Cr(VI) data were not collected within the Klamath Mountains, or Modoc Plateau and Cascades hydrogeologic provinces in northern California as part of the GAMA-PBP. The Klamath Mountains have the most extensive occurrence of Cr-containing mafic rocks in California and high-chromium concentrations in surface soils (Fig. 1). Despite the abundance of chromium-containing source material, Cr(t) concentration in water from 39 wells in the Klamath Mountains sampled as part of the GAMA-PBP (Mathany and Belitz, 2014) ranged from less than the SRL of 0.42–6.9  $\mu\text{g/L}$ , with 15 percent of sampled wells greater than or equal to 1  $\mu\text{g/L}$ . Similar to the Sierra Nevada hydrogeologic province, this area also has few defined groundwater basins (Table 1), and all of the wells sampled by GAMA-PBP were in fractured-rock. The wells in this province had (Table 1), and the shallowest median well depth of any hydrogeologic province (Table 2). In addition, many wells are near channels of major rivers and streams and pumping may induce infiltration of surface water from those sources potentially affecting the chemistry of water from the wells. Water from sampled wells was generally oxic and slightly acidic with a median pH of 6.9. Slightly acidic water increases sorption of Cr(VI), potentially limiting the occurrence of Cr(t) and Cr(VI) in water from wells. The Modoc Plateau and Cascades hydrogeologic provinces do not contain extensive areas of Cr-containing mafic rock (Fig. 1A), but the area does have high-chromium concentrations in surface soils (Fig. 1B). Cr(t) concentrations in water from 90 wells in the Modoc Plateau and Cascades sampled as part of the GAMA-PBP (Sheldon et al., 2013) ranged from less than the SRL to 8.9  $\mu\text{g/L}$ , with 40 percent of sampled wells greater than or equal to 1  $\mu\text{g/L}$ . Although water from sampled wells was generally oxic, it was near-neutral pH, with a median pH of 7.2, potentially limiting the occurrence of Cr(VI).

### 3.2. Other factors affecting Cr(VI) occurrence

In addition to factors such as pH, redox, land use, well construction, and differences in geology and hydrologic conditions within the various hydrogeologic provinces, Cr(VI) occurrence also

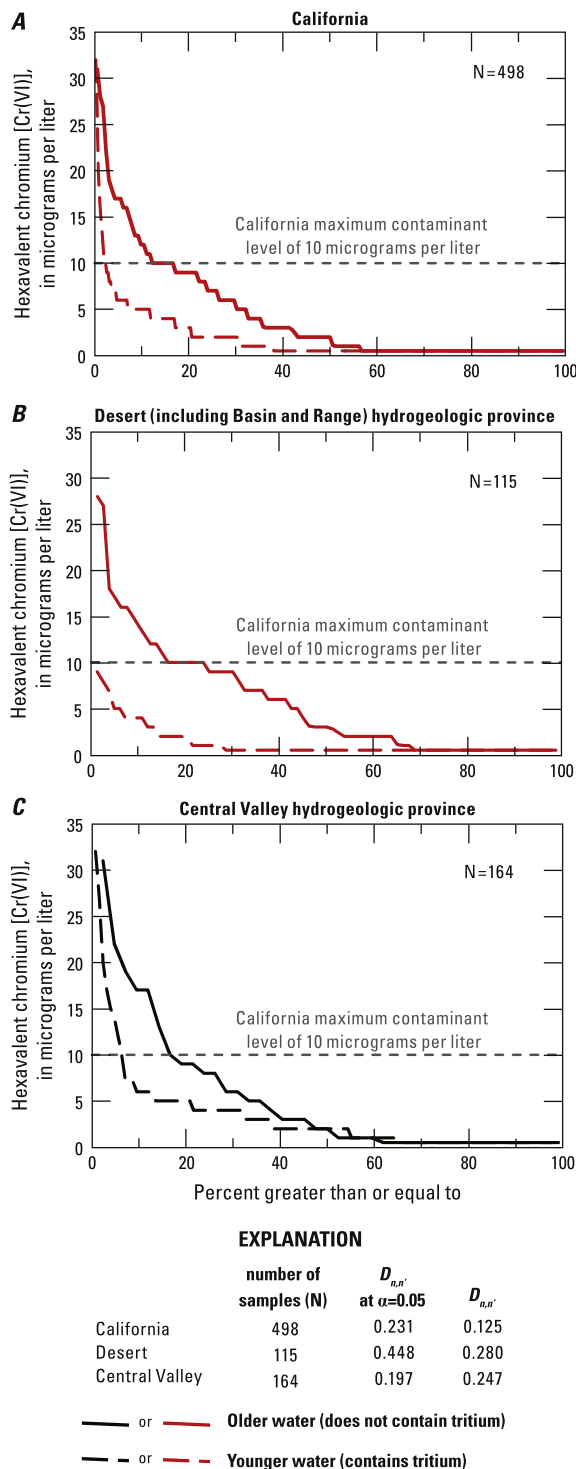
may be affected by other hydrologic factors including groundwater age and recharge processes. All these factors are linked in environmental systems, and it is often difficult to identify primary and secondary controls on Cr(VI) occurrence. Because Cr(VI) concentrations are higher in the Desert and Central Valley hydrogeologic provinces, differences in groundwater age and recharge processes that affect Cr(VI) occurrence are compared for these two areas.

#### 3.2.1. Groundwater age

As groundwater age increases in oxic alluvial aquifers, pH gradually increases as a result of weathering of primary silicate minerals. As pH becomes increasing alkaline, Cr(VI) and other trace elements may desorb from exchange sites on the surfaces of mineral grains and enter solution (Rai and Zachara, 1984; Izbicki et al., 2008). The effect is most pronounced in large aquifers having long groundwater flowpaths, low recharge rates, and long residence times. In this study, groundwater age in oxic water from wells was evaluated on the basis of tritium and carbon-14 data. Tritium is a radioactive isotope of hydrogen having a half-life of about 12.3 years. Its presence in the environment increased as a result of atmospheric testing of nuclear weapons beginning in about 1952. Water from wells containing measurable tritium is interpreted as containing at least some water recharged after 1952. Carbon-14 is a radioactive isotope of carbon having a half-life of about 5730 years. Unlike tritium, carbon-14 is not part of the water molecule and carbon-14 activities can be affected by reactions other than radioactive decay. For the purposes of this paper, only uncorrected carbon-14 activities that do not account for reactions with aquifer material are presented.

Statewide, Cr(VI) concentrations were greater in water from wells having only older groundwater that does not contain tritium than from wells having younger groundwater containing tritium (Fig. 8A). Water from 17 percent of wells containing older groundwater that does not contain tritium exceeded the MCL of 10  $\mu\text{g/L}$  for Cr(VI), compared to water from 3 percent of wells having younger water.

In the Desert (including Basin and Range) hydrogeologic province, Cr(VI) concentrations were greater in water from wells having older groundwater than younger groundwater (Fig. 8B). Cr(VI) concentrations in 23 percent of wells yielding only older groundwater not containing tritium exceed the California MCL, compared to wells containing younger groundwater that does not contain tritium. There was a statistically significant negative correlation



Data shown in red if Cr(VI) distribution in oxic water containing detectable tritium are statistically different from Cr(VI) distribution in oxic water not containing detectable tritium on the basis of the the Kolmogorov-Smirnov D statistic at a confidence criterion of  $\alpha=0.05$ ; where  $D_{n,n'}$  is greater than the critical value  $D_{n,n'}$  at  $\alpha=0.05$  (Taylor and Emerson, 2011).

**Fig. 8.** Hexavalent chromium, Cr(VI), as a function of groundwater age in water from public-supply wells in A) California, and the B) the Desert (including Basin and Range), and C) Central Valley Hydrogeologic Provinces sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.

between Cr(VI) concentrations and carbon-14 activity as percent modern carbon (reflecting increasing Cr(VI) concentrations with groundwater age) in the Antelope Valley study unit within the Desert hydrogeologic province (Kendall's Tau =  $-0.378$ ; significant at a confidence criterion of  $\alpha = 0.10$ ). The Antelope Valley study unit has the highest percentage of Cr(VI) concentrations in water from wells in excess of the MCL within California, and the data suggest that Cr(VI) concentrations would continue to increase along groundwater flowpaths as long as groundwater remains oxic. Similar increases in Cr(VI) concentrations with increasing groundwater age have been observed in flowpath studies in alluvial aquifers elsewhere in the Desert hydrogeologic province (Izbicki et al., 2008a).

In the Central Valley hydrogeologic province, Cr(VI) concentrations were not statistically different in water from wells having older and younger groundwater (Fig. 8C). However, Cr(VI) concentrations in water from wells yielding older groundwater that does not containing tritium exceeded the California MCL in about 17 percent of sampled wells, compared to 6 percent of wells containing younger groundwater (Fig. 8C). Because wells sampled as part of the GAMA-PBP are mostly public supply-wells, typically having long screen lengths, many of the samples containing tritium may be mixtures of older and younger water that entered the well from different depths within the aquifer. It also is possible that naturally occurring high-chromium rock eroded to form alluvial aquifers along the west-side of the Central Valley can weather rapidly and influence groundwater Cr(VI) concentrations (Morrison et al., 2009; Mills et al., 2011). Unlike the Desert hydrogeologic province, areal recharge occurs in the Central Valley province and Cr(VI) in younger groundwater may be associated with groundwater recharge in areas where water moved through thick unsaturated zones and reacted with Cr-containing rock prior to recharge. In addition, the presence of irrigation return water that would have moved through the unsaturated zone was identified on the basis of high-nitrate concentrations in water from some wells having high Cr(VI) concentrations (Mills et al., 2011; Manning et al., 2015).

### 3.2.2. Groundwater recharge processes

The effect of differences in groundwater recharge processes on Cr(VI) concentrations in the Desert and Central Valley hydrogeologic provinces was evaluated on the basis of dissolved noble gas concentrations. Noble gasses do not react chemically in water, but their concentration in water is a function of temperature, pressure, and salinity at the time of recharge according to Henry's Law (Stumm and Morgan, 1996). For focused recharge as a result of winter stormflows, dissolved noble-gas concentrations in groundwater may reflect cooler winter recharge temperatures if the unsaturated zone is comparatively thin, typically less than 5–10 m (Bense and Kooi, 2004; Manning, 2011). For thicker unsaturated zones, water infiltrated from winter stormflows commonly warms to near the average annual temperature of the area prior to recharge. Water recharged as a result of stormflows also commonly has additional gas entrapped during the recharge process, known as excess air (Cey et al., 2008). Dissolved gas in groundwater from excess air is contributed according to the atmospheric proportions of those gases, rather than as a function of temperature, pressure, or salinity according to Henry's Law. For water recharged areally as a result of infiltrating precipitation, or as a result of irrigation return, dissolved-gas concentrations at recharge reflect the temperature at the water table (Cey et al., 2009). For sufficiently thick unsaturated zones, between 5 and 10 m, this temperature approximates the average annual temperature (Stute and Schlosser, 2000). In irrigated areas, dissolved-gas concentrations in recharge from irrigation return may reflect warmer summer (growing season) temperatures. Recharge temperature and excess air were estimated

using the computer program NOBLEBOOK (Aeschbach-Hertig et al., 1999, 2000). Input to the program included a suite of noble gas data (including helium, neon, argon, krypton, and xenon) collected as part of the GAMA-PBP (Bryant Jurgens, U.S. Geological Survey, written commun., 2015).

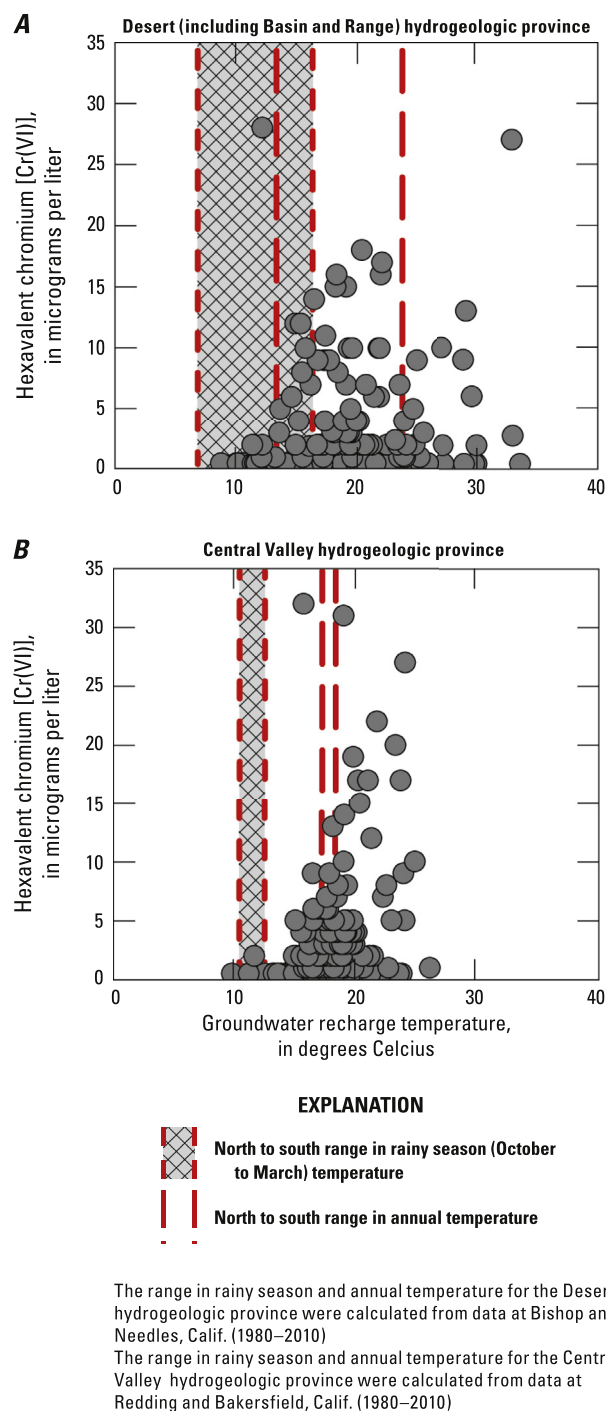
Within the Desert hydrogeologic province there is a wide range in rainy season (October–March) average daily temperatures and annual average temperatures (Fig. 9A). Cooler recharge temperatures in the Desert hydrogeologic province were from wells in the Owens Valley study unit, and to a lesser extent from the floodplain aquifer along the Mojave River within the Mojave River study unit (Fig. 1). As a group, these samples contained tritium, were recently recharged, and had low Cr(VI) concentrations. Otherwise, little relation was apparent for either recharge temperature (Fig. 9A), or excess-air (not shown on Fig. 9A), and Cr(VI) concentrations. This lack of relationship is consistent with recharge from a variety of sources (including sources no longer active under present-day climatic conditions) where Cr(VI) concentrations are controlled by a combination of source abundance and changes in pH and exchange along groundwater flowpaths.

Within the Central Valley hydrogeologic province there is less range and no overlap between rainy season (October–March) average daily temperatures and average annual temperatures (Fig. 9B). Cooler recharge temperatures and lower Cr(VI) concentrations were observed in water from wells along the east side of the Central Valley where recharge from rivers containing winter snowmelt from the higher altitudes of the Sierra Nevada occurs. Similar to the Desert hydrogeologic province, water from these wells contains tritium, was recently recharged, and has generally low Cr(VI) concentrations (Fig. 9B). Younger water containing tritium, warmer recharge temperatures, and higher Cr(VI) concentrations predominates in water from wells along the west-side of the Central Valley. In this area higher Cr(VI) concentrations are consistent with recharge processes through thick unsaturated zones that promote mobilization of Cr(VI) from source chromium-containing materials. Unlike the Desert hydrogeologic province, Cr(VI)-containing groundwater along the west-side of the Central Valley contains tritium, consistent with rapid mobilization of Cr(VI) during recharge from chromium-containing alluvium within the unsaturated zone. Rapid mobilization of Cr(VI) from the unsaturated zone rather than changes in pH and exchange along groundwater flowpaths may be responsible for the high groundwater Cr(VI) concentrations in this area. The presence of Cr(VI) in water from wells in the west-side of the Central Valley having warm recharge temperatures, presumably associated with areal recharge processes, was previously observed by Manning et al. (2015).

### 3.3. Cr VI co-occurrence with selected trace elements and nitrate

In addition to chromium and Cr(VI), 21 other trace elements (including the reduced and oxidized forms of arsenic, As(III) and As(VI), and of iron, Fe(II) and Fe(III)), were analyzed in water from wells as part of the GAMA-PBP. Kendall's Tau correlation coefficients and Principal Component Analysis (PCA) were used to evaluate similarities and differences in the co-occurrence of selected trace elements with Cr(VI) under different pH and redox conditions.

Kendall's Tau correlation coefficients show significant positive correlations (confidence criterion of  $\alpha = 0.05$ ) between Cr(VI) and the elements vanadium, selenium, uranium and with barium. Most correlation coefficients were comparatively low in magnitude with the largest magnitude correlation,  $r = 0.398$ , for vanadium (Table S1). With the exception of barium, these elements form oxyanions having similar chemical properties. Vanadium and



**Fig. 9.** Hexavalent chromium, Cr(VI), as a function of groundwater recharge temperature in A) the Desert (including Basin and Range), and B) Central Valley Hydrogeologic Provinces in water from public-supply wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.

selenium form soluble oxyanions in the +6 oxidation state, and uranium in the +4 oxidation state. These elements also form comparatively insoluble cations and cationic complexes under reduced conditions. PCA groups these different elements similarly near Cr(VI) (Fig. 10). Barium, while positively correlated with Cr(VI), does not form an oxyanion under alkaline, oxic conditions and does not group closely with Cr(VI) or the other elements (Fig. 10).

Arsenic and its oxyanion, As(V), were not correlated with Cr(VI) in oxic water (Table S1), and were not grouped together in PCA results. In contrast, As(III), which is soluble under reduced conditions, was significantly negatively correlated with Cr(VI). Kendall's Tau correlation coefficients also show significant negative correlations between Cr(VI) and molybdenum, and tungsten. Molybdenum and tungsten in the +6 oxidation state also form oxyanions, but these oxyanions are complex polyatomic ions that differ from Cr(VI) in chemical behavior. Because of the polyatomic nature of

molybdenum and tungsten oxyanions, analyses of filtered water samples commonly measure only the dissolved cationic forms. Negative correlation coefficients also were obtained between Cr(VI) and Fe(II), lithium, and boron. Collectively, results of PCA analyses group molybdenum, tungsten, As(III), Fe(II), lithium, and boron separately from Cr(VI), and the (non-polyatomic) oxyanion forming elements vanadium, selenium, and uranium (Fig. 10A). Cadmium, manganese, and nickel also are negatively correlated with Cr(VI). These elements form divalent cations soluble in reduced water but comparatively insoluble in oxic water, and form a separate group on the basis of the PCA results.

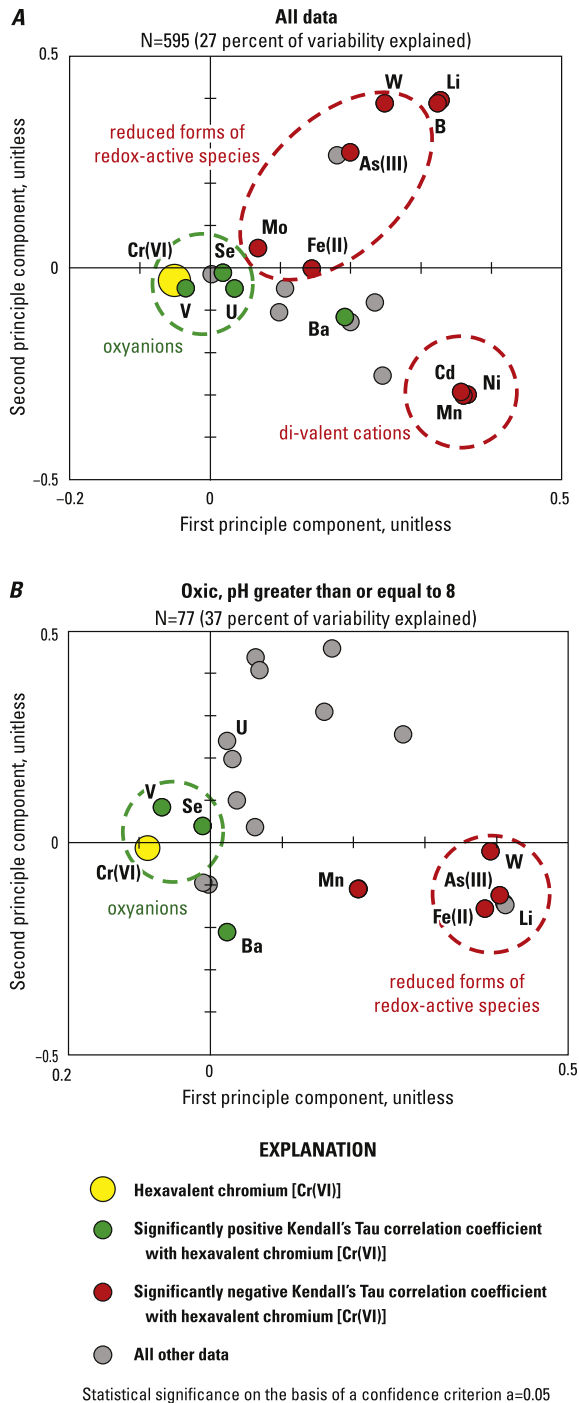
Fewer elements were significantly correlated with Cr(VI) under alkaline ( $\text{pH} \geq 8$ ) oxic conditions (possibly because fewer data are available) (Fig. 10B). However, the data show the same general pattern; with the oxyanion-forming elements, vanadium and selenium, grouping near Cr(VI), and the reduced forms of redox-active species Fe(II) and As(III) and tungsten plotting differently. The data are consistent with Cr(VI) co-occurrence with oxyanion-forming elements as a result of similarities in their aqueous chemistry over a range of pH and redox conditions within aquifers, rather than as a result of similarities in their occurrence within source rock. Co-occurrence of these elements may increase as pH increases along groundwater flowpaths, as long as oxic conditions persist.

In addition to trace elements, Cr(VI) also was positively correlated with nitrate (Kendall's correlation coefficient of 0.358). This occurs, in part, because both constituents occur primarily in oxic groundwater, although Cr(VI) may persist in reduced groundwater until nitrate is completely denitrified (Izbicki, 2008; Izbicki et al., 2008b; Chovanec et al., 2012) (Fig. 5B). If only oxic water from wells is considered, the correlation coefficient increases to 0.592. These data are consistent with increased Cr(VI) occurrence in areas of agricultural land use (Fig. 6), a finding that with the noble-gas data (Fig. 9) suggests that areal recharge and recharge associated with irrigation return may increase Cr(VI) concentrations in groundwater as a result of increased contact with chromium-containing minerals in the unsaturated zone prior to recharge (Mills et al., 2011; Manning et al., 2015). Cr(VI) was not correlated with either Ca or Mg, despite a tendency for Cr(VI) to form complexes with these ions (Lelli 204).

#### 4. Conclusions

Statewide Cr(VI) was detected in 31 percent of public-supply wells sampled as part of the GAMA-PBP, and exceeded the recently established (2014) California Maximum Contaminant Level of 10  $\mu\text{g/L}$  in 4 percent of sampled wells. Almost all dissolved chromium, about 90 percent, was present as Cr(VI). Data collected for public-health and regulatory purposes by the DDW had a higher frequency of detection compared to the spatially distributed data collected as part of the GAMA-PBP, as a result of clustering of analyses in the DDW database from wells in areas known to have natural or anthropogenic Cr(VI) occurrence. Use of public-health or regulatory data to assess the occurrence of Cr(VI), and other trace elements, over large areas may overestimate the occurrence of these constituents compared to data collected using spatially-distributed sample designs (Belitz et al., 2015).

Statewide, about 20 percent of the public-supply wells in California have high concentrations of one or more constituents, and trace-elements, specifically arsenic, manganese, and uranium, were more prevalent in public-supply wells than nitrate or organic compounds (Belitz et al., 2015). Arsenic and uranium occur naturally in rock and alluvium, with whole-rock concentrations almost two orders of magnitude lower than chromium (Nriagu and Niebor, 1988; Reimann and Caritat, 1998), but occur commonly in water



**Fig. 10.** Principal component analysis (PCA) of hexavalent chromium, Cr(VI), and selected trace element in water from wells in California sampled as part of the Groundwater Ambient Monitoring and Assessment-Priority Basin Project (GAMA-PBP), 2004–2012.

from public-supply wells, especially in the Central Valley and Desert hydrogeologic provinces because of alkaline, oxic groundwater and hydrologic conditions in these areas (Belitz et al., 2015). (Although arsenic, as As(III), concentration increased in reduced groundwater because arsenic also is soluble under reduced conditions.) Although commonly detected at the SRL of 1 µg/L, the occurrence of Cr(VI) in groundwater was less than what might be expected on the basis of its relative abundance in the continental crust (compared to arsenic and uranium), and the widespread occurrence of chromium-containing rock and soil in California. Cr(VI) was most abundant in aquifers having chromium-containing source rock and alkaline oxic groundwater, especially alluvial aquifers in the Desert and west-side of the Central Valley hydrogeologic provinces.

Within the Desert hydrogeologic province, Cr(VI) was more commonly detected and present at concentrations greater than the California MCL in the Antelope and Coachella Valley study units. In both study units the combination of chromium-containing source rock and alkaline, oxic groundwater contributed to the both the high frequency of Cr(VI) occurrence and the high Cr(VI) concentrations. These data suggest that geologic, hydrologic, and geochemical factors do not individually control Cr(VI) occurrence, but in combination these factors can create a high frequency of occurrence, and high Cr(VI) concentrations. However, Cr(VI) in excess on the California MCL was widely distributed throughout the Desert independent of chromium abundance in geologic materials, and data show increases in pH resulting from silicate weathering in comparatively non-reactive alluvial aquifers contributes to high chromium occurrence in groundwater, as long as dissolved oxygen and oxic conditions persist.

In contrast, within the Central Valley hydrogeologic province, chromium-containing geologic material, coupled with areal groundwater recharge (from both infiltrating precipitation and recharge from irrigation return), facilitate interaction of water with unsaturated sediments prior to groundwater recharge—resulting in increased Cr(VI) occurrence and concentrations in water from public supply wells. However, the presence of chromium-containing material does not solely explain occurrence of Cr(VI) in groundwater. Parts of California having large areas of chromium-containing rock or soil, such as the Klamath Mountains, or Modoc Plateau and Cascades hydrogeologic provinces, do not have high concentrations of Cr(VI) in water from public supply wells (on the basis of California DPHS data) because of hydrologic and geochemical factors. Hydrology can play a role in limiting Cr(VI) concentrations in areas having shallow aquifers with short groundwater flowpaths that limit interaction between groundwater and aquifer materials, especially where wells located near streams and rivers are influenced by nearby surface water. Similarly, Cr(VI) concentrations also are low in both the Desert hydrogeologic province and the east-side of the Central Valley in areas where focused recharge from streams and rivers contribute large amounts of recent groundwater recharge. Rapid recharge of large quantities of water and the relatively young age of water in parts of these systems also limits interaction between groundwater and aquifer materials.

Interpretation of data in this paper is at a large, statewide scale, and is intended to highlight major geologic, hydrologic, and geochemical controls on Cr(VI) occurrence. Additional interpretation may be useful for evaluation of more localized processes that control Cr(VI) occurrence within individual within smaller-scale study units and groundwater basins that compose larger areas.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2015.08.007>.

## References

- Aeschbach-Hertig, W., Peeters, W., Beyerle, U., Kipfer, R., 1999. Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resour. Res.* 35 (9), 2779–2792.
- Aeschbach-Hertig, W., Peeters, W., Beyerle, U., Kipfer, R., 2000. Paleotemperature reconstruction from noble gases in groundwater taking into account equilibration with entrapped air. *Nature* 405, 1040–1044.
- ATSDR, September 2012. Toxicological Profile for Chromium. Agency for Toxic Substances and Disease Registry, Public Health Service, US Department of Health and Human Services. <http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=62&tid=17> (accessed 03.12.14.).
- Ayotte, J.D., Gronberg, J.M., Apodaca, L.E., 2011. Trace Elements and Radon in Groundwater across the United States, 1992–2003. U.S. Geological Survey Scientific Investigations Report 2011–5059, 115 p. <http://pubs.usgs.gov/sir/2011/5059> (accessed 06.11.14.).
- Ball, J.W., McCleskey, R.B., 2003a. A new cation-exchange method for accurate field speciation of hexavalent chromium. *Talanta* 61 (3), 305–313.
- Ball, J.W., McCleskey, R.B., 2003b. A New Cation-exchange Method for Accurate Field Speciation of Hexavalent Chromium. U.S. Geological Survey Water-Resources Investigations Report 03-4018, 17 p. [http://www.wrri.cr.usgs.gov/projects/GWC\\_chemtherm/pubs/WRIR%2003-4018.pdf](http://www.wrri.cr.usgs.gov/projects/GWC_chemtherm/pubs/WRIR%2003-4018.pdf) (accessed 04.11.14.).
- Ball, J.W., Izbicki, J.A., 2004. Occurrence of hexavalent chromium in ground water in the western Mojave Desert, California. *Appl. Geochem.* 19 (7), 1123–1135. <http://www.sciencedirect.com/science/article/pii/S088329270400023X> (accessed 24.03.15.).
- Beaumont, J.J., Sedman, R.M., Reynolds, S.D., Sherman, C.D., Li, L., Howd, R.A., Sandy, M.S., Zeise, L., Alexeeff, G.V., 2008. Cancer mortality in a Chinese population exposed to hexavalent chromium in drinking water. *Epidemiology* 19 (1), 12–23.
- Belitz, K., Dubrovsky, N.M., Burrow, K., Jurgens, B., Johnson, T., 2003. Framework for a Ground-water Quality Monitoring and Assessment Program for California. U.S. Geological Survey Water-Resources Investigations Report 03-4166, 78 p. <http://pubs.usgs.gov/wri/wri034166/> (accessed 31.10.14.).
- Belitz, K., Fram, M.S., Johnson, T.D., 2015. Metrics for assessing the quality of groundwater used for public supply, CA, USA: equivalent-population and area. *Environ. Sci. Technol.* 49 (14), 8330–8338. <http://dx.doi.org/10.1021/acs.est.5b00265>.
- Beller, H.R., Yang, L., Varadharajan, C., Ruyang, H., Lim, H.C., Karaoz, U., Molins, S., Marcus, M.A., Brodie, A.L., Steefel, C.I., Nico, P.S., 2014. Divergent aquifer biogeochemical systems converge on similar and unexpected Cr(VI) reduction products. *Environ. Sci. Technol.* 48 (18), 10699–10706.
- Bense, V.F., Kooi, H., 2004. Temporal and spatial variations of shallow subsurface temperature as a record of lateral variations in groundwater flow. *J. Geophys. Res. B Solid Earth* 109 (4), B04103 1–13.
- Blowes, D.W., 2002. Tracking hexavalent Cr in groundwater. *Science* 295 (5562), 2024–2025.
- California Department of Water Resources, 2003. California's groundwater. Bulletin 118. <http://www.water.ca.gov/groundwater/bulletin118/index.cfm> (accessed 08.04.15.).
- California State Water Resources Control Board, 2014a. Groundwater Information Sheet: Hexavalent Chromium. [http://www.waterboards.ca.gov/water\\_issues/programs/gama/docs/coc\\_hexchromcr6.pdf](http://www.waterboards.ca.gov/water_issues/programs/gama/docs/coc_hexchromcr6.pdf) (accessed 03.12.14.).
- California State Water Resources Control Board, 2014b. Chromium-6 Drinking Water MCL. [http://www.waterboards.ca.gov/drinking\\_water/certlic/drinkingwater/Chromium6.shtml](http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chromium6.shtml) (accessed 03.12.14.).
- Cey, B.D., Hudson, G.B., Moran, J.E., Scanlon, B.R., 2008. Impact of artificial recharge on dissolved noble gases in groundwater in California. *Environ. Sci. Technol.* 42 (4), 1017–1023.
- Cey, B.D., Hudson, G.B., Moran, J.E., Scanlon, B.R., 2009. Evaluation of noble gas recharge temperatures in a shallow unconfined aquifer. *Ground Water* 47 (5), 646–659.
- Charlet, L., Manceau, A.A., 1992. X-ray absorption spectroscopic study of the sorption of Cr (III) at the oxide-water interface. II. Adsorption, coprecipitation, and surface precipitation on hydrous ferric oxide. *J. Colloid Interface Sci.* 148 (2), 443–458.
- Chovanec, P., Sparacino-Watkins, C., Zhang, N., Basu, P., Stolz, J.F., 2012. Microbial reduction of chromate in the presence of nitrate by three nitrate respiring organisms. *Front. Microbiol.* 3, 146–158.
- Chung, J.-B., Burau, R.G., Zasoski, R.J., 2001. Chromate generation by chromate depleted subsurface materials. *Water Air Soil Pollut.* 138, 407–417.

- Daugherty, M.L., 1992. Toxicity Summary for Chromium. Oak Ridge National Laboratory Chemical Hazard Evaluation and Communication Group, Oak Ridge, TN.
- Dawson, B.J.M., Bennett, G.L., Belitz, K., 2008. Ground-water Quality Data in the Southern Sacramento Valley, California, 2005 – Results from the California GAMA Program. In: US Geological Survey Data Series 285, 93 p. <http://pubs.usgs.gov/ds/285/> (accessed 10.04.15.).
- Davis, T.A., Olsen, L.D., Fram, M.S., Belitz, K., 2014. Updated Study R 903 Eporting Levels (SRLs) 904 for Trace-element Data Collected for the California Groundwater Ambient Monitoring and 905 Assessment (GAMA) Priority Basin Project, October 2009–March 2013. U.S. Geological Survey Scientific Investigations Report 2014–5105, 52 p. <http://dx.doi.org/10.3133/sir20145105> (accessed 04.11.14.).
- Eary, L.E., Rai, D., 1987. Kinetics of Chromium (III) oxidation to chromium (VI) by reaction with manganese dioxide. *Environ. Sci. Technol.* 21, 1187–1193.
- Emsley, John, 2001. *Nature's Building Blocks: an A–Z Guide to the Elements*. Oxford University Press, Oxford, England, UK, pp. 495–498.
- Fram, M.S., Belitz, Kenneth, 2014. Status and Understanding of Groundwater Quality in the Sierra Nevada Regional Study Unit, 2008—California GAMA Priority Basin Project. U.S. Geol. Survey Scientific Investigations Report 2014-5174, 118 p. <http://pubs.usgs.gov/sir/2014/5174/> (accessed 21.01.15.).
- Gnanadesikan, R., 1977. *Methods for Statistical Data Analysis of Multivariate Observations*. John Wiley and Sons, New York.
- Gonzalez, A.R., Ndung'u, K., Flegal, A.R., 2005. Natural occurrence of hexavalent chromium in the Aromas Red Sands Aquifer, California. *Environ. Sci. Technol.* 39 (15), 5505–5511.
- Guha, H., Saiers, J.E., Brooks, S., Jardine, P., Jayachandran, K., 2000. Chromium transport, oxidation, and adsorption in manganese-coated sand. *Contam. Hydrol.* 49 (1–2), 311–334.
- Han, R., Geller, J.T., Yang, L., Brodie, E.L., Chakraborty, R., Larsen, J.T., Beller, H.R., 2010. Physiological and transcriptional studies of Cr(VI) reduction under aerobic and denitrifying conditions by an aquifer-derived *Pseudomonas*. *Environ. Sci. Technol.* 44 (19), 7491–7497.
- Hem, J.D., 1959. Study and Interpretation of the Chemical Characteristics of Natural Water, first ed. U.S. Geological Survey Water-Supply. Paper 1473, 269 p.
- Hitchon, B., Perkins, E.H., Gunter, W.D., 1999. *Introduction to Groundwater Geochemistry*. Geoscience Publishing Ltd., Sherwood Park, Alberta, Can., 310 p.
- Izbicki, J.A., 1996. Source, Movement, and Age of Groundwater in a California Coastal Aquifer. U.S. Geological Survey Fact Sheet 126-96, 4 p. <http://pubs.er.usgs.gov/publication/fs12696> (accessed 12.12.14.).
- Izbicki, J.A., Martin, P., 1997. Use of Isotopic Data to Evaluate Recharge and Geologic Controls on the Movement of Groundwater in Las Posas Valley, Ventura County, California. U.S. Geological Survey Water Resources Investigations Report 97-4035, 12 p. <http://pubs.er.usgs.gov/publication/wri974035> (accessed 12.12.14.).
- Izbicki, J.A., Borchers, J.W., Leighton, D.A., Kulongoski, J.T., Fields, L., Galloway, D.L., Michel, R.L., 2003. Hydrogeology and Geochemistry of Aquifers Underlying the San Lorenzo and San Leandro Areas of the East Bay Plain, Alameda County, California. U.S. Geological Survey Water-Resources Investigations Report 2002-4250, 71 p. <http://pubs.er.usgs.gov/publication/wri024259> (accessed 12.12.14.).
- Izbicki, J.A., Stamos, C.L., Nishikawa, T., Martin, P., 2004. Comparison of groundwater flow model particle-tracking results and isotopic data in the Mojave River ground-water basin, southern California, USA. *J. Hydrol.* 292, 30–47. <http://pubs.er.usgs.gov/publication/70026967> (accessed 12.12.14.).
- Izbicki, J.A., Michel, R.L., 2004. Movement and Age of Ground Water in the Western Part of the Mojave Desert, Southern California, USA. USGS Water-Resources Investigations Report: 2003-4314, 42 p. <http://pubs.er.usgs.gov/publication/wri034314> (accessed 12.12.14.).
- Izbicki, J.A., 2007. Physical and temporal isolation of mountain headwater streams in the western Mojave Desert, southern California. *J. Am. Water Resour. Assoc.* 43 (1), 26–40. <http://pubs.er.usgs.gov/publication/70033123> (accessed 12.12.14.).
- Izbicki, J.A., 2008. Chromium Concentrations, Chromium Isotopes, and Nitrate in the Unsaturated Zone at the Water–table Interface, El Mirage, California. Written comm. to the Lahontan Regional Water Quality Control Board, December 24, 2008. [http://www.swrcb.ca.gov/lahontan/publications\\_forms/available\\_documents/molycorp\\_elmirage1208.pdf](http://www.swrcb.ca.gov/lahontan/publications_forms/available_documents/molycorp_elmirage1208.pdf) (accessed 05.11.14.).
- Izbicki, J.A., Ball, J.W., Bullen, T.D., Sutley, S.J., 2008a. Chromium, chromium isotopes and selected trace elements, western Mojave Desert, USA. *Appl. Geochem.* 23 (5), 1325–1352. <http://ca.water.usgs.gov/news/2008/Chromium-report.pdf> (accessed 24.03.15.).
- Izbicki, J.A., Kulp, T.R., Bullen, T.D., Ball, J.W., O'Leary, D., 2008b. Chromium mobilization from the unsaturated zone (Abs.). In: Proc. 2008 Goldschmidt Conf. Canada, Vancouver. July 13–18, 2008.
- Izbicki, J.A., Flint, A.L., Stamos, C.L., 2008c. Artificial recharge through a thick, heterogeneous unsaturated zone. *GroundWater* 46 (3), 475–488.
- Izbicki, J.A., Bullen, T.D., Martin, P., Schroth, B., 2012. Delta chromium-53/52 isotopic composition of native and contaminated groundwater, Mojave Desert, USA. *Appl. Geochem.* 27 (4), 841–853. <http://ca.water.usgs.gov/pubs/IzbickiEtAl2012-2.pdf> (accessed 24.03.15.).
- Jacobson, C.E., Barth, A.P., Grove, M., 2000. Late Cretaceous protolith age and provenance of the Pelona and Orocopia Schists, southern California: implications for evolution of the Cordilleran margin. *Geology* 28 (3), 219–222.
- Johnson, T.D., Belitz, K., 2009. Assigning land use to supply wells for the statistical characterization of regional groundwater quality: correlating urban land use and VOC occurrence. *J. Hydrol.* 370 (1–4), 100–108. [http://ca.water.usgs.gov/projects/gama/pdfs/Johnson\\_2009\\_1-s2.0-S0022169409001462-main.pdf](http://ca.water.usgs.gov/projects/gama/pdfs/Johnson_2009_1-s2.0-S0022169409001462-main.pdf) (accessed 04.11.14.).
- Kendall, M., 1938. A new measure of rank correlation. *Biometrika* 30 (1–2), 81–89.
- Kotas, J., Stasicka, Z., 2000. Chromium occurrence in the environment and methods of its speciation. *Environ. Pollut.* 107 (3), 263–283.
- Kruckeberg, A.R., 1984. *California serpentines: Flora, Vegetation, Geology, Soils, and Management Problems*. University of California Press, Ltd., Berkeley, 180 p.
- Kshirsagar, A.M., 1972. *Multivariate Analysis*. Marcel Dekker, New York.
- Kulongoski, J.T., Hilton, D.R., Izbicki, J.A., 2003. Helium isotope studies in the Mojave Desert, California: implications for groundwater chronology and regional seismicity. *Chem. Geol.* 202, 95–113. <http://pubs.er.usgs.gov/publication/70025023> (accessed 12.12.14.).
- Kulongoski, J.T., Hilton, D.R., Izbicki, J.A., 2005. Source and movement of helium in the eastern Morongo groundwater Basin: the influence of regional tectonics on crustal and mantle helium fluxes. *Geochim. Cosmochim. Acta* 69 (15), 3857–3872. <http://pubs.er.usgs.gov/publication/70031458> (accessed 12.12.14.).
- Lelli, M., Grassi, S., Amadori, M., Franceschini, F., 2014. Natural Cr(VI) contamination of groundwater in the Cecina coastal area and its inner sectors (Tuscany, Italy). *Environ. Earth Sci.* 71 (9), 3907–3919.
- Manning, A.H., 2011. Mountain-block recharge, present and past, in the eastern Espanola Basin, New Mexico, USA. *Hydrogeol. J.* 19, 379–397.
- Manning, A.H., Mills, C.T., Morrison, J.M., Ball, L.B., 2015. Insights into controls on hexavalent chromium in groundwater provided by environmental tracers, Sacramento Valley, California, USA. *Appl. Geochem.* 61. <http://www.sciencedirect.com/science/article/pii/S0048969702002310> (accessed 16.07.15.).
- Mathany, T.M., Belitz, K., 2014. Groundwater-quality Data in the Klamath Mountains Study Unit, 2010: Results from the California GAMA Program. In: U.S. Geological Survey Data Series 803, 82 p. <http://pubs.usgs.gov/ds/803/> (accessed 20.01.15.).
- Mayer, L.M., Schick, L.L., 1981. Removal of hexavalent chromium from estuarine waters by model substrates and natural sediments. *Environ. Sci. Technol.* 15 (12), 1482–1484.
- McMahon, P.B., Chapelle, F.H., 2008. Redox processes and water quality of selected principal aquifer systems. *GroundWater* 46 (2), 259–271.
- Mills, C.T., Morrison, J.M., Goldhaber, M.B., Ellefsen, K.J., 2011. Chromium(VI) generation in vadose zone soils and alluvial sediments of the southwestern Sacramento Valley, California: a potential source of geogenic Cr(VI) to groundwater. *Appl. Geochem.* 26 (8), 1488–1501.
- Morrison, J.M., Goldhaber, M.B., Lee, L., Holloway, J.M., Wamty, R.B., Wolf, R.E., Ranville, J.F., 2009. A regional-scale study of chromium and nickel in soils of northern California, USA. *Appl. Geochem.* 24 (8), 1500–1511.
- Morrison, J.M., Goldhaber, M.B., Mills, C.T., Breit, G.N., Hooper, R.L., Holloway, J.M., Diehl, S.F., Ranville, J.F., 2015. Weathering and transport of chromium and nickel from serpentinite in the coast range ophiolite to the Sacramento Valley, California, USA. *Appl. Geochem.* 62, 72–86. <http://www.sciencedirect.com/science/article/pii/S0883292715001407> (accessed 16.07.15.).
- Motzer, W.E., 2005. In: Guertin, J., Jacobs, J.A., Avkian, C.P. (Eds.), *Chemistry, geochemistry, and geology of chromium and chromium compound*, Chapt. 2, Chromium (VI) Handbook, 784 p.
- Neter, J., Wasserman, W., 1974. *Applied Linear Statistical Models*, vol. 1. Richard D. Irwin Inc., Homewood, IL, 152 p.
- Nriagu, J.O., Niebor, E. (Eds.), 1988. *Chromium in the Natural and Human Environments*. John Wiley & Sons, New York, 571 p.
- Olsen, L.D., Fram, M.S., Belitz, K., 2010. Review of Trace-element Field-blank Data Collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program, May 2004–January 2008. U.S. Geological Survey Scientific Investigations Report 2009-5220, 47 p. <http://pubs.usgs.gov/sir/2009/5220/pdf/sir20095220.pdf> (accessed 04.11.14.).
- Oze, C., Fendorf, S., Bird, D.K., Coleman, R.G., 2004a. Chromium geochemistry of serpentinite soils. *Int. Geol. Rev.* 46 (2), 97–126.
- Oze, C., Fendorf, S., Bird, D.K., Coleman, R.G., 2004b. Chromium geochemistry in serpentinitized ultramafic rocks and serpentinite soils from the Franciscan Complex of California. *Am. J. Sci.* 304 (1), 67–101.
- Oze, C., Bird, D.K., Fendorf, S., 2007. Genesis of hexavalent chromium from natural sources in soil and groundwater. *Proc. Natl. Acad. Sci.* 104 (16), 6544–6549.
- Perlmutter, N.M., Liber, M., Frauenthal, H.L., 1963. Movement of Waterborne Cadmium and Hexavalent Chromium Wastes in South Farmingdale, Nassua County, Long Island, pp. C170–C184. US Geological Survey Professional Paper 475C. <http://pubs.usgs.gov/pp/0475c/report.pdf> (accessed 03.12.14.).
- Rai, D., Zachara, J.M., 1984. Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration: Volume 1: a Critical Review. Battelle Pacific Northwest Laboratories, Richland, WA. EA-3336 Volume 1, Research Project 2198–1, variously pagged.
- Rajapasha, A.U., Vithanage, M., Sik, Y., Oze, C., 2013. Cr(VI) formation related to Cr(III)-muscovite and birnessite interactions in ultramafic environments. *Environ. Sci. Technol.* 47 (17), 9722–9729.
- Reimann, C., de Caritat, P., 1998. *Chemical Elements in the Environment*. Springer-Verlag, Berlin, 398 p.
- Robertson, F.N., 1975. Hexavalent chromium in the ground water, in Paradise Valley, Arizona. *GroundWater* 13 (6), 516–527.
- Robertson, F.N., 1991. *Geochemistry of Ground Water in Alluvial Basins of Arizona and Adjacent Parts of Nevada, New Mexico, and California*. US Geological Survey Professional Paper 1406-C, 90 p. <http://pubs.er.usgs.gov/publication/pp1406> (accessed 05.12.14.).
- Scancar, J., Milacic, R., 2014. A critical overview of Cr speciation analysis based on high performance liquid chromatography and spectrometric techniques. *J. Anal. Atomic Spectrom.* 29, 427–443.

- Schroeder, D.C., Lee, G.F., 1975. Potential transformations of chromium in natural waters. *Water Air Soil Pollut.* 4, 355–365.
- Scott, J.C., 1990. Computerized Stratified Random Site-selection Approaches for Design of a Ground-water-quality Sampling Network. U.S. Geological Survey, Water-Resources Investigations Report 90-4101, 109 p. <http://pubs.er.usgs.gov/publication/wri904101>.
- Sedman, R.M., Beaumont, J., McDonald, T.A., Reynolds, S., Krowech, G., Howd, R., 2006. Review of the evidence regarding carcinogenicity of hexavalent chromium in drinking water. *J. Environ. Sci. Health Part C* 24 (1), 155–182.
- Shelton, J.L., Fram, M.S., Belitz, Kenneth, 2013. Groundwater-quality Data in the Cascade Range and Modoc Plateau Study Unit, 2010—Results from the California GAMA Program. In: U.S. Geol. Survey Data Series 688, 124 p. <http://pubs.usgs.gov/ds/688/> (accessed 21.01.15.).
- Smith, D.B., Cannon, W.F., Woodruff, L.G., Solano, F., Ellefsen, K.J., 2014. Geochemical and Mineralogical Maps for Soils in the Conterminous United States. U.S. Geological Survey Open-File Report 2014-1082, 368 p. <http://pubs.usgs.gov/of/2014/1082/> (accessed 12.12.14.).
- Steinpress, M.G., 2005. In: Guertin, J., Jacobs, J.A., Avakian, C.P. (Eds.), Naturally-occurring chromium(VI) in groundwater. Chapt. 3, Chromium (VI) Handbook, 784 p.
- Stumm, W., Morgan, J.J., 1996. *Aquatic Chemistry*. Wiley, New York, 1022 p.
- Stute, M., Schlosser, P., 2000. Atmospheric noble gases. In: Cook, P., Herezeg, A.L. (Eds.), *Environmental Tracers in Subsurface Hydrology*. Kluwer, Boston, 529 p.
- U.S. Environmental Protection Agency, 1991. Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography. [http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007\\_07\\_10\\_methods\\_method\\_218\\_6.pdf](http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_218_6.pdf) (accessed 04.11.14.).
- U.S. Environmental Protection Agency, 2008. Addressing Chromium Contamination in the San Fernando Valley. U.S. Environmental Protection Agency, Region 9, San Francisco, Calif. <http://www.epa.gov/Region9/superfund/chromium/index.html> (accessed 03.12.14.).
- U.S. Environmental Protection Agency, 2009. National Primary Drinking Water Regulations. EPA 816-F-09-004 6 p. <http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf> (accessed 03.12.14.).
- U.S. Geological Survey, 2015. Groundwater Ambient Monitoring and Assessment Program. [http://ca.water.usgs.gov/gama/includes/GAMA\\_publications.html](http://ca.water.usgs.gov/gama/includes/GAMA_publications.html) (accessed 15.07.15.).
- U.S. Geological Survey, Various Dated, National Field Manual for the Collection of Water-quality data: U.S. Geological Survey Techniques of Water-resources Investigations, Book 9, Chaps. A1–A9 <http://pubs.water.usgs.gov/twri9A>, (accessed 04.11.14.).
- Wright, M.T., Belitz, K., 2010. Factors controlling the regional distribution of vanadium in groundwater. *Ground Water* 48 (4), 515–525. <http://pubs.er.usgs.gov/publication/70003992> (accessed 05.11.14.).
- Wright, M.T., Stollenwerk, K.G., Belitz, K., 2014. Assessing solubility controls on vanadium in groundwater, northeastern San Joaquin Valley, CA. *Appl. Geochem.* 48, 41–52. <http://www.sciencedirect.com/science/journal/08832927> (accessed 26.03.15.).