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

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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 Program—Priority Basin Project (GAMA—PBP) ranged from less than the study reporting limit (SRL) of 1 microgram per liter (μg/L) to 32 μg/L. Statewide, Cr(VI) was reported in 31 percent of sampled wells and equaled or exceeded the recently established (2014) California Maximum Contaminant Level (MCL) for Cr(VI) of 10 μg/L in 4 percent of sampled wells. Cr(VI) data collected for regulatory purposes overestimate Cr(VI) occurrence. Ninety percent of chromium was present as Cr(VI), which was detected more frequently and at higher concentrations in alkaline (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 abundance in source rock eroded to form those aquifers, and areal recharge processes (including irrigation return) that 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.

## Highlights

1. Cr(VI) exceed the California MCL of 10 μg/L in 4 percent of sampled wells.
2. Data collected for regulatory purposes overestimate Cr(IV) occurrence.
3. Geology, hydrology, and geochemistry combine to control Cr(VI) occurrence.
4. Cr(VI) occurrence is greater in alkaline oxic groundwater, independent of geology.
5. Areal recharge and interaction with unsaturated zone increases Cr(VI) occurrence.

## 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 2,400 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 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 2,860 square kilometers ($km^2$) 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. in review), 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 chromium of 100 micrograms per liter (μg/L) (US Environmental Protection Agency 2009).

**Figure 1A and 1B near here**

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 μg/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 Program–Priority Basin Project (GAMA-PBP) Program.

### 1.1 Geochemistry of chromium

The most common chromium-containing mineral, chromite ($FeCr_2O_4$), 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 $CrO_4^{2-}$ (fig. 2), or as neutral complexes with calcium and magnesium ($CaCrO_4^0$ and $MgCrO_4^0$ , 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).

**Figure 2 near here**

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(IV), 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 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, and 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 largest provinces 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 greatest areal extent of groundwater basins. Although population is greatest in the Transverse and Selected Peninsular Range province and Coast Ranges province; the largest numbers of public supply wells, and presumably 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 (Table 1).

**Table 1 near here**

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 and 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 Program were divided into an equal-area grid (Scott, 1990). Statewide, the median grid-cell size was 25 $km^2$, with a median of 20 cells per study unit (Belitz et al. 2015). The objective was to sample one public-supply well 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 2,400 wells were sampled as part of the GAMA-PBP Program (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 in 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 hydrologic provinces (Northern and Southern Coast Ranges; and 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 and 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 hyrochloric acid and shipped to the U.S. Geological Survey National Research Laboratory in Boulder, Colo. For analyses of chromium (http://wwwbrr.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-hour 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).

Additional data from the California Department of Public Health (CDPH) also were compiled and interpreted as part of this study. CDPH 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.

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) on-line data bases.

225 **2.2 Quality assurance and statistical methods**

226 Data from equipment and field blanks were used for quality assurance and to establish
227 study reporting levels (SRL) for Cr(VI) and trace elements (Olsen et al., 2010; Davis et al. 2014)
228 (Table S1). Least-squares regression analysis of 91 replicate sample pairs having Cr(VI)
229 concentrations ranging from <1 to 28 μg/L, showed data compared favorably with a $R^2$ of 0.98
230 and mean square error of 0.30 μg/L. The average difference between replicate pairs was 4
231 percent, and in most cases the replicate sample values were identical. As part of this study
232 1,261 samples were collected and analyzed for Cr(VI). Contamination, traced to corroded metal
233 parts in a field pipette used to preserve samples with hydrochloric acid, was identified in 17 of
234 112 field blank samples collected between September 2004 and December 2005 resulted in the
235 removal of 343 samples, for a total of 918 samples discussed in this paper. The pipette was
236 replaced with a pipette that did not contain metal parts and contamination issues ceased
237 (Appendix A). Contamination contributed to the less rigorous statewide spatial distribution of
238 Cr(VI) data compared to most other GAMA-PBP data discussed previously.

239 Most Cr(VI) data were less than the SRL for this study. Non-parametric descriptive
240 statistics such as medians (and even upper 25-percent quartiles) and associated statistical tests,
241 such as the Median or Wilcoxon rank-sum test (Neter and Wasserman, 1974), are not
242 meaningful for data having a high-occurrence of less than values. As a consequence, differences
243 in Cr(VI) occurrence were evaluated on the basis of the two-sample Kolmogorov- Smirnov test
244 (Taylor and Emerson 2011) (Appendix A). Co-occurrence of Cr(VI) and other trace elements was
245 evaluated using Kendall's Tau correlation coefficients (Kendall 1938) and Principle Component
246 Analyses (PCA) (Kshirsagar 1972; Gnanadesikan 1977).

**Appendix A near here**

# 3. Results and discussion

## 3.1 Cr(VI) occurrence

Cr(VI) concentrations in 918 public-supply wells sampled 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).

**Figures 3 and 4 near here**

Cr(VI) concentrations in more than 1,480 wells within the CDPH data base 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 not sampled by the GAMA-PBP study within the southern part of the Central Valley, and the Northern and Southern Coast Ranges hydrogeologic provinces. CDPH 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 CDPH data using least-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 CDPH data (not shown in figures). Some of the Cr(VI) excess in the CDPH data may occur because Cr(VI) samples analyzed as part of the GAMA-PBP Program were filtered and Cr(VI) was separated from Cr(t) in the field; whereas, Cr(VI) samples in the CDPH data base 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 CDPH data for samples collected at the same well more than 3 years apart was poor, with an $R^2$ of 0.58 and a Cr(VI) excess of 30 percent in the CDPH data. This difference may result from changing sample collection, preservation, and laboratory methods in the longer period of record represented by the CDPH data, or because of trends in Cr(VI) concentrations with time in water from some sampled wells.

CDPH 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 CDPH 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 wells sampled for Cr(VI) were less rigorously distributed statewide than most wells sample as part of the GAMA-PBP Program, 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 CDPH 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 established by adjusting the divisions at 0.1 unit intervals to maximize the difference between 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

310 39 percent of sampled wells and greater than the California MCL in 4 percent of sampled wells.
311 In water from wells having a pH less than 7, Cr(VI) was present at concentrations greater than
312 the SRL in 8 percent of sampled wells and did not exceed the California MCL in any sampled
313 wells.

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

321 **Figure 5 near here**

322 Differences in Cr(VI) occurrence by redox status were evaluated by grouping data into
323 two categories, oxic, and reduced. Oxic water had dissolved oxygen concentrations greater than
324 0.5 milligrams per liter. Reduced water had dissolved oxygen concentrations less than 0.5 mg/L.
325 In the absence of dissolved oxygen data, nitrate (less than 0.5 mg/L as N), manganese (greater
326 than or equal to 0.05 mg/L), or iron concentrations (greater than or equal to 0.1 mg/L) were
327 used to characterize reduced water (McMahon and Chapelle 2008). A similar approach was
328 used to characterize the redox status of water from wells for analysis of the occurrence of
329 vanadium in California (Wright and Belitz 2010; Wright et al. 2014).

330 Statewide, Cr(VI) was detected more frequently and at higher concentrations in oxic
331 water; with Cr(VI) present at concentrations greater than the SRL in 46.4 percent of sampled
332 wells and greater than the MCL in 7.4 percent of sampled wells. In reduced water, Cr(VI) was
333 detected at concentrations greater than the SRL in only 4.9 percent of sampled wells and water
334 from only one well exceeded the MCL of 10 μg/L (fig. 3). In 10 of 14 samples in reduced water
335 having reportable Cr(VI) concentrations, nitrate was present at concentrations ranging from 0.7
336 to 12.7 mg/L as N. In some studies, reduction of Cr(VI) to Cr(III) is reported to increase when
337 nitrate is present (Han et al., 2010); however, other studies (Izbicki 2008; Izbicki et al. 2008b;
338 Chovanec et al., 2012) show nitrate interferes with microbially mediated reduction of Cr(VI) to
339 Cr(III). Inhibition of Cr(VI) reduction may occur in some settings because many of the same
340 microorganisms that reduce Cr(VI) also reduce nitrate (Chovanec et al., 2012), and these
341 microorganisms may preferentially utilize nitrate, which is commonly present at higher
342 concentrations than Cr(VI).

343 **3.1.2 Occurrence with land use and well construction**

344 Land use within a 500-m radius around wells is a useful predictor of water quality within
345 wells in California (Johnson and Belitz, 2009). Examination of Cr(VI) occurrence in wells showed
346 a statistically significant difference (Kolmolgorov-Smirnov two-sample test at a confidence
347 criterion of $\alpha = 0.05$) between Cr(VI) concentrations in water from wells in natural
348 (undeveloped) land compared to agricultural, and urban land uses (fig. 6). Cr(VI) occurrence at
349 concentrations greater than the SRL was greater in water from wells in both agricultural and
350 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, and processes that that alter the hydrology or geochemistry in agricultural and urban areas also may increase the occurrence of Cr(VI).

**Figure 6 near here**

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 Program 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 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

372 desorption of Cr(VI) from aquifer materials. In areas where aquifer materials are more reactive,
373 and groundwater is reducing, Cr(VI) may not be present at depth if dissolved oxygen has been
374 consumed.

375 ### 3.1.3 Occurrence by hydrogeologic province

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

380 **Figure 7 near here**

381 Cr(VI) concentrations greater than the California MCL were found in water from wells
382 throughout the Desert (including Basin and Range) hydrogeologic province. However, Cr(VI)
383 concentrations were highest in alluvial aquifers within the Antelope Valley and Coachella Valley
384 study units (fig. 1) where concentrations exceeded the SRL in 94 and 74 percent of sampled
385 wells, and exceeded the California MCL in 26 and 20 percent of sampled wells, respectively. The
386 chromium-containing Pelona Schist and related schists (Jacobson et al. 2000) that crop out in
387 these areas (not shown on fig. 1) may be a source of chromium (Izbicki et al. 2008a). Oxic,
388 alkaline groundwater (with dissolved oxygen concentrations greater than 0.5 mg/L in 95 and 83
389 percent of sampled wells, and median pH's of 8 and 7.8, respectively), coupled with low
390 groundwater recharge rates and long flowpaths through aquifers within the Antelope and
391 Coachella Valley study units, enable chromium weathered from chromium-containing minerals,
392 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) 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, 2015). Water from sampled wells in the west-side of the Central Valley was oxic 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 μg/L than statewide (fig. 7B). Cr(VI) concentrations 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 hydrologeologic provinces (Kolmolgorov-Smirnov two-sample test at a confidence criterion of $\alpha$

415 = 0.05) (fig. 7). The Coast Ranges province has large areas of chromium-containing rock (fig. 1),
416 but Cr(VI) concentrations exceed the California MCL in only 3 percent of sampled wells with
417 detections above the SRL in only 18 percent of sampled wells. Cr(VI) concentrations in the Coast
418 Ranges may be limited by the comparatively large percentage of wells in this area having
419 reduced groundwater (about 65 percent) compared to other parts of the state (Table 2). Water
420 from only one well exceeded the MCL in the Transverse Range province and no wells exceeded
421 the California MCL in the Sierra or San Diego provinces, although Cr(VI) concentrations were
422 greater than the SRL in 18 to 16 percent of sampled wells in these areas (Table 2). Comparison
423 with CDPH data (fig. 3) shows a number of wells in urban areas near Los Angeles that have
424 Cr(VI) concentrations greater than the California MCL. This may occur because wells near areas
425 of known contamination would have been excluded from the GAMA-PBP Program, while these
426 wells may have been preferentially sampled and included within the CDPH data base.

427 **Table 2 near here**

428 Cr(VI) concentrations in the Sierra Nevada hydrogeologic province were statistically
429 different from statewide concentrations and plot below the statewide distribution (fig. 7). Wells
430 in areas having chromium-containing rock within the Sierra Nevada were not sampled as part of
431 the GAMA-PBP Program. However CDPH data show a number of wells having Cr(VI) greater
432 than 1 μg/L in areas where chromium-containing rock occurs (fig. 3B), although Cr(VI)
433 concentrations greater than the California MCL were not present. The Sierra Nevada has fewer
434 defined groundwater basins than other hydrogeologic provinces within California (Table 1) and
435 groundwater flow paths are commonly short, limiting the potential interactions between
436 groundwater and aquifer material. In addition, wells near channels of major rivers, streams,

437 and lakes may induce infiltration of water from those sources affecting the chemistry (including
438 pH, redox, and Cr(VI) concentrations) of water from those wells.
439 Cr(VI) data were not collected within the Klamath Mountains, or Modoc Plateau and
440 Cascades hydrogeologic provinces in northern California as part of the GAMA-PBP Program. The
441 Klamath Mountains have the most extensive occurrence of Cr-containing mafic rocks in
442 California and high-chromium concentrations in surface soils (fig. 1). Despite the abundance of
443 chromium-containing source material, Cr(t) concentration in water from 32 wells in the
444 Klamath Mountains sampled as part of the GAMA-PBP Program (Mathany and Belitz 2014)
445 ranged from less than the SRL of 0.07 to 6.3 μg/L, with 22 percent of sampled wells greater
446 than or equal to 1 μg/L. Similar to the Sierra Nevada hydrogeologic province, this area also has
447 few defined groundwater basins (Table 1), and the shallowest median well depth of any
448 hydrogeologic province (Table 2). In addition, many wells are near channels of major rivers and
449 streams and may induce infiltration of surface water from those sources potentially affecting
450 the chemistry of water from the wells. Water from sampled wells was generally oxic and slightly
451 slightly acidic with a median pH of 6.9. Slightly acidic water increases sorption of Cr(VI),
452 potentially limiting the occurrence of Cr(t) and Cr(VI) in water from wells. The Modoc Plateau
453 and Cascades hydrogeologic provinces do not contain extensive areas of Cr-containing mafic
454 rock (fig. 1A), but the area does have high-chromium concentrations in surface soils (fig. 1B).
455 Cr(t) concentrations in water from 88 wells in the Modoc Plateau and Cascades sampled as part
456 of the GAMA-PBP Program (Shelton et al., 2013) ranged from less than the SRL to 8.9 μg/L, with
457 46 percent of sampled wells greater than or equal to 1 μg/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 province, 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 as least some water recharged after 1952. Carbon-14 is a radioactive

479 isotope of carbon having a half-life of about 5,730 years. Unlike tritium, carbon-14 is not part of
480 the water molecule and carbon-14 activities can be affected by reactions other than radioactive
481 decay. For the purposes of this paper, only uncorrected carbon-14 activities that do not account
482 for reactions with aquifer material are presented.

483 Statewide, Cr(VI) concentration were greater in water from wells having older
484 groundwater that does not contain tritium than for younger groundwater containing tritium
485 percent of wells (fig. 8A). Water from 17 percent of wells containing older groundwater that
486 does not contain tritium exceeded the MCL of 10 μg/L for Cr(VI), compared to water from 3
487 percent of wells having younger water.

488 **Figure 8A, B, and C near here**

489 In the Desert (including Basin and Range) hydrogeologic province, Cr(VI) concentrations
490 were greater in water from wells having older groundwater than younger groundwater (fig. 8B).
491 Cr(VI) concentrations in 23 percent of wells yielding older groundwater not containing tritium
492 exceed the California MCL, compared to no wells containing younger groundwater. There was a
493 statistically significant negative correlation between Cr(VI) concentrations and carbon-14
494 activity as percent modern carbon (reflecting increasing Cr(VI) concentrations with
495 groundwater age) in the Antelope Valley study unit within the Desert hydrogeologic province
496 (Kendalls Tau = -0.378; significant at a confidence criterion of a = 0.10). The Antelope Valley
497 study unit has the highest percentage of Cr(VI) concentrations in water from wells in excess of
498 the MCL within California, and the data suggest that Cr(VI) concentrations would continue to
499 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). 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 Program are 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'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 unstaturated zone is comparatively thin, typically less than 5 to 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. Dissolved gas in groundwater from excess air is contributed according to the atmospheric proportions those gases, rather than as a function of temperature, pressure, or salinity according to Herny's Law. For water recharged areally through comparatively thick unsaturated zones 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. 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 Program (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 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.

**Figure 9A and 9B near here**

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 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 hydreogeologic province water form these wells contains tritium, was recently recharged, and Cr(VI) concentrations in these areas are generally low (fig. 9B). Younger water containing

tritium, warmer recharge temperatures, and higher Cr(VI) concentrations predominate 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 in 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, rather than changes in pH and exchange along groundwater flowpaths. The presence of Cr(VI) in water from wells in the west-side of the Central Valley having warm recharge temperatures, presumable 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 iron, Fe(II) and Fe(III), were analyzed in water from wells as part of the GAMA-PBP Program. 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). These elements form oxyanions having similar chemical properties. Vanadium and selenium form soluble oxyanions in the +6 oxidation state, and uranium in the +4 oxidation state. These elements also form comparatively

584 insoluble cations under reduced conditions. PCA groups these different elements similarly near
585 Cr(VI) (fig. 10). Barium, while positively correlated with Cr(VI), does not form an oxyanion under
586 alkaline, oxic conditions and does not group closely with Cr(VI) or the other elements (fig. 10).
587 Arsenic, and its oxyanion, As(V), were not correlated with Cr(VI), and were not grouped
588 together in PCA results. In contrast, As(III), which is soluble under reduced conditions, was
589 significantly negatively correlated with Cr(VI). Kendall's Tau correlation coefficients also show
590 significant negative correlations between Cr(VI) and molybdenum, and tungsten. Molybdenum
591 and tungsten in the +6 oxidation state also form oxyanions, but these oxyanions are complex
592 polyatomic ions that differ from Cr(VI) in chemical behavior. Because of the polyatomic nature
593 of molybdenum and tungsten oxyanions, analyses of filtered water samples commonly measure
594 only the dissolved cationic forms. Negative correlation coefficients also were obtained between
595 Cr(VI) and Fe(II), lithium, and boron. Collectively, results of PCA analyses group molybdenum,
596 tungsten, As(III), Fe(II), lithium, and boron separately from Cr(VI), and the (non-polyatomic)
597 oxyanion forming elements vanadium, selenium, and uranium (fig. 10a). Cadmium, manganese,
598 and nickel also are negatively correlated with Cr(VI). These elements form divalent cations
599 soluble in reduced water but comparatively insoluble in oxic water, and form a separate group
600 on the basis of the PCA results.

601 **Figure 10A and 10B near here**

602 Fewer elements were significantly correlated with Cr(VI) under alkaline (pH $\geq$ 8) oxic
603 conditions (possibly because fewer data are available) (fig. 10b). However, the data show the
604 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 aqueous chemistry as pH and redox conditions change within aquifers, rather than as a result of similarities in 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), and with noble-gas data (fig. 9) that suggest 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 sampled wells, and exceeded the recently established (2014) California Maximum Contaminant Level of 10 μg/L in 4 percent of sampled wells. Almost all dissolved chromium, about 90 percent, was present as Cr(VI). Data

626 collected for public-health and regulatory purposes by the CDPH had a higher frequency of
627 detection compared to the spatially distributed data collected as part of the GAMA-PBP
628 Program, as a result of clustering of analyses in the CDPH database from wells in areas known
629 to have natural or anthropogenic Cr(VI) occurrence. Use of public-health or regulatory data to
630 assess the occurrence of Cr(VI), and other trace elements, over large areas may overestimate
631 the occurrence of these constituents compared to data collected using spatially-distributed
632 sample designs.

633 Statewide, about 20 percent of the public-supply wells in California have high
634 concentrations of one or more constituents, and trace-elements, specifically arsenic,
635 manganese, and uranium, were more prevalent in public-supply wells than nitrate or organic
636 compounds (Belitz et al., 2015). Arsenic and uranium occur naturally in rock and alluvium at
637 bulk, continental-scale concentrations almost two orders of magnitude lower than chromium
638 (Nriagu and Niebor 1988; Reimann and Caritat 1998), but occur commonly in water from
639 public-supply wells, especially in the Central Valley and Desert hydrogeologic provinces because
640 of alkaline, oxic groundwater and hydrologic conditions in these areas (Belitz et al., 2015).
641 (Although arsenic, as As(III), concentration increased in reduced groundwater because arsenic
642 also is soluble under reduced conditions.) Although commonly detected at the SRL of 1 μg/L,
643 the occurrence of Cr(VI) in groundwater was less than what might be expected on the basis of
644 its relative abundance in the continental crust (compared to arsenic and uranium), and the
645 widespread occurrence of chromium-containing rock and soil in California. Cr(VI) was most
646 abundant in aquifers having chromium-containing source rock and alkaline oxic groundwater,

647 especially alluvial aquifers in the Desert and west-side of the Central Valley hydrogeologic
648 provinces.

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

660 In contrast within the Central Valley hydrogeologic province, chromium-containing
661 geologic material, coupled with areal groundwater recharge (from both infiltrating precipitation
662 and recharge from irrigation return), facilitate interaction of water with unsaturated sediments
663 prior to groundwater recharge—resulting in increased Cr(VI) occurrence and concentrations in
664 water from public supply wells. However, the presence of chromium-containing material does
665 not solely explain occurrence of Cr(VI) in groundwater. Parts of California having large areas of
666 chromium-containing rock or soil, such as the Klamath Mountains, or Modoc Plateau and
667 Cascades hydrogeologic provinces, do not have high concentrations of Cr(VI) in water from
668 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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## 6. Supplementary information

**Appendix A:** Data sources and field procedures, quality assurance, and statistical methods

**Table S1.--** Long-term method detection levels, study reporting levels, percent analyses exceeding study reporting level, and Kendall's Tau correlation coefficient between Cr VI and selected constituents, Groundwater Ambient Monitoring Assessment-Priority Basin Project (GAMA-PBP) Program, California 2004 to 2012.

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