



Insights into controls on hexavalent chromium in groundwater provided by environmental tracers, Sacramento Valley, California, USA



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ABSTRACT

Environmental tracers are useful for determining groundwater age and recharge source, yet their application in studies of geogenic Cr(VI) in groundwater has been limited. Environmental tracer data from 166 wells located in the Sacramento Valley, northern California, were interpreted and compared to Cr concentrations to determine the origin and age of groundwater with elevated Cr(VI), and better understand where Cr(VI) becomes mobilized and how it evolves along flowpaths. In addition to major ion and trace element concentrations, the dataset includes $\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H concentration, ^{14}C activity (of dissolved inorganic C), $\delta^{13}\text{C}$, $^3\text{He}/^4\text{He}$ ratio, and noble gas concentrations (He, Ne, Ar, Kr, Xe). Noble gas recharge temperatures (NGTs) were computed, and age-related tracers were interpreted in combination to constrain the age distribution in samples and sort them into six different age categories spanning from <60 yr old to >10,000 yr old. Nearly all measured Cr is in the form of Cr(IV). Concentrations range from <1 to 46 $\mu\text{g L}^{-1}$, with 10% exceeding the state of California's Cr(VI) maximum contaminant level of 10 $\mu\text{g L}^{-1}$. Two groups with elevated Cr(VI) ($\geq 5 \mu\text{g L}^{-1}$) were identified. Group 1 samples are from the southern part of the valley and contain modern (<60 yr old) water, have elevated NO_3^- concentrations ($>3 \text{ mg L}^{-1}$), and commonly have $\delta^{18}\text{O}$ values enriched relative to local precipitation. These samples likely contain irrigation water and are elevated due to accelerated mobilization of Cr(VI) in the unsaturated zone (UZ) in irrigated areas. Group 2 samples are from throughout the valley and typically contain water 1000–10,000 yr old, have $\delta^{18}\text{O}$ values consistent with local precipitation, and have unexpectedly warm NGTs. Chromium(VI) concentrations in Group 2 samples may be elevated for multiple reasons, but the hypothesis most consistent with all available data (notably, the warm NGTs) is a relatively long UZ residence time due to recharge through a deep UZ near the margin of the basin. A possible explanation for why Cr(VI) may be primarily mobilized in the UZ rather than farther along flowpaths in the oxic portion of the saturated zone is more dynamic cycling of Mn in the UZ due to transient moisture and redox conditions.

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1. Introduction

A growing number of studies have reported geogenic Cr(VI) in groundwater at concentrations that approach or exceed the World Health Organization's recommended total Cr standard of 50 $\mu\text{g L}^{-1}$ (Fantoni et al., 2002; Fariás et al., 2003; Ball and Izbicki, 2004; Morrison et al., 2009; Wood et al., 2010; Bertolo et al., 2011; Moraetis et al., 2012; Lelli et al., 2014). These elevated concentrations are concerning given that Cr(VI) is a known carcinogen (Salnikow and Zhitkovich, 2007; Stout et al., 2008). The primary source of geogenic Cr(VI) is widely believed to be Cr-rich minerals (mainly chromite, Cr-magnetite, and Cr-bearing silicates) within or derived from ultramafic rocks commonly associated with ophiolite complexes (Oze et al., 2007). However, the dissolution of

Cr(III) within mineral phases, the oxidation of Cr(III) to Cr(VI) on Mn oxides, and the subsequent transport of Cr(VI) in groundwater are complex redox- and pH-dependent processes, and how these occur in aquifers (versus the laboratory) remains unclear (e.g., Rajapaksha et al., 2013). Previous studies have primarily utilized major and trace element data, statistical techniques, geochemical modeling, and laboratory experiments to survey the spatial distribution of Cr(VI) in aquifers, determine the likelihood of geogenic versus anthropogenic sources, and develop hypotheses regarding the geochemical processes responsible for observed concentrations. Although a great deal has been learned, these studies generally lack reliable information on the specific origin (recharge source and location) and residence time of sampled waters. As a result, knowledge of Cr(VI) sources and the manner in which Cr(VI) concentrations evolve along groundwater flowpaths remains vague and/or speculative.

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Environmental tracers such as carbon isotopes, helium isotopes, and dissolved noble gases are powerful tools for determining groundwater age and recharge source (Cook and Herczeg, 2000). The application of environmental tracers in studies of Cr(VI) in groundwater has been limited. Izbicki et al. (2008a) used stable isotopes of water (^{18}O and ^2H) to help identify a high-Cr industrial waste-water source, and used ^{14}C activity of dissolved inorganic carbon to identify relationships between Cr(VI) and relative groundwater age. Lelli et al. (2014) employed $\delta^{18}\text{O}$ and ^3H (along with NO_3^-) to distinguish recently recharged water from older water, and found different Cr(VI) concentrations in these two groups. These studies demonstrate the potential value of environmental tracer methods in groundwater Cr investigations, but in both cases the tracer data were presented for a modest number of samples, actual groundwater ages were not computed, and only two different tracers were utilized. Age and source determinations are considerably more robust when multiple types of tracer data are employed together, particularly in the case of constraining the age distribution in mixed-age samples from long-screened wells or springs (e.g., Manning et al., 2012).

The Sacramento Valley in Northern California, USA, is a 17,000 km² regional aquifer with geogenic Cr concentrations ranging up to 50 $\mu\text{g L}^{-1}$ (Morrison et al., 2009). The apparent source is Cr-rich minerals in soils and sediments derived from ultramafic rocks, which crop out extensively in the adjacent Sierra Nevada and Coast Range mountains (Morrison et al., 2009). Laboratory incubations of unsaturated-zone (UZ) soils collected in the southwestern Sacramento Valley suggest that precipitation and irrigation water may acquire high Cr(VI) concentrations while infiltrating through the UZ, where both Cr and Mn oxides are abundant (Chung et al., 2001; Mills et al., 2011). However, an examination of groundwater Cr(VI) concentrations for the whole Sacramento Valley has not been performed, and the fundamental question of why certain groundwater samples in a given area are high in Cr(VI) while others are not remains largely unanswered. Understanding which types of groundwater are most likely to contain elevated geogenic Cr(VI) is of particular interest in the state of California where naturally-elevated groundwater Cr concentrations occur in multiple locations (Deverel et al., 1984; Ball and Izbicki, 2004; Gonzalez et al., 2005), and a new state drinking water maximum contaminant level (MCL) for Cr(VI) of 10 $\mu\text{g L}^{-1}$ was recently implemented (California State Water Resources Control Board, <http://www.swrcb.ca.gov/>).

In this study, environmental tracer data collected from 166 wells located throughout the Sacramento Valley were interpreted and compared to Cr concentrations in order to better understand the origin and age of groundwater with elevated geogenic Cr(VI), gain new insight into controlling factors, and focus future research efforts. The dataset was collected as part of the California Groundwater Ambient Monitoring and Assessment (GAMA) Program (Belitz et al., 2003), and is unusual in the number and diversity of tracer measurements. In addition to major and trace elements and Cr(VI), it includes stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), carbon isotopes of dissolved inorganic carbon (^{14}C activity, $\delta^{13}\text{C}$), tritium (^3H), helium isotope ratio ($^3\text{He}/^4\text{He}$), and dissolved noble gases (He, Ne, Ar, Kr, Xe). Apparent $^3\text{H}/^3\text{He}$ ages (applicable for waters <60 yr old) were computed from ^3H concentrations, $^3\text{He}/^4\text{He}$ ratios, and noble gas concentrations. Unadjusted radiocarbon ages were computed from ^{14}C activities and $\delta^{13}\text{C}$. Computed ages along with other age indicators (mainly terrigenous ^4He concentration) were used to sort samples into six different age categories spanning from <60 yr old to >10,000 yr old. Noble gas concentrations were also used to compute noble gas recharge temperature (NGT), the temperature at the water table at the recharge location. Noble gas recharge temperatures in combination with $\delta^{18}\text{O}$ values allow for the identification of the following types of

recharge: high-elevation precipitation that recharges in the mountains and flows as groundwater to the valley (mountain-block recharge); high-elevation precipitation that becomes streamflow in the mountains, flows as surface water to the valley, then infiltrates as focused stream loss; low-elevation precipitation that recharges in a diffuse manner in the valley; and water that recharges through a relatively deep (>50 m) UZ. Comparison of these tracer results to Cr concentrations revealed which types of water were most likely to contain elevated Cr(VI), and pointed to likely controlling mechanisms.

2. Site description

The Sacramento Valley is the northern portion of California's Central Valley (Fig. 1A), which supplies about 25% of the food and 20% of the groundwater demand of the U.S. (Faunt, 2009). Land use in the Sacramento Valley is a mixture of agricultural, urban, and native grasslands and woodlands. Elevations predominantly range from 0 to 300 masl, generally increasing from south to north and from the Sacramento River (valley axis) toward the valley margins. The valley is bound to the east by the Sierra Nevada mountains (up to 3000 masl), to the west by the Coast Range (up to 2400 masl), and to the north by the southern end of the Klamath Mountains and Cascade Range (up to 2700 masl). It has a Mediterranean climate with mild, wet winters and hot, dry summers. Mean annual air temperature ranges from 15 to 17 °C. Mean annual precipitation ranges from 35 to 75 cm throughout most of the valley (the extreme northern end receives 115 cm), generally increasing from south to north and with elevation (Western Regional Climate Center, <http://www.wrcc.dri.edu/precip.html>). Nearly all precipitation falls from October to April as rain. Upper elevations of the surrounding mountains receive an average of up to 250 cm yr⁻¹ of precipitation, maintain a winter snowpack, and host montane and sub-alpine forests. Streamflow from the mountains is highly seasonal, with about 80% occurring January through June (Williamson et al., 1989). East-side streams and rivers account for about 75% of the surface-water flow entering the valley (Sacramento River excluded; Fig. 1B; Faunt, 2009).

The mountains west and north of the valley are composed predominantly of Mesozoic and Paleozoic clastic marine sedimentary rocks (sandstone, shale, and conglomerate) and metasedimentary rocks (mainly schist), the latter including the highly deformed Franciscan mélangé (Gutierrez et al., 2010). Marine sedimentary rocks (Great Valley Sequence) crop out along the foot of the adjacent Coast Range, and metasedimentary rocks are exposed at higher elevations further west. Bedrock in the mountains east of the valley consists mainly of Cenozoic volcanics (flow rocks and pyroclastics), Paleozoic and Mesozoic volcanic and metavolcanic rocks (andesite and rhyolite flow rocks, greenstone, diabase, and pillow lavas), and granitic intrusives, as well as some of the same sedimentary and metasedimentary rocks exposed west and north of the valley (Gutierrez et al., 2010). The metasedimentary and metavolcanic units contain numerous packages of ultramafic rocks east, west, and north of the valley, consisting mainly of serpentinite with minor peridotite and gabbro (Fig. 1A). Morrison et al. (2009) collected samples of ultramafic rock and overlying soils in the mountains adjacent to the southern part of the valley and measured total Cr concentrations of 990–5900 mg kg⁻¹ in the rock and 1100–11,670 mg kg⁻¹ in the soils. In the soils, Cr primarily occurs within chromite and other mixed-composition spinels (Al, Mg, Fe, Cr).

The shallow (<300 m) valley-fill, which composes the valley aquifer, consists of late Tertiary to Quaternary alluvial and fluvial sediments shed from the surrounding mountains (Page, 1986; Fig. 1A). The older Plio-Pleistocene sediments form low hills and

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