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Delta Chromium-53/52 isotopic composition of native and contaminated groundwater, Mojave Desert, USA

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ABSTRACT

Chromium(VI) concentrations in groundwater sampled from three contaminant plumes in aquifers in the Mojave Desert near Hinkley, Topock and El Mirage, California, USA, were as high as 2600, 5800 and 330 μg/L, respectively. $\delta^{53/52}$Cr compositions from more than 50 samples collected within these plumes ranged from near 0‰ to almost 4‰ near the plume margins. Assuming only reductive fractionation of Cr(VI) to Cr(III) within the plume, apparent fractionation factors for $\delta^{53/52}$Cr isotopes ranged from $\varepsilon_{app} = 0.3$ to 0.4 within the Hinkley and Topock plumes, respectively, and only the El Mirage plume had a fractionation factor similar to the laboratory derived value of $\varepsilon = 3.5$. One possible explanation for the difference between field and laboratory fractionation factors at the Hinkley and Topock sites is localized reductive fractionation of Cr(VI) to Cr(III), with subsequent advective mixing of native and contaminated water near the plume margin. Chromium(VI) concentrations and $\delta^{53/52}$Cr isotopic compositions did not uniquely define the source of Cr near the plume margin, or the extent of reductive fractionation within the plume. However, Cr(VI) and $\delta^{53/52}$Cr data contribute to understanding of the interaction between reductive and mixing processes that occur within and near the margins of Cr contamination plumes. Reductive fractionation of Cr(VI) predominates in plumes having higher ε_{app}, these plumes may be suitable for monitored natural attenuation. In contrast, advective mixing predominates in plumes having lower ε_{app}, the highly dispersed margins of these plumes may be difficult to define and manage.

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1. Introduction

Chromium is the 21th most abundant element in the earth's crust (Emsley, 2001). The average concentration of Cr in the earth's crust is about 100 mg/kg (Nriagu and Niebor, 1988; Reimann and Caritat, 1998). 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 Caritat, 1998). The most common Cr-containing mineral is chromite ($FeCr_2O_4$). Chromium also is commonly substituted within minerals such as amphiboles, garnets, micas, pyroxenes and spinels (Reimann and Caritat, 1998). In most minerals Cr is in the +3 oxidation state (Nriagu and Niebor, 1988).

Chromium occurs naturally in groundwater in the Mojave Desert (Ball and Izbicki, 2004; Izbicki et al., 2008a) and in other parts of the world (Robertson, 1975, 1991; Chung et al., 2001; Gray 2004; Gonzalez et al., 2005; Morrison et al., 2009; Aragon, 2009; Mills et al., 2011). In water, Cr is present in either the Cr(III) or Cr(VI) oxidation state. Chromium(III), an essential micronutrient for humans, is only sparingly soluble in most groundwater. Where geologic and geochemical conditions are favorable, naturally-occurring Cr(VI) concentrations in groundwater underlying the Mojave Desert can exceed the California Maximum Contaminant Limit (MCL) of 50 μg/L (Ball and Izbicki, 2004; Izbicki et al., 2008a).

Chromium(VI) is a known carcinogen if inhaled (Daugherty, 1992; ATSDR, 2000) and recent work suggests Cr(VI) may be a carcinogen if ingested (Sedman et al., 2006; Beaumont et al., 2008). Concern over chronic exposure to low-levels of Cr(VI) has prompted establishment of a California Public Health Goal of 0.02 μg/L Cr(VI) in drinking water (California Environmental Protection Agency, 2011).

Chromium has a wide range of industrial uses in electroplating, leather tanning, wood preservation, and as an anti-corrosive in cooling tower water (Nriagu and Niebor, 1988). As a consequence, Cr is a common industrial contaminant. Chromium(VI) is highly soluble and mobile in alkaline, oxic groundwater; and Cr(VI) contamination can migrate for kilometers with only limited attenuation (Perlmutter et al., 1963; Blowes, 2002). In some areas, identifying the extent of Cr(VI) contamination near plume margins can be complicated by the presence of naturally-occurring Cr(VI) (Izbicki et al., 2008a).

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Chromium isotopes have been suggested as a tool to determine the source of Cr in groundwater, and to more accurately define the extent of contamination in areas having high natural background Cr(VI) concentrations (Ellis et al., 2002; Bullen, 2007; Izbicki et al., 2008a). There are 4 naturally occurring isotopes of Cr having masses of approximately 50, 52, 53 and 54 (Coplen et al., 2002). The two most abundant isotopes, ^{52}Cr and ^{53}Cr have global abundances of 83.8 and 9.5%, respectively. Chromium isotopic abundances are expressed in delta (δ) notation as ‰ differences relative to the ^{53}Cr/^{52}Cr ratio in a sample and the ^{53}Cr/^{52}Cr ratio in the certified Cr isotope standard NIST979. Small variations in Cr isotope compositions can be used to differentiate Cr from different sources, or to identify chemical processes involving Cr (Ellis et al., 2002, 2004; Bullen, 2007; Izbicki, 2008; Berna et al., 2009; Aragon, 2009).

Differences in Cr isotope composition are induced during chemical reactions through fractionation where one isotope (usually the lighter isotope) is preferentially incorporated into the product, leaving the heavier isotope in the remaining reactant. Weathering of Cr from primary minerals, and oxidation of Cr(III) to Cr(VI) have not been shown to fractionate Cr in natural settings (Izbicki et al., 2008a). Speciation of Cr(VI) between bichromate ($HCrO_4^-$) and chromate (CrO_4^{-2}) also has not been shown to fractionate Cr (Ellis et al., 2004). However, Cr isotopes fractionate during the reduction of Cr(VI) to Cr(III) as the strong Cr-O bonds in the chromate and bichromate oxyanions are broken. The lighter Cr isotopes are preferentially reduced, leaving the heavier isotopes in the remaining Cr(VI) (Ellis et al., 2004). $\delta^{53/52}$Cr compositions as high as 5.1‰ have been measured in native groundwater as a result of this process (Izbicki et al., 2008a). In contrast, industrial Cr compounds have $\delta^{53/52}$Cr compositions near-0‰; therefore, anthropogenic Cr(VI) within contamination plumes that has not been partially reduced to Cr(III) has $\delta^{53/52}$Cr compositions near 0‰ (Ellis et al., 2002, 2004; Bullen, 2007; Izbicki et al., 2008a; Berna et al., 2009).

Berna et al. (2009) used changes in $\delta^{53/52}$Cr isotopic composition to show that reduction of Cr(VI) to Cr(III) occurred within a Cr contamination plume in an alluvial aquifer near Berkeley, California having anoxic groundwater. The plume was monitored from 2001 to 2008. Stable Cr(VI) concentrations within the plume between 2004 and 2008 suggest the plume is no longer advancing, and $\delta^{53/52}$Cr isotopic data suggest that the areal extent of contamination at the site is limited by reduction of Cr(VI) to Cr(III). However, the apparent fractionation factor measured at the site, $\varepsilon_{app} = 1.4$, differs from laboratory derived fractionation factors ranging from $\varepsilon = 3.4$ to 4.5 (Ellis et al., 2002; Kitcher et al., 2004; Sikora et al., 2008). Berna et al. (2009) explained this difference through a combination of reductive fractionation and advective mixing with native groundwater having low Cr(VI) concentrations near the plume margin. In contrast, Raddatz et al. (2011) showed limited reduction of Cr(VI) contamination in oxic groundwater within a basaltic aquifer underlying the Snake River Plain in Idaho, and that Cr(VI) concentrations near the plume margin were controlled largely by mixing with native groundwater containing naturally occurring Cr(VI). However, small amounts of reduction of Cr(VI) were identified on the basis of $\delta^{53/52}$Cr isotopic data as a result of reactions with reduced Fe in the host rock. Additional data from field settings can be used to evaluate the use of the $\delta^{53/52}$Cr isotopic data to (1) estimate the extent of Cr contamination at sites having high background Cr concentrations and (2) evaluate the effects of reduction and mixing on Cr concentrations and plume migration in a range of hydrogeologic settings.

1.1. Purpose and scope

The purpose of this paper is to (1) evaluate the usefulness of $\delta^{53/52}$Cr compositions to distinguish Cr(VI) originating from natural and anthropogenic sources near Cr contamination plumes, and (2) evaluate reductive and mixing processes that control Cr concentrations and isotope compositions within, and near the margins of, contaminant plumes. The scope of this work included measurement of Cr(VI) concentrations and $\delta^{53/52}$Cr compositions in native and contaminated groundwater at the Hinkley, Topock and El Mirage Cr contamination sites in the Mojave Desert, California (Fig. 1).

2. Hydrologic setting

The Hinkley, Topock and El Mirage sites represent a range of geologic and hydrologic conditions found in alluvial aquifers throughout the Mojave Desert. The Mojave Desert is hot and dry in the summer with daytime temperatures commonly exceeding 40 °C. Temperatures below 0 °C are not uncommon during the winter. Average annual precipitation at all three sites is less than 150 mm, and average annual evaporation is greater than 390 mm (Western Region Climate Center, http://www.wrcc.dri.edu/, accessed September 14, 2009).

2.1. Hinkley

The Hinkley site is located in the Hinkley Valley approximately 1.5 km north of the Mojave River near Barstow, California (Fig. 1). Alluvial deposits at the site were largely eroded from granitic rock in the San Bernardino and San Gabriel Mountains 70 km to the west and deposited by the Mojave River. The alluvial deposits are composed primarily of sand and gravel from 30 to 90 m thick, and are underlain by granitic rock (CH2M Hill, Inc., 2007a). Groundwater in the Hinkley Valley is recharged by infiltration of intermittent streamflow in the Mojave River to the south of the

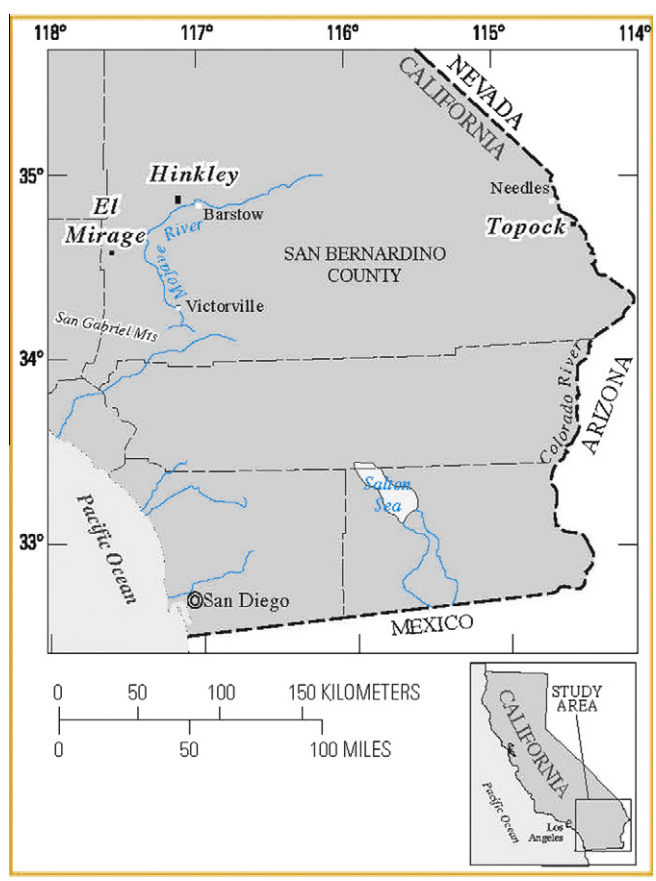

Fig. 1. Location of study areas.

valley (Izbicki, 2004; Stamos et al., 2009) (Fig. 2). Prior to groundwater pumping, groundwater movement in Hinkley Valley was from the Mojave River towards Harper (dry) Lake in the north, where groundwater discharged by evaporation (Izbicki, 2004; Izbicki and Michel, 2004). Currently groundwater follows the same general pattern (Stamos et al., 2009), with local changes in the direction of movement caused by pumping wells. Groundwater generally contains ^{3}H and was recharged after the onset of nuclear weapons testing in 1952 (Izbicki and Michel, 2004). Uncontaminated groundwater in the area is oxic, neutral to alkaline with pH ranging from 6.9 to 8.8, and fresh with specific conductance ranging from 170 to 2760 μS/cm (CH2M Hill, Inc., 2007a).

Chromium(VI) contamination at the Hinkley site originated from a compressor station along a natural gas pipeline where Cr(VI) was used as an anti-corrosive. Releases of untreated Cr(VI) at the compressor station began in 1952 and continued until 1964 (LRWQCB, 2008). Since that time, Cr(VI) has moved to the north with the groundwater, and in 2006 the plume was more than 4 km long (Fig. 2). Historical maximum Cr(VI) concentrations within the plume were as high as 5000 μg/L (LRWQCB, 2008).

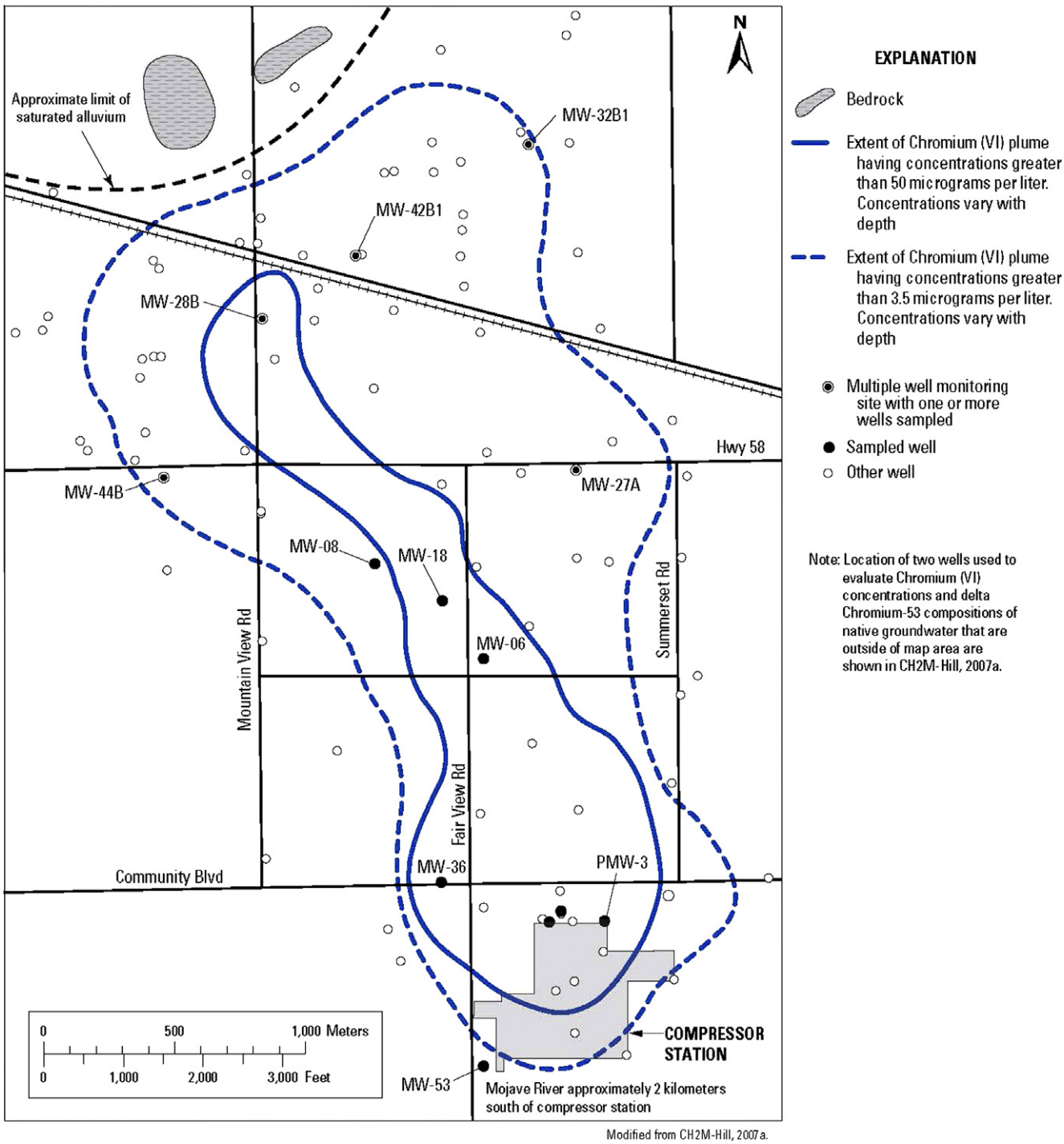

Fig. 2. Extent of Cr(VI) contamination near Hinkley, Calif., 2006.

2.2. Topock

The Topock site is located west of the Colorado River, near Needles, California (Fig. 1). Although the site is in California it derives its name from the small town of Topock on the Arizona side of the Colorado River. Aquifer materials consist of alluvial-fan deposits and fluvial deposits along the Colorado River (Metzger and Loeltz, 1973; Howard et al., 1997). Alluvial fan deposits at the site are composed of poorly-sorted silty, clayey gravel eroded from metamorphic, igneous and volcanic rock in the surrounding mountains. Deposits beneath the water table are older, more consolidated, and less permeable than deposits above the water table. The saturated thickness of the alluvial fan deposits is greater than 80 m to the north and west of the site and the deposits thin to the south near the mountain front. Fluvial deposits along the Colorado River are composed of sandy gravel with interspersed layers of fine-grained sand, silt, and clay eroded largely from more distant sources (CH2M Hill, Inc., 2007b). The fluvial deposits are about 30 m thick throughout the area, and have similar thickness through the gorge in the mountains cut by the Colorado River. The fluvial deposits contain organic material, and groundwater in these deposits is generally anoxic. The unconsolidated alluvial and fluvial deposits are underlain by relatively impermeable consolidated conglomerate and igneous and metamorphic rock.

Although groundwater regionally discharges to the Colorado River, the gradient is relatively flat, with water levels generally within 1 m of the river altitude. Groundwater levels in the fluvial deposits and adjacent alluvial fan deposits respond to changes in river level resulting from regulation by a downstream dam. Carbon-14 data suggest that water in the alluvial fan deposit was

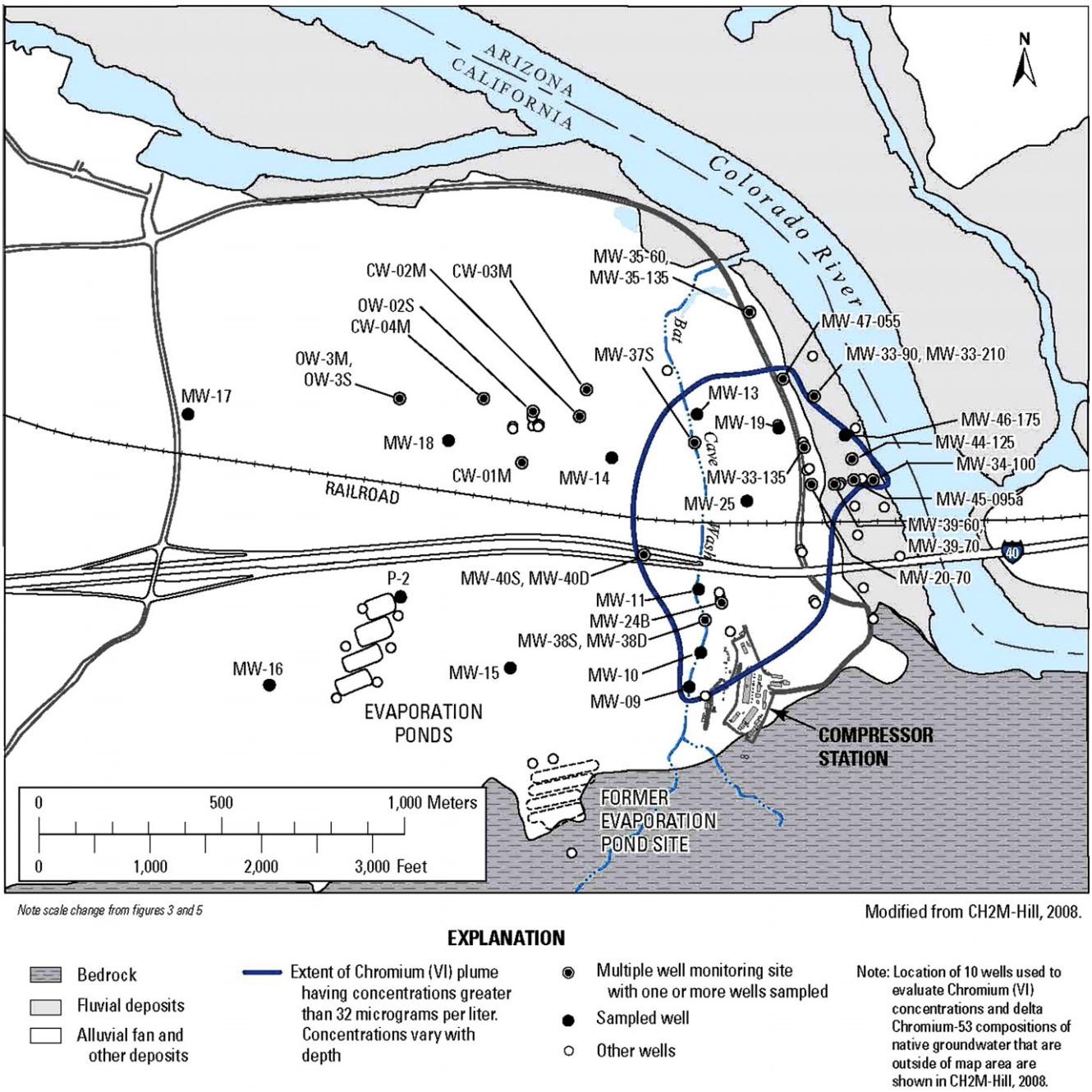

Fig. 3. Extent of Cr(VI) contamination near Topock, Calif., 2007.

recharged many thousands of years ago (Goldrath et al., 2010). Native groundwater in the alluvial fan deposits at the site is suboxic to oxic, and neutral to alkaline with pH ranging from 6.9 to 8.2, and fresh to saline with specific conductance ranging from 600 μS/cm to more than 40,000 μS/cm (CH2M Hill, Inc., 2007b). Deeper deposits tend toward suboxic and have higher specific conductance.

Contamination at the site originated from a compressor station along the same natural gas pipeline as the Hinkley site. Similar to the Hinkley site, Cr(VI) was also used as an anti-corrosive at the Topock site. Releases of untreated Cr(VI) to a dry wash crossing the alluvial-fan deposits began in 1951 and continued until 1964. After 1964, Cr(VI) was reduced to Cr(III) and removed from the waste solution, and the remaining wastewater was disposed of in the wash, injected into deep wells, or disposed of in lined ponds near the site. Chromium(VI) moved with groundwater to the north, opposite the direction of surface flow in the river, and then turned abruptly to the east toward the Colorado River. In 2006, the plume was almost 1000 m long, with historical maximum Cr(VI) concentrations of 12,000 μg/L (CH2M Hill, Inc., 2009) (Fig. 3).

2.3. El Mirage

The El Mirage site is located on the distal part of the Sheep Creek fan near El Mirage (dry) Lake about 30 km west of Victorville, California. Alluvial deposits of the Sheep Creek fan were eroded from metamorphic rock in the San Gabriel Mountains, 13 km to the south. Some of these rocks are mafic and are known to contain high concentrations of Cr (Izbicki et al., 2008a). Water from some wells on the upgradient portions of the Sheep Creek fan naturally exceeds the California Maximum Contaminant Level for Cr of 50 μg/L (Ball and Izbicki, 2004; Izbicki et al., 2008a). The distal part of the Sheep Creek fan near the El Mirage site is composed of fine-grained sand and silt, with interbedded layers of sand and gravel to a depth of about 70 m (Balderman Consulting, Inc., 2004). Locally these deposits are known as the "perched aquifer". Deeper alluvial deposits at the site composing the regional aquifer were eroded from granitic rocks to the north. The distal part of the Sheep Creek fan is near El Mirage (dry) Lake. Caliche deposits associated with groundwater discharge to the lake were encountered during test drilling near this site (Izbicki et al., 2008a).

Groundwater in the El Mirage area was recharged as infiltration of streamflow near the front of the San Gabriel Mountains 20 km to the south (Izbicki, 2007; Izbicki et al., 2007). Carbon-14 data suggests that this water was recharged many thousands of years ago (Izbicki and Michel, 2004). Prior to groundwater pumping the water table may have sloped to the north toward the dry lake (Balderman Consulting, Inc., 2004), under present-day conditions groundwater movement in the perched aquifer is to the NE. Groundwater at the site is oxic to suboxic with pH ranging from 7.5 to 8.6, and fresh with specific conductance ranging from 510 μS/cm to 1520 μS/cm. Prior to agricultural development native groundwater upgradient from the site was suboxic to reducing as a result of natural reductants in aquifer materials (primarily organic C, associated with lacustrine deposits associated with the dry lake). Irrigation return may have contributed to oxic conditions near the water table and may have mobilized Cr from the overlying unsaturated deposits (Izbicki, 2008; Izbicki et al., 2008b).

Water containing neutralized acids and other waste from the chemical milling of aircraft parts was discharged to an unlined pond at the El Mirage site between 1967 and 1980 where it infiltrated to underlying groundwater. The source of Cr(VI) contamination is not precisely known, but may have occurred within the facility and could be unrelated to the discharge of other wastes (Balderman Consulting, Inc., 2004). Chromium(VI) has moved to the NE with the groundwater and in 2002 the plume was approximately

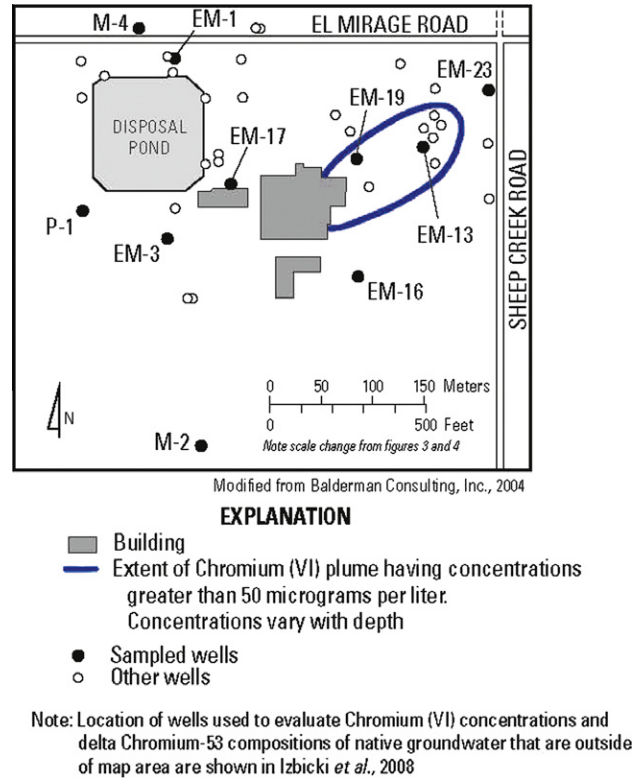

Fig. 4. Extent of Cr(VI) contamination near El Mirage, Calif., 2002.

150 m long with maximum Cr(VI) concentrations of 310 μg/L (Balderman Consulting, Inc., 2004) (Fig. 4). The El Mirage plume is small in comparison to the Hinkley or Topock plumes. Due to the uncertain episodic nature of Cr release, the presence of other industrial compounds (including Cr(VI) at concentrations in excess of 50 μg/L outside the mapped plume) and the potential for episodic Cr(VI) contamination throughout the site, all on-site wells are identified as "plume wells" for the purposes of this paper. Off-site wells showing evaporative evidence of industrial water use (32E1) or water from irrigation related sources (25M2) (Izbicki et al., 2008a) have been identified as native groundwater even though they may not strictly represent Cr(VI) concentrations and $\delta^{53/52}$Cr compositions of native water in the "perched aquifer" near the site.

3. Methods

Samples from the Hinkley and Topock sites were collected from wells within and near the contamination plume by CH2M Hill, Inc. in 2006. Chromium speciation at these sites was determined in a laboratory within 24 h of collection using US EPA method 218.6 (Arar et al., 1991). Samples from the El Mirage site were collected by the US Geological Survey in 2002. Chromium speciation at this site was determined within minutes of sample collection in a field laboratory using US EPA Method 218.6, and a direct colorimetric method (Hach Company, Inc., 1992). In addition, samples for Cr(VI) analysis were preserved using a field speciation procedure with later analysis in the laboratory (Ball and McCleskey, 2003a, b). Total dissolved Cr, Cr(T), was measured by inductively coupled plasma mass spectrometry (ICP-MS) at the Hinkley and Topock sites and by graphite furnace at the El Mirage site. Chromium(III) was calculated as the difference between total dissolved Cr(T), and Cr(VI). The analytical precision for chromium data analyzed using this technique is 0.2 μg/L (Ball and McCleskey, 2003a,b; Izbicki et al., 2008a).

Field parameters (temperature, specific conductivity, pH, dissolved O_2) were measured at each site at the time of collection. Portable meters were used to make measurements of specific conductivity and pH. Portable meters were used to make measurements of dissolved O_2 at the Topock and Hinkley sites and the Indigo-Carmine method was used at the El Mirage site. Samples for determination of a number of dissolved constituents (including major and minor ions, trace elements, and nutrients), and the stable isotopes of O and H were also collected and analyzed, although these samples are not discussed in this paper.

At all three sites, 1 L of filtered, unacidified water was collected for Cr isotope analysis from each well. Chromium isotope samples were immediately chilled on ice and shipped to the USGS laboratory in Menlo Park for processing. Upon receipt, each sample was analyzed for total Cr, Cr(T), using ICP-MS. Sample processing prior to isotopic analysis was initiated by separating the hexavalent, Cr(VI), and trivalent, Cr(III), fractions using ion exchange chromatography (Ellis et al., 2002; Izbicki et al., 2008a) to obtain approximately 500 ng of Cr(VI) for isotopic analysis. The processing steps are described in detail by Bullen (2007) and were intended to ensure the Cr(VI) for isotopic analysis was sufficiently pure to minimize interference from organic compounds and SO_4 in the sample water. Sample processing also included the addition of a mixed ^{50}Cr–^{54}Cr "double spike" solution as an internal standard during mass spectroscopy (Bullen, 2007). The isotopic composition of Cr in groundwater samples and the double spike standard were measured using thermal ionization mass spectrometry (TIMS, Finnigan MAT 261). Data were collected as a series of scans each consisting of two measurements: ^{50}Cr and ^{52}Cr simultaneously for 4 s, then ^{52}Cr, ^{53}Cr and ^{54}Cr simultaneously for 4 s. Blocks of data consisting of 10 scans each, separated by baseline and peak center measurements, were collected over a period ranging from 1 to 2 h. The raw block values for $^{50}Cr/^{52}Cr$, $^{53}Cr/^{52}Cr$ and $^{54}Cr/^{52}Cr$ ratios were entered into a spreadsheet algorithm to mathematically extract the double spike from the measured composition of the mixture (Johnson et al., 2000). Data are reported as $\delta^{53/52}Cr$, the ‰ difference between the $^{53}Cr/^{52}Cr$ ratio measured for the sample and that measured for the NIST979 Cr standard.

Twelve determinations of the $^{53}Cr/^{52}Cr$ ratio of the NIST979 Cr standard over the course of work on the Hinkley samples yielded an average value of 0.113381 with a 2σ precision of 0.11‰. The value compares well with the NIST value for this standard of 0.113392 (Shields et al. 1966). Analyses of 17 duplicate samples from the three sites agreed with a Mean Square Error (MSE) of 0.29‰ (Fig. 5). The MSE of replicate and duplicate samples from this study is only slightly greater than the MSE of replicate analysis of samples from the El Mirage site of 0.17 (Izbicki et al., 2008a).

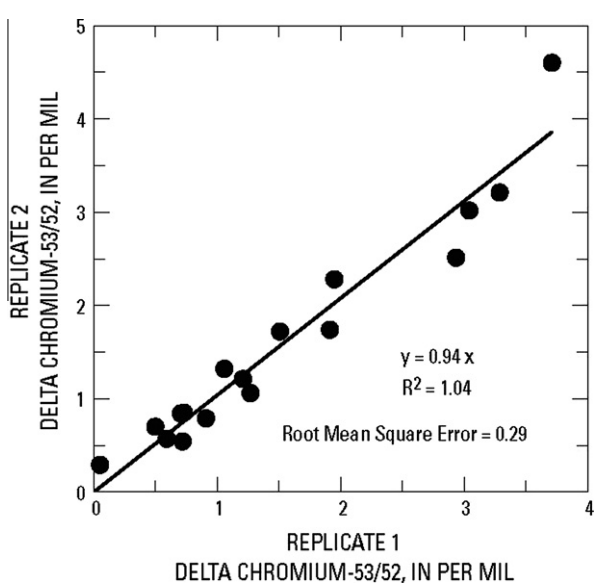

Fig. 5. Comparison of analysis of duplicate samples of delta Cr-53/52 ($\delta^{53/52}Cr$) from selected samples from the Hinkley, Topoc and El Mirage areas of southern California, May 2001–2007.

4. Results

4.1. Hinkley

A total of 13 wells were sampled to determine the $\delta^{53/52}Cr$ composition of water at the Hinkley site, with three wells representative of native water and 10 wells within the contamination plume.

Chromium(VI) concentrations of samples from the three wells representative of native water in the Hinkley area ranged from 0.8 to 3.7 μg/L (Table 1). These concentrations were similar to the average Cr(VI) concentration of 1.4 μg/L in 41 sampled wells sampled to assess background Cr(VI) concentrations near the site (CH2M Hill, Inc., 2007a). The maximum Cr(VI) concentration from these 41 wells was 2.7 μg/L. The $\delta^{53/52}Cr$ composition of water from the three sampled wells considered to be representative of native water ranged from 2.7 to 4.1‰ (Table 1).

Chromium(VI) concentrations in water from the 10 wells sampled within the defined contamination plume (Cr(VI) concentrations greater than 4 μg/L) downgradient from the compressor station ranged from 15.4 to 2660 μg/L (Table 1). Almost all the Cr within the plume is in the form of Cr(VI), with Cr(III) accounting for about 5% of the total dissolved Cr in the sampled water. The $\delta^{53/52}Cr$ compositions of sampled wells within the plume ranged from −0.2 to 1.9‰ (Table 1), with a median composition of 1.2‰.

4.2. Topock

A total of 51 wells were sampled to determine the $\delta^{53/52}Cr$ composition of water at the Topock site, with 23 wells representative of native water, 19 wells in the contamination plume, and eight wells on the margin of the plume.

Chromium(VI) concentrations of samples from the 23 wells representative of native water in the Topock area ranged from 1.2 to 38 μg/L (Table 2), with a median concentration of 15.1 μg/L. These samples included wells from both the California and Arizona side of the Colorado River. The $\delta^{53/52}Cr$ composition of water from those wells ranged from 0 to 3.2‰ (Table 2), with a median composition of 1.5‰.

Chromium(VI) concentrations in water from the 19 wells sampled within the defined contamination plume (Cr(VI) concentrations greater than 32 μg/L) downgradient from the compressor station ranged from 1.1 to 5760 μg/L (Table 2). Almost all the Cr in the plume was in the form of Cr(VI) with Cr(III) accounting for about 3% of the total dissolved Cr in the sampled water. $\delta^{53/52}Cr$ compositions of sampled wells within the plume ranged from −0.2 to 1.5‰ (Table 2) with a median composition of 0.7‰.

The Cr(VI) concentrations in water from the eight wells on the margin of the defined contamination plume ranged from 5.7 to 32.6 μg/L (Table 2). Given the range of Cr(VI) concentrations, these wells were difficult to identify as native or contaminated groundwater. The $\delta^{53/52}Cr$ composition of water from these wells ranged from 0.6 to 4.0‰ (Table 2), with a median composition of 3.4‰L.

4.3. El Mirage

A total of 16 wells were sampled to determine the $\delta^{53/52}Cr$ composition of water at the El Mirage site, with six wells representative of native water, and 10 wells in the contamination plume.

Table 1
Field data, Cr concentrations, and delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic composition of water from selected wells, near Hinkley, Calif., April–October, 2006. [μSiesmens/cm, microSiesmens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; Cr, chromium;Cr(T), dissolved Cr(VI) plus dissolved Cr(III);Cr(VI), the oxidized hexavalent form of chromium; Cr(III), the reduced trivalent form of chromium].

Well number	Date	pH (standard units)	Specific conductance (μS/cm)	Dissolved oxygen (mg/L)	Chromium			Delta Chromium-53/52 (per mil)	Replicate delta Chromium (per mil)
					Cr (T) (μg/L)	Cr (VI) (μg/L)	Cr (III) (μg/L)		
Native groundwater									
BGS-04	04/26/06	8.0	559	6.8	4.3	3.7	0.6	2.7	–
MW-32B1	04/25/06	8.5	782	5.3	3.6	3.3	0.3	2.8	–
MW-53	04/24/06	9.1	459	5.5	1.2	0.8	0.4	4.1	–
Contaminated groundwater									
MW-06	07/27/06	7.0	1687	6.3	106	102	4.8	0.5	0.7
MW-08	04/26/06	7.6	1262	4.4	21.2	20.6	0.6	1.9	–
MW-18	10/24/06	7.0	2254	4.6	54.5	51.1	3.4	0.7	0.9
MW-23B	04/25/06	8.5	1800	7.5	29.7	28.9	0.7	1.4	–
MW-27A	04/24/06	9.6	1797	8.9	20.6	19.5	1.1	1.4	–
MW-28B	04/26/06	7.8	1810	8.3	46.1	44.4	1.8	1.1	–
MW-36	10/24/06	7.3	1027	5.8	142	133	9.5	0.3	–
MW-42B1	04/24/06	8.6	2287	10.4	33.7	32.2	1.6	1.2	1.3
MW-44B	04/24/06	8.3	1170	7.4	17.5	15.4	2.1	1.3	–
PMW-03	04/26/06	7.1	1055	5.8	2780	2660	120	−0.2	–

Chromium(VI) concentrations of samples from the six wells representative of native water from the "perched aquifer" in the El Mirage area ranged from 3.0 to 60 μg/L (Table 3), with a median concentration of 8.5 μg/L. The $\delta^{53/52}$Cr compositions of samples from these wells ranged from 1.7 to 4.6‰, with a median composition of 3.5‰ (Table 3).

Chromium(VI) concentrations in water from 10 wells located onsite at the chemical milling facility were as high as 330 μg/L (Table 3). Almost all the Cr was in the form of Cr(VI), with Cr(III) accounting for about 7% of the total Cr in the sampled water, although as much as 18% of the Cr in water from well EM-19 was in the form of Cr(III) (Table 3). The $\delta^{53/52}$Cr compositions of sampled wells within the plume ranged from −0.1 to 3.3‰ with a median value of 1.4‰ (Table 3).

5. Discussion

Background Cr(VI) concentrations were lowest at the Hinkley site where a concentration of 3.5 μg/L was used to delineate the plume margin (CH2M Hill, Inc., 2007a). These concentrations were independent of pH (Fig. 6), and were consistent with the lower Cr abundance in alluvium eroded from granitic rock (Izbicki et al., 2008a). Low Cr(VI) concentrations in the Hinkley area are also consistent with recent recharge (less than 60 a) of groundwater from the Mojave River (Izbicki and Michel, 2004), and consequently limited contact time (in a geologic sense) between groundwater and alluvial deposits. Low Cr(VI) concentrations were also measured in recently recharged groundwater in alluvial deposits eroded from granitic rock elsewhere along the Mojave River upstream from the Hinkley site (Ball and Izbicki, 2004; Izbicki et al., 2008a).

In contrast, background Cr(VI) concentrations were higher in alluvium eroded from metamorphic, igneous and volcanic rock at the Topock site, and in alluvium eroded, in part, from mafic rock at the El Mirage site (Fig. 6). The background Cr(VI) concentration of 32 μg/L used to delineate the plume margin at the Topock site is consistent with the higher Cr abundance in alluvium eroded from rock at the site, and also with the older age of groundwater (Goldrath et al., 2010), and consequently greater contact time, between groundwater and alluvial deposits.

The higher fraction of Cr(III) at the El Mirage site compared to the Hinkley and Topock sites is interesting given the smaller size of the El Mirage plume and its consequently greater interaction with the native groundwater. Reduction of Cr(VI) to Cr(III) and subsequent fractionation of $\delta^{53/53}$Cr isotopes has been demonstrated to occur in native groundwater at this site (Izbicki et al., 2008a), and may be occurring within the plume. Neither Topock or El Mirage show the positive correlation between pH and Cr(VI) concentrations that was apparent in regional studies of Cr(VI) in the Mojave Desert (Ball and Izbicki, 2004; Izbicki et al., 2008a). This may be because only small parts of the flow system were sampled as part of this study, and processes that occur over larger temporal and spatial scales along groundwater flowpaths were not adequately represented in the data.

Median $\delta^{53/52}$Cr compositions in native groundwater were 2.8‰ at Hinkley, 1.4‰ at Topock, and 3.1‰ at El Mirage (Fig. 7). These values were significantly fractionated with respect to the $\delta^{53/52}$Cr composition of 0‰ for Cr in rock. Higher $\delta^{53/52}$Cr compositions in native water at El Mirage are consistent with the location of the site on the distal portion of the Sheep Creek fan, and the presence of natural reductants within aquifer material near El Mirage (dry) Lake that promote the reduction of Cr(VI) to Cr(III). The $\delta^{53/52}$Cr values near Hinkley indicate that reduction of Cr(VI) to Cr(III) and subsequent isotopic fractionation has occurred in native groundwater at that site, despite the low Cr(VI) concentrations and short contact time between aquifer materials and groundwater. Similarly, positive $\delta^{53/52}$Cr values were measured in recently recharged water from wells having low Cr(VI) concentrations near the mountain front along the San Gabriel Mountains (Izbicki et al., 2008a). These values show that positive $\delta^{53/52}$Cr compositions in groundwater can be established by reactions occurring before large concentrations of Cr(VI) enter solution.

The wide range in $\delta^{53/52}$Cr compositions of native groundwater at the Topock site, from 0 to 3.2‰ (Fig. 7), reflects the complex geologic and geochemical conditions at that site. The near-0 values extend the range of $\delta^{53/52}$Cr compositions in native groundwater beyond the range of 0.7–5.1‰ reported by (Izbicki et al., 2008a). Recent work (Izbicki, 2008; Izbicki et al., 2008b) shows Cr(VI) concentrations in excess of 200 μg/L, having $\delta^{53/52}$Cr compositions near-0‰, in water from the unsaturated zone near El Mirage. This water is unrelated to the contamination site discussed in this paper. These samples had specific conductance as high as 39,200 μS/cm. It is possible that conditions, such as high salinity, may inhibit the bacterially mediated reduction of Cr(VI) to Cr(III), and subsequent fractionation of Cr isotopes. Although some of the near-0 $\delta^{53/52}$Cr values for native groundwater at the Topock site were from waters having a specific conductance as high as 8620 μS/cm, other samples were from wells having specific conductance as low as 522 μS/cm (Table 3). Near-0‰ $\delta^{53/52}$Cr values, make it difficult to use $\delta^{53/52}$Cr compositions independently to establish the extent of Cr contamination at the Topock site.

Table 2
Field data, chromium concentrations, and delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic composition of water from selected wells, near Topock, Calif., May 2006 to July, 2007. [(μSiesmens/cm, microSiesmens per centimeter; mg/L, milligrams per liter; (μg/L, micrograms per liter; Cr, chromium; Cr(T), dissolved Cr(VI) plus dissolved Cr(III);Cr(VI), the oxidized hexavalent form of chromium; Cr(III), the reduced trivalent form of chromium. Replicate analysis in italics].

Well number	Date	pH (standard units)	Specific conductance (μS/cm)	Dissolved oxygen (mg/L)	Chromium			Delta Chromium-53/52 (per mil)	Replicate delta Chromium (per mil)
					Cr (T) (μg/L)	Cr (VI) (μg/L)	Cr (III) (μg/L)		
Native groundwater									
CA Ag. station	05/01/06	6.9	1820	7.2	3.3	2.8	0.5	3.2	–
CW-01M	05/02/06	7.7	6260	2.5	17.1	15.1	2	2.1	–
CW-02M	05/02/06	7.6	6360	2.2	15.7	15.5	0.2	2.6	–
CW-03M	05/02/07	7.7	8620	2.8	11.4	11.4	<1	0.0	1.1
CW-04M	05/01/07	7.5	5720	3.8	21.8	20.8	1	0.4	–
EPNG-2	05/02/07	8.2	971	5.5	9.4	9.6	<1	2.9	2.5
GSRV-2	07/10/07	8.1	600	8.1	25.6	25	0.6	0.9	–
GSWC-2	05/02/07	7.8	808	2.4	3.0	1.5	1.5	1.2	–
GSWC-4	05/02/07	7.7	522	3.6	11.0	10.7	0.3	0.5	–
Langmaack	05/02/07	7.9	519	6.6	18.0	18.1	<1	1.5	–
Lily Hill	05/01/06	7.1	4040	3.9	3.1	2.6	0.5	2.6	–
MW-15	05/04/07	7.6	2060	8.2	21.0	21.1	<1	0.6	–
MW-16	05/03/06	7.3	1570	7.4	9.7	8.2	1.5	1.8	–
MW-17	05/09/06	7.1	1670	5.2	15.8	14.6	1.2	2.5	–
MW-18	05/01/06	7.3	2140	8.2	37.4	37.6	<1	2.7	–
Needles MW-11	05/02/07	7.5	2160	1.1	2.5	2.4	0.1	1.2	–
OW-02S	04/30/07	7.8	1780	8.2	37.4	35	2.4	1.8	–
OW-03M	05/04/06	7.9	6650	2.6	20.0	18	2	0.9	–
OW-03M	*05/01/07*	*8.0*	*5240*	*3.6*	*18.2*	*17.8*	*0.4*	*0.6*	–
OW-03S	04/30/07	7.7	1850	7.8	23.4	20	3.4	1.7	–
OW-05S	04/30/07	7.7	1760	7.7	25.6	24.1	1.5	2.5	–
P-2	05/02/07	7.7	5340	–	2.7	2.5	0.2	0.1	0.3
Tayloe	05/02/07	7.9	848	2.5	1.3	1.2	0.1	1.2	–
TMLP-2	05/03/07	7.9	415	6.2	23.0	20.2	2.8	0.6	0.6
Contaminated groundwater									
MW-09	05/03/07	7.6	2880	7.6	341	286	55	1.2	–
MW-10	05/04/06	7.5	4500	5.0	1780	1610	170	−0.1	–
MW-11	05/03/07	7.6	2100	7.8	337	350	<1	0.7	0.5
MW-19	05/02/06	7.3	2450	3.3	1120	1130	<1	0.6	–
MW-20-070	05/05/06	7.7	3050	7.2	4440	4100	340	−0.1	–
MW-24B	05/04/06	7.6	24,000	2.7	6260	5760	500	−0.2	–
MW-25	05/03/06	7.1	2110	7.7	1300	1390	<1	0.5	–
MW-31-135	05/01/07	7.9	10,600	2.8	47	46	1.3	1.5	–
MW-34-100	05/03/06	7.6	18,200	0.3	877	900	<1	0.9	–
MW-34-100	*04/30/07*	*7.6*	*16,300*	*2.1*	*599*	*626*	*<1*	*0.7*	*0.8*
MW-37D	05/03/06	7.1	33,000	3.2	1880	1970	<1	0.9	–
MW-38D	05/03/07	7.8	21,000	<0.2	70	69	0.7	0.1	–
MW-38S	05/04/06	7.4	5620	3.4	846	812	34	0.0	–
MW-39-060	05/02/06	6.4	12,000	<0.2	1.4	1.1	0.3	1.3	–
MW-39-070	05/02/06	6.3	11,200	<0.2	123	137	<1	1.0	–
MW-40D	05/04/07	7.6	15,300	2.0	80	78	1.6	1.4	–
MW-44-125	05/03/07	7.5	11,700	1.9	309	300	9.0	1.3	1.1
MW-45-095a	05/04/07	7.6	10,100	0.3	140	169	<1	1.2	–
MW-46-175	05/04/07	8.4	16,100	<0.2	114	86	28	0.2	–
MW-47-055	05/04/07	7.6	3990	2.4	32	30	1.3	0.6	–
Margin wells									
MW-13	05/02/06	7.2	1990	4.2	19.2	21.4	<1	4.0	–
MW-14	05/02/06	7.4	1610	3.9	27.6	32.6	<1	3.2	–
MW-33-090	05/03/06	6.8	10,400	0.4	16.4	16.1	0.3	3.6	–
MW-33-210	05/05/06	6.5	20,100	0.4	8.8	10	<1	3.9	–
MW-35-060	05/02/06	7.2	6770	–	26.4	25.7	0.7	2.5	–
MW-35-135	05/02/06	7.4	13,000	2.7	20.7	21	<1	2.8	–
MW-35-135	*05/04/07*	*7.4*	*10,500*	*2.2*	*25.2*	*27.8*	*<1*	*0.9*	*0.8*
MW-37S	05/04/06	7.6	6080	3.5	9.3	8.1	1.2	0.6	–
MW-40S	05/03/06	7.0	3080	8.5	6.7	5.7	1	3.7	–

Median $\delta^{53/52}$Cr compositions within the 3 Cr contamination plumes were 0.6‰ at Hinkley, 0.7‰ at Topock and 1.2‰ at El Mirage. Median $\delta^{53/52}$Cr compositions at all three sites were significantly lower within the contamination plumes than the median $\delta^{53/52}$Cr composition of the surrounding native groundwater (Fig. 7) (on the basis of the Median Test, Neter and Wasserman, 1974, with a confidence criterion of $\alpha = 0.05$). However, there is overlap between range of native $\delta^{53/52}$Cr groundwater compositions and anthropogenic values, especially at the Topock site (Fig. 7). This overlap makes it difficult to use $\delta^{53/52}$Cr compositions to independently delineate the margins of the contamination plumes.

Within all three plumes $\delta^{53/52}$Cr compositions increase with decreasing Cr(VI) concentrations (Fig. 8). However, data at Hinkley and Topock are not consistent with the expected fractionation of Cr isotopes, assuming the laboratory derived fractionation factor of $\varepsilon = 3.5$ (Ellis et al., 2002). The apparent fractionation factor calculated from data at Hinkley is $\varepsilon = 0.3$ (Fig. 8a), and the apparent fractionation at Topock appears bimodal with values ranging from $\varepsilon = 0.4$ to $\varepsilon = 0.1$ (Fig. 8b). Apparent fraction factors that are lower

Table 3
Field data, Cr concentrations, and delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic composition of water from selected wells, near El Mirage, Calif., May 2001 to January 2003. [(μS/cm, microSiesmens per centimeter; mg/L, milligrams per liter; (μg/L, micrograms per liter; Cr, chromium; Cr(T), dissolved Cr(VI) plus dissolved Cr(III); Cr(VI), the oxidized hexavalent form of chromium; Cr(III), the reduced trivalent form of chromium. Replicate analysis in italics.]

Well number	Date	pH (standard units)	Specific conductance (μS/cm)	Dissolved oxygen (mg/L)	Chromium			Delta Chromium-53/52 (per mil)	Replicate delta Chromium (per mil)
					Cr (T) (μg/L)	Cr (VI) (μg/L)	Cr (III) (μg/L)		
Native groundwater									
6N/7W-24D1	06/03/02	7.8	531	–	9.3	8.3	1.0	4.6	
6N/7W-24E2	06/06/02	7.7	554	–	22.4	22.1	0.3	1.9	1.7
6N/7W-25M2	05/18/01	8.0	1520	6.1	–	55	–	2.0	2.3
6N/7W-25M2	*06/05/02*	*8.0*	*1520*	*6.1*	*59.6*	*60.5*	*<0.1*	*2.3*	–
6N/7W-26J2	06/05/02	8.3	702	1.2	3.9	2.7	1.2	5.1	–
6N/7W-27B8	01/23/03	8.6	513	12.2	8.9	8.6	0.3	3.1	–
6N/7W-29N2	06/03/02	7.5	513	<0.2	4.0	3.0	1.1	4.0	–
Contaminated groundwater									
EM-1	06/04/02	8.4	812	–	14.5	13.7	0.8	3.3	3.2
EM-3	06/03/02	8.4	562	–	21.0	20.2	0.8	3.0	3.0
EM-13	06/05/02	7.4	4850	7.3	330	310	20.0	0.5	–
EM-16	06/05/02	7.5	3350	2.9	34.8	30.8	4.0	−0.1	–
EM-17	06/03/02	7.5	6070	6.5	34.5	30.9	3.6	1.1	–
EM-19	06/04/02	7.4	3440	5.5	130	107	23	1.9	–
EM-23	06/04/02	7.5	4920	–	31.2	28.8	2.4	1.1	1.3
EM-M2	06/05/02	7.7	2380	5.1	38.6	37.4	<0.1	1.5	1.7
EM-M4	06/05/02	7.1	5180	4.5	60.8	56.8	4.0	1.2	–
EM-P1	06/03/02	7.4	6180	4.9	44.5	44.0	0.5	2.0	–

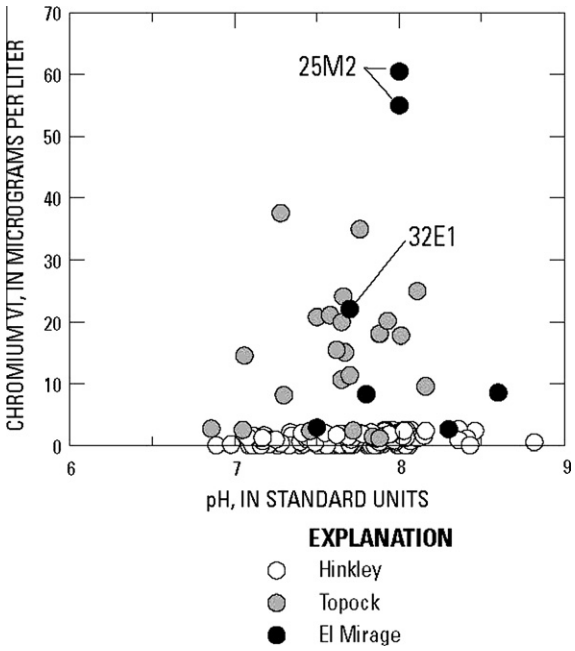

Fig. 6. Cr (VI) as a function of pH in native groundwater near contamination plumes at Hinkley (2006), Topock (2006–2007), and El Mirage (2001–2003), Calif. [Cr(VI) data at the Hikley site are from CH2M Hill, Inc., 2007a].

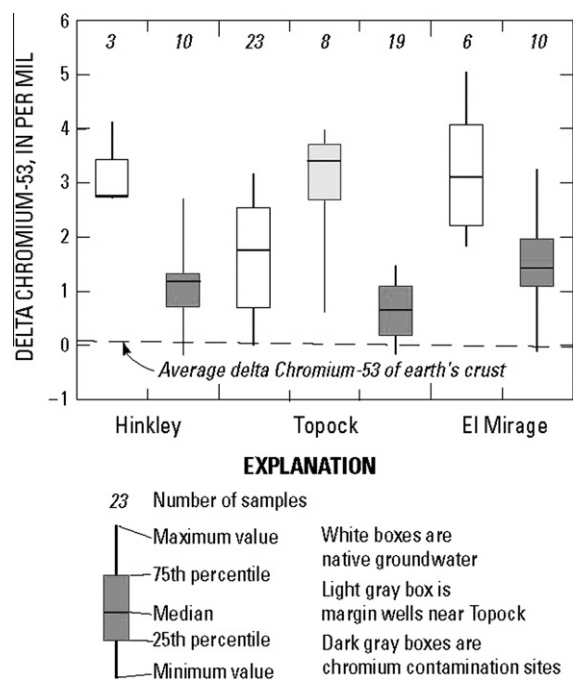

Fig. 7. Delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic compositions in native and contaminated groundwater near Hinkley (2006), Topock (2006–2007), and El Mirage (2001–2003), Calif.

than laboratory derived values also have been reported for Cr contamination plumes at other sites (Berna et al., 2009). Izbicki et al. (2008a) were able to match field data to a laboratory derived fractionation factor, $\varepsilon = 3.5$, by assuming a range of initial contaminant concentrations represented by water from two wells (EM-13 and EM-16) having near-zero $\delta^{53/52}$Cr compositions but greatly different Cr(VI) concentrations (Fig. 8c).

Variations in contaminant source concentrations cannot be invoked to explain data at either the Hinkley or Topock sites given the large volumes and consistent Cr(VI) releases from these facilities. Similarly, simple advective mixing of water within the plume and native groundwater (well BGS-04 at Hinkley, and wells GSWC-2 and MW-18 at Topock) does not adequately explain measured Cr(VI) concentrations and $\delta^{53/52}$Cr compositions at Hinkley (Fig. 9a) or at Topock (Fig. 10a). The position of the data above the mixing lines in Figs. 9a and 10a shows reduction of Cr(VI) to Cr(III) has occurred in addition to mixing at both sites.

A combination of reductive fractionation and advective mixing with native groundwater coupled with subsequent mixing with unfractionated water within the plume was invoked by Bullen (2007) to explain observed Cr(VI) concentrations and $\delta^{53/52}$Cr compositions at the Hinkley site (Fig. 9b). This is similar to the process

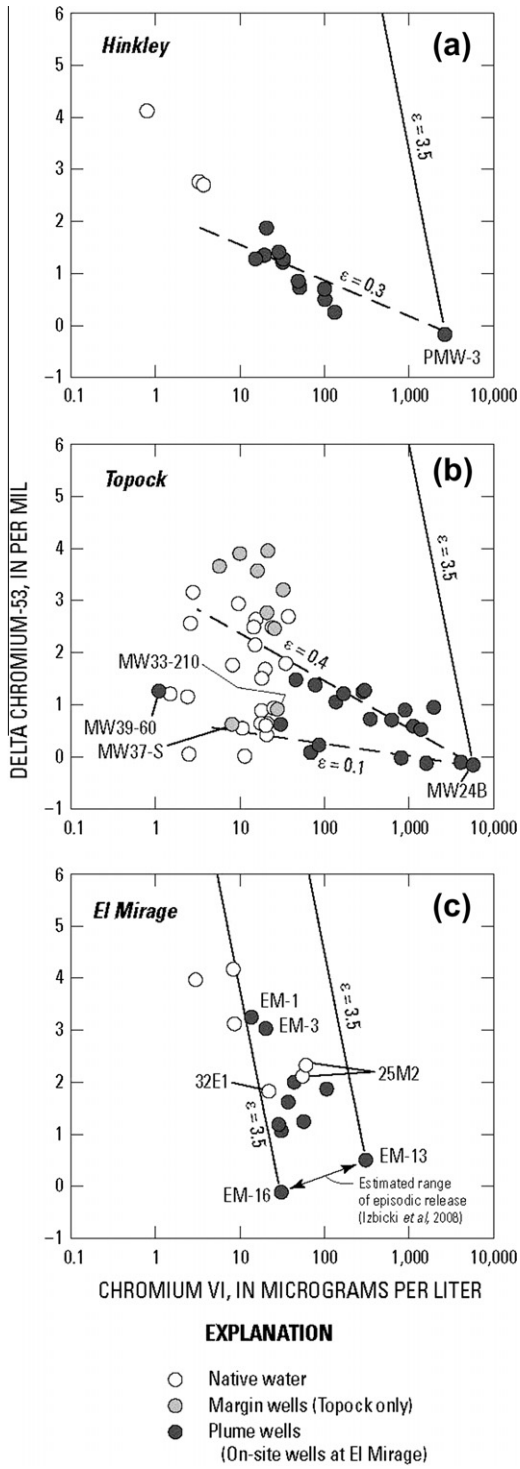

Fig. 8. Delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic compositions as a function of Cr(VI) concentrations with apparent fractionation factors in contaminated groundwater near Hinkley (2006), Topock (2006–2007), and El Mirage (2001–2003), Calif.

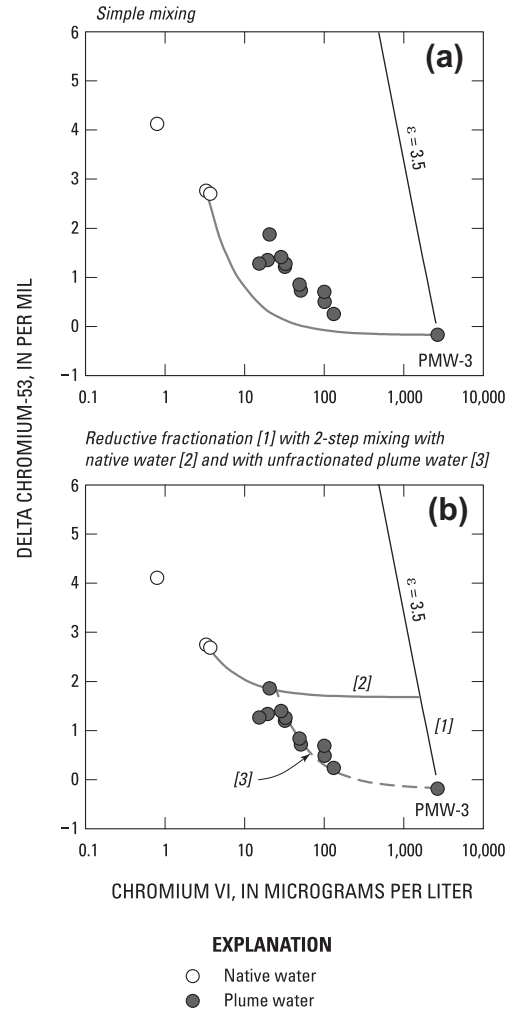

Fig. 9. Delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic compositions as a function of Cr(VI) concentrations with examples of fractionation and mixing between native and contaminated groundwater near Hinkley, Calif., 2006.

described by Berna et al. (2009). The process involves reduction of Cr(VI) as the plume initially moved through aquifer deposits and encountered natural reductants (step 1, Figs. 9b and 10b). These natural reductants consist primarily of organic material within the aquifer deposits. Although abundant at the site studied by Berna et al. (2009), their abundance in alluvium in arid areas such as the Mojave Desert is limited. In these settings, available reductants are rapidly consumed in the leading edge of the plume by Cr(VI), a strong oxidant, and Cr(VI) in the core of the plume passing through these deposits later is not reduced. Near the plume margin, the initial water with reduced Cr(VI) mixes with native groundwater (step 2, Figs. 9b and 10b). The chemical and isotopic composition of this mixed water is subsequently altered by mixing with Cr in water in the core of the plume (step 3, Figs. 9b and 10b). This combination of processes can create a wide range of chemical and isotopic compositions depending on the extent of reduction, mixing with native water, and mixing with unreduced plume water as indicated by data and the bimodal distribution of ε_{app} from the Topock site (Fig. 10b).

Sample collection from the eight wells near the margin of the Topock plume revealed Cr(VI) concentrations ranging from 5.7 to 33 μg/L, with $\delta^{53/52}$Cr compositions ranging from 0.6 to 4.0‰ (Fig. 11). The source of the Cr(VI) in these wells was of special interest given their proximity to the plume, and because the Cr(VI) concentrations in water from some of these wells approached the 32 μg/L threshold used to define the plume margin. The range in $\delta^{53/52}$Cr compositions for the margin wells is large, with some values more positive than compositions for native groundwater sampled at the site (Fig. 7). In addition, the $\delta^{53/52}$Cr compositions from two of the margin wells were less than 1‰ and have $\delta^{53/52}$Cr compositions similar to the composition of anthropogenic Cr within the plume (Fig. 11). The combination of reductive fractionation, mixing

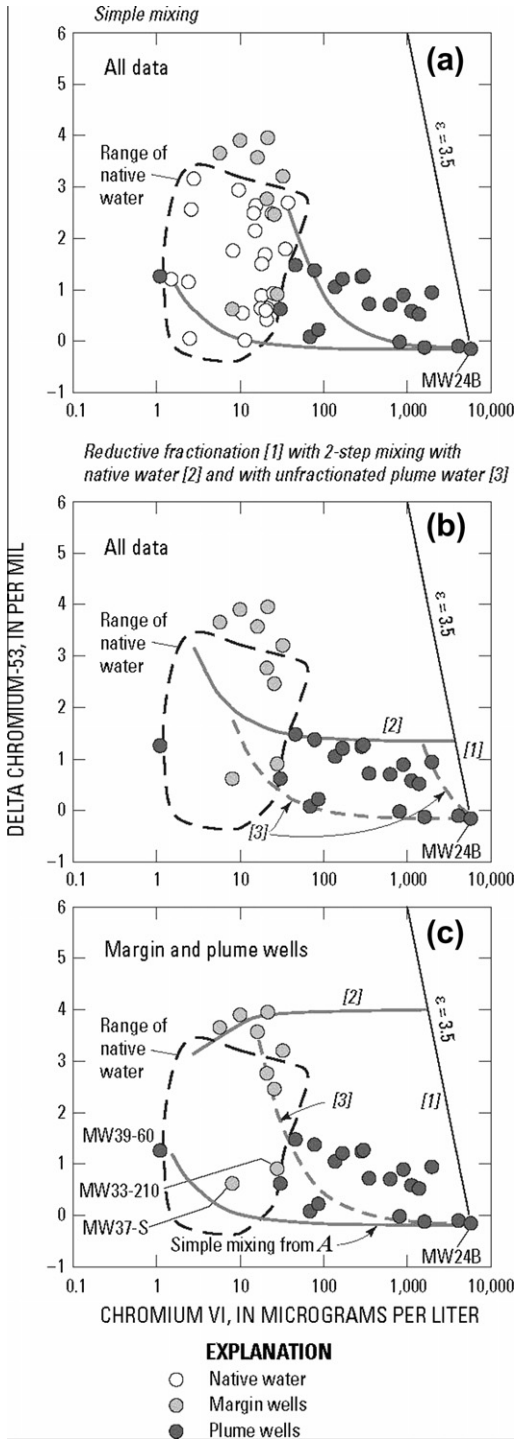

Fig. 10. Delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic compositions as a function of Cr(VI) concentrations with examples of fractionation and mixing between native and contaminated groundwater near Topock, Calif., 2006–2007.

with native water, and mixing with unreduced water within the plume provides an adequate fit to the observed data at the Topock site (Fig. 10c) with water from only one well, MW-37S, failing to plot on the calculated lines. Collectively, the margin wells appear to describe the maximum historical extent of the contaminant plume. The extent of the plume identified on the basis of $\delta^{53/52}$Cr data from the margin wells was used to constrain hydraulic properties used as inputs to a groundwater flow and transport model of the site (CH2M Hill, Inc., 2008).

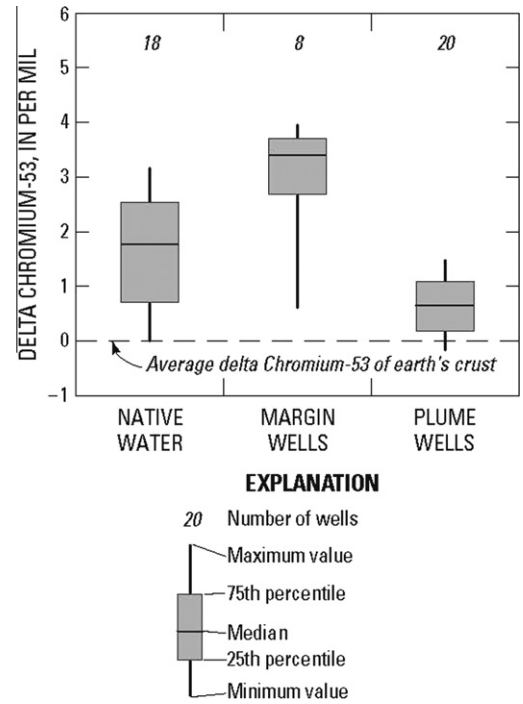

Fig. 11. Delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic compositions in native, margin, and plume wells, near Topock, Calif., 2006–2007.

In contrast to the other margin wells, well MW-37S is near Bat Cave Wash, the largest ephemeral stream at the Topock site (Fig. 10c). Although this well is within the defined plume, it is shallow and located beneath the wash. Since the end of Cr(VI) discharges to this wash in 1964, intermittent flow in the wash has recharged the aquifer with water having low Cr(VI) concentrations. Infiltration of intermittent, uncontaminated streamflow from Bat Cave Wash would explain the combination of low Cr(VI) and low $\delta^{53/53}$Cr compositions. A deeper well at this location, MW-37D, has elevated Cr(VI) concentrations and near-0‰ $\delta^{53/52}$Cr values consistent with plume water.

6. Conclusions

Background Cr(VI) concentrations at the Hinkley, Topock and El Mirge sites differed with local geologic conditions (Table 4). Chromium(VI) concentrations were lower in alluvial aquifers eroded from granitic rock containing recently recharged groundwater near the Hinkley site. Chromium(VI) concentrations were higher in alluvial aquifers eroded from mafic (El Mirage) and metamorphic (Topock) rock, especially where those aquifers contained older groundwater. Positive $\delta^{53/52}$Cr values for native groundwater suggest that reduction of Cr(VI) to Cr(III) occurs in the presence of the small amounts of natural reductants and that the $\delta^{53/52}$Cr isotopic composition is established before large amounts of Cr enter solution. However, natural water from a few wells at the Topock site had $\delta^{53/52}$Cr values near-0‰. This overlap in natural and anthropogenic $\delta^{53/52}$Cr values in groundwater makes it difficult to use $\delta^{53/52}$Cr compositions to independently delineate the margins of the contamination plumes.

Three types of processes occurring near the plume margin were identified: (1) reduction of Cr(VI) in the leading edge of the contamination plume by naturally occurring reductants within aquifer deposits, producing increasingly positive $\delta^{53/52}$Cr values, (2) mixing of reduced plume and non-plume groundwater, and (3) subsequent mixing of this water with water in the core of the plume

Table 4
Median delta Cr-53/52 ($\delta^{53/52}$Cr) isotopic composition of native and contaminated groundwater, apparent epsilon (ε_{app}), and hydrologic setting of study Cr(VI) contamination plumes near Hinkley (2006), Topock (2006–2007), and El Mirage (2001–2003), western Mojave Desert, Calif. [Includes data from a plume in Berkeley, Ca (northern California, near San Francisco) Berna et al., 2009.]

Site	Median $\delta^{53/52}$Cr, in per mil			Hydrologic setting
	Native water	Contaminated water	Apparent epsilon (ε_{app})	
Increasing ε_{app}, reductive fractionation dominates				
El Mirage	3.1	1.2	3.5	Alluvium eroded, in part, from mafic rock. Older, alkaline groundwater having regionally reducing conditions. Plume size ±100's of meters, reduction of Cr(VI) to Cr(III) occurring within plume
Berkeley (2006 data from Berna et al., 2009)	–	1.9	1.4	Alluvium eroded from consolidated marine, metamorphic, and volcanic rock. Heterogeneous distribution of reductants within aquifer deposits. Plume size 100's of meters, reduction of Cr(VI) to Cr(III) occurring within plume, areal extent of plume stable and not advancing
Decreasing ε_{app}, advective mixing dominates				
Topock	1.4	0.7	0.1–0.4	Alluvium eroded from metamorphic, igneous, and volcanic rock. Older, alkaline groundwater, regionally oxic conditions within alluvial fan deposits and, dispersed plume margins. Plume size ±1 km. Rapid reduction of Cr(VI) to Cr(III) in anoxic fluvial deposits along Colorado River (ε_{app} in fluvial deposits not characterized)
Hinkley	2.8	0.6	0.3	Alluvium eroded from granitic rock. Younger, near-neutral pH groundwater, regionally oxic conditions. Plume size ±3–4 km, dispersed plume margins

having unreduced Cr(VI) as the plume moved downgradient. The combination of these processes can produce a wide range of Cr(VI) concentrations and $\delta^{53/52}$Cr compositions, and differences in the apparent fractionation factors, ε_{app}, at each study site.

Apparent fractionation factors for the reduction of Cr(VI) to Cr(III) at the Hinkley and Topock sites, ε_{app} = 0.3–0.4, were lower than laboratory derived fractionation factors, ε = 3.4–4.5 (Ellis et al., 2002; Kitcher et al., 2004; Sikora et al., 2008), and lower than apparent fractionation factors estimated from Cr contamination plumes in reducing aquifers, ε_{app} = 1.7 (Berna et al., 2009). The lower fractionation factors may result from the decreased importance of reductive fractionation and increased importance of advective mixing with native groundwater having naturally occurring Cr(VI) in oxic aquifers (Table 4). In contrast to the Hinkley and Topock sites, reduction of Cr(VI) to Cr(III) appears to dominate advective mixing at the El Mirage site located within a more reducing hydrologeologic setting (Izbicki et al., 2008a). High $\delta^{53/52}$Cr values near the plume margin at the Topock site may have resulted from greater reduction of Cr(VI) as the plume first encountered natural reductants within aquifer materials. As plume migration continued and natural reductants were oxidized by Cr(VI) within the contaminant plume, advective mixing may have increasingly dominated and controlled Cr concentrations and isotopic compositions.

On the basis of data from these three sites, differences in apparent fractionation factors between Cr contamination plumes may provide a useful tool for characterization of reductive and mixing processes occurring within and near the margins of Cr contamination plumes in different hydrogeologic settings. The relative importance of mixing increases as the ε_{app} decreases and the importance of reduction of Cr(VI) to Cr(III) increases as ε_{app} approaches laboratory derived values. The magnitude of ε_{app} is likely a function of both the availability of natural reductants within the aquifer deposits, and the magnitude of the release (size of the plume).

Knowledge of the interaction between reductive and mixing processes that control Cr concentrations within and near the margins of contamination plumes can lead to management opportunities to control contaminant concentrations and facilitate clean-up at Cr contamination sites. For example, smaller contamination plumes in reducing environments such as those at El Mirage and described by Berna et al. (2009) may be suitable for Monitored Natural Attenuation (MNA) (Palmer and Puls, 1994); whereas, larger contaminant plumes such as those at Topock can overwhelm naturally occurring reductants and assume characteristics of plumes in more oxic aquifers having fewer natural reductants, such as Hinkley. Plumes having lower apparent fraction factors are likely to have highly dispersed margins that are difficult to define without detailed sample collection and monitoring near the plume margins, and more aggressive management than MNA may be needed to control plume migration.

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