Alpha-emitting isotopes and chromium in a coastal California aquifer

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A B S T R A C T

The unadjusted 72-h gross alpha activities in water from two wells completed in marine and alluvial deposits in a coastal southern California aquifer 40 km north of San Diego were 15 and 25 picoCuries per liter (pCi/L). Although activities were below the Maximum Contaminant Level (MCL) of 15 pCi/L when adjusted for uranium activity; there is concern that new wells in the area may exceed MCLs, or that future regulations may limit water use from the wells. Coupled well-bore flow and depth-dependent water-quality data collected from the wells in 2011 (with analyses for isotopes within the uranium, actinium, and thorium decay-chains) show gross alpha activity in marine deposits is associated with decay of naturally-occurring 238U and its daughter 234U. Radon activities in marine deposits were as high as 2230 pCi/L. In contrast, gross alpha activities in overlying alluvium within the Piedra de Lumbre watershed, eroded from the nearby San Onofre Hills, were associated with decay of 232Th, including its daughter 228Ra. Radon activities in alluvium from Piedra de Lumbre of 450 pCi/L were lower than in marine deposits. Chromium VI concentrations in marine deposits were less than the California MCL of 10 µg/L (effective July 1, 2014) but δ53Cr compositions were near zero and within reported ranges for anthropogenic chromium. Alluvial deposits from the nearby Las Flores watershed, which drains a larger area having diverse geology, has low alpha activities and chromium as a result of geologic and geochemical conditions and may be more promising for future water-supply development.

1. Introduction

Selected radionuclide activities and chromium concentrations are elevated in some wells in marine and alluvial deposits in a coastal California aquifer. Radiation may be contributed to water from naturally-occurring isotopes within the uranium, actinium, and thorium decay chains (Fig. 1). Gross alpha and gross beta measurements, intended as screening tools for rapid quantification of radioactivity in water, are sensitive to the combined activity of a number of isotopes. However, these methods do not measure (1) volatile isotopes such as radon, and (2) gross beta measurements can be affected by ingrowth of radioactive progeny between sample collection and analyses (Thomas et al., 1993). Radon-222 (222Rn), an alpha-emitter within the uranium decay-chain, poses the largest risk to human health of naturally-occurring radionuclides (National Research Council, 1999), but other naturally-occurring radioactive isotopes such as uranium, and radium also have Maximum Contaminant Levels (MCL’s) for drinking water established by the U.S. Environmental Protection Agency (http://water.epa.gov/drink/contaminants#List, accessed December 3, 2013). Understanding the chemistry and distribution of isotopes within the uranium, actinium, and thorium decay-chains allows increased understanding of the sources of radiation in water from wells, and facilitates planning future water supply development and management practices intended to limit these constituents in wells.

1.1. Uranium, other radionuclides, and chromium occurrence in groundwater

Uranium is soluble in oxic groundwater and insoluble in reduced groundwater (Rai and Zachara, 1984; Szabo and Zapecka, 1991). In the absence of complexing ions, uranium in oxic groundwater is present in the +6 valance as the uranyl (UO₂²⁺) ion. In this form, the solubility of uranium is limited by sorption to iron coatings on mineral grains, clay mineral-edge structures, and organic material (Langmuir, 1978). Uranyl complexes with fluoride, phosphate, or most commonly with inorganic carbon (carbonate) enhance uranium solubility (Langmuir, 1978; Hsi and Langmuir, 1978).
There are two naturally-occurring primordial isotopes of uranium, uranium-238 (238U) and uranium-235 (235U), and a naturally-occurring radiogenic isotope uranium-234 (234U), formed as part of the uranium decay series (Fig. 1). The half-lives of these isotopes are long: 4.47 × 10^9, 7.04 × 10^8, and 2.45 × 10^5 years, respectively (Osmond and Cowart, 2000). 235U, the most abundant isotope, composes about 99.275% of crustal uranium; 238U, the fissionable form used in reactors and nuclear weapons, composes about 0.72% of the crustal uranium; while 234U, a daughter of 235U decay, composes only about 0.005% of the crustal abundance. Uranium isotope abundance is measured as an activity in picoCuries per liter (pCi/L). Despite the difference in crustal abundance, the activity ratio (AR) of 235U and 234U in sediments is commonly near 1 as a result of secular equilibrium, a steady-state condition where the rate of production of a shorter-lived daughter isotope equals the rate of decay of the longer-lived parent isotope. Departures from this ratio result from a combination of alpha-recoil and specific geochemical conditions within aquifers. Activity ratios characteristic of groundwater from different settings can be used to evaluate geochemical reactions and the hydrologic history of groundwater (Osmond and Cowart, 1976 and Osmond and Cowart, 2000).

Radium is soluble in acidic, anoxic, chloride-rich groundwater with elevated total dissolved solids (Tanner, 1964; Dickson, 1985; Szabo and Zapecza, 1991). There are four naturally-occurring radium isotopes. Radium-226 (226Ra), within the uranium decay-chain (Fig. 1), is the longest lived radium isotope having a half-life of about 1,600 years. Radium-223 (223Ra), within the actinium (235U) decay-chain (Fig. 1b), has a half-life of 11.4 days. Radium-228 and radium-224 (228Ra and 224Ra, respectively) within the thorium decay-chain have half-lives of 5.7 years and 3.6 days, respectively. 228Ra is a beta-emitter and does not contribute to gross alpha activity. However, the MCL for combined activity of 228Ra and 226Ra is 5 pCi/L. Consistent with the low abundance of its parent isotope, 223Ra activity is usually much lower than the activity of the other radium isotopes.

Radon is a noble gas and, although soluble, radon is otherwise non-reactive in groundwater (Szabo and Zapecza, 1991). As previously discussed, of the naturally-occurring radionuclides, radon poses the largest risk to human health (National Research Council, 1999). 222Rn is part of the uranium decay-chain that includes 235U, 238U and 226Ra (Fig. 1). 222Rn is produced directly by alpha decay of 226Ra and has a half-life of 3.8 days. Radium is insoluble and radon in solution is released from the solid phase as a result of direct recoil during alpha decay, and to a lesser extent by indirect recoil and subsequent diffusion (Cecil and Green, 2000). Because of its relatively short half-life, 222Rn is reflective of geo-logic conditions near the sample collection location, and 222Rn activities can differ greatly over short distances even within the same geologic unit (Cecil and Green, 2000). Radon-219 and radon-220, produced as part of the actinide and thorium decay chains, have half-lives of 4 and 56 s, respectively—too short for most hydrologic applications (Cecil and Green, 2000).

Chromium and uranium have similar aquatic chemistry, in that both elements are present in the +6 valance, soluble under alkaline,oxic conditions, and insoluble under reduced conditions (Rai and Zachara, 1984). In that in alkaline, oxic groundwater chromium is present as the oxyanion form, CrO_4^{2-}, while uranium is present as the uranyl ion, or as uranyl complexes with either fluoride, phosphate, or most commonly with carbonate ions (Langmuir, 1978; Hsi and Langmuir, 1985; and Jurgens et al., 2009). Chromium is higher in mafic rocks and uranium is higher in granitic rock (Reimann and de Caritat, 1998). Although these trace elements are not commonly associated with the same geologic source materials or hydrologic processes, co-occurrence of chromium and uranium has been observed in unconsolidated sand and gravel.

Fig. 1. Decay series for (a) Radon (Uranium-238), (b) actinium (Uranium-235) and (c) thorium (Note: isotopes measured as part of this study are shown in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

1985; and Jurgens et al., 2009) and the presence of calcium can enhance desorption of uranyl-carbonate complexes from aquifer material (Fox et al., 2006).
1.2. Hydrogeology

The study area is in the lower part of the Las Pulgas Watershed at MCB Camp Pendleton, California, about 40 km north of San Diego (Fig. 2). The climate is Mediterranean with annual temperatures averaging 18 °C, and average annual precipitation of about 330 mm falling mostly during the October–March rainy season (California Regional Water Quality Control Board, 1994).

The Las Pulgas Watershed covers an area of about 78 km², and is composed of two sub-watersheds, the Las Flores and Piedra de Lumbre (Fig. 2), named for the streams that drain the areas. The area is underlain by marine deposits including the Santiago, San Onofre Breccia, Monterey, and San Mateo Formations (California Department of Conservation, Division of Mines and Geology, 2007). The San Onofre Breccia is composed of clasts of metamorphic rocks of blueschist and greenschist, including serpentinite, actinolite, fuchsite (chrome mica), and glaucophane clasts, within a well lithified mudstone matrix. Clasts and mudstone matrix composing the San Onofre Breccia are potential sources of chromium. The Santiago, San Onofre Breccia, and Monterey Formations are generally consolidated and not pumped for water supply. The San Mateo Formation is pumped for water supply. Recent marine terrace deposits along the coast (older paralic deposits in Fig. 2) are generally above the regional water table.

Uplift of the San Onofre Hills during the Pleistocene left a series of marine terrace platforms, which have been incised by valleys on

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**Fig. 2.** Location of study area and surficial geology within the Las Flores and Piedra de Lumbre Watersheds, southern California. (See above-mentioned references for further information).
the west slope and partly back-filled by alluvium (Edwards et al., 2009). The higher altitudes of the San Onofre Hills in the upper part of the Piedra de Lumbre watershed are composed of southwestern-dipping sedimentary rock derived from plutonic and metavolcanic rocks of the Peninsular Ranges batholiths (Crandall et al., 2010). Las Flores Creek cut a narrow canyon through the San Onofre Hills to drain lower altitude granitic bedrock to the east. Air-borne gamma-ray spectrometry surveys (Duval et al., 2005) show comparatively uniform uranium concentrations of about 2 ppm (ppm) throughout the area. In contrast, thorium concentrations range from about 9 ppm in the higher altitudes of the San Onofre Hills to about 4 ppm along the coast and interior areas to the east. Although the depth of penetration of these surveys is limited to the near-surface soil horizon (Pitkin, 1968), the results reflect underlying geology.

Recent and older alluvial deposits within the Piedra de Lumbre watershed were eroded from local marine deposits and sedimentary and metavolcanic rocks of the San Onofre Hills; whereas, alluvium within the Las Flores drainage has a more diverse geologic source that includes lower altitude granitic bedrock east of the San Onofre Hills. Land in both watersheds is generally undeveloped. However, small areas of residential development (military barracks) are present with the Las Flores watershed, and small areas formerly used for disposal of unknown materials are present in other areas on the base.

The main aquifers pumped for water supply are the alluvial deposits along Las Flores and Piedra de Lumbre creeks and the underlying San Mateo Formation. About 277 acre-feet are pumped annually (Daniel Bartu, written commun., 2014) to supply approximately 8900 personnel (Jessica Spurlock, written commun., 2014). Alluvial deposits along Las Flores creek are about 60 m thick, whereas deposits along Piedra de Lumbre creek are thinner, about 50 m thick. The San Mateo Formation within the study area is 30 m thick, but can exceed 400 m in other parts of MCB Camp Pendleton (Palmer, 1990).

3. Purpose and scope

The purpose of this study was to evaluate the occurrence andpotential sources of alpha radiation, uranium and associated radio-nuclides, and chromium in existing 41 Area supply wells on MCB Camp Pendleton in southern California to determine possible limitations on future water supply development in the area. This analysis contributes to the discussion of radionuclide occurrences in groundwater and drinking water in coastal aquifers. Although a regional study, it is applicable on an international scale.

The scope of the study included coupled well-bore flow and depth-dependent sample collection to determine the quantity and quality of water entering supply wells from different depths within the aquifer. Details about this method and the equipment used for the sampling are described in Izbicki et al. (2014). Depth-dependent samples were analyzed for chemical and isotopic constituents including 72-h and 30-day gross alpha and gross beta activities, uranium (total of all isotopes) and $^{238}$U, $^{235}$U, $^{234}$U activities; $^{226}$Rn and $^{228}$Ra activities within the uranium decay series; $^{223}$Ra activity within the actinium decay series; and $^{228}$Ra and $^{224}$Ra activities within the thorium decay series also were measured. In addition, chromium and Cr VI concentrations, and $^{60}$Cr composition of Cr VI were measured.

2. Methods

2.1. Field methods

Natural gamma, caliper, fluid resistivity, and fluid temperature and well-bore flow logs were collected from wells 410621 and 41611 (California State well numbers 10S/5W-18E3 and 10S/5W-18M3, respectively) within the Piedra de Lumbre watershed at MCB Camp Pendleton. To permit access, production pumps were removed from these wells prior to collection of log data. Natural gamma and caliper logs were collected from these wells under unpumped conditions to provide geologic information and to confirm well-construction data. Fluid resistivity, fluid temperature, and well-bore flow logs were collected under unpumped and pumped conditions to provide information on water quality and well yield with depth in the wells. It was not possible to remove the production pump from well 410613 (10S/5W-18M5) within the Las Flores watershed; as a consequence, geophysical logs, flow data, and depth-dependent water-quality samples were not collected from this well. However, water-quality data from the surface discharge of this well were collected.

Well-bore flow data were collected using an electromagnetic (EM) flowmeter (Paillet, 2000). The EM flowmeter measures flow, in accordance with Faraday’s Law, as the voltage generated by an electrical conductor (water) passing through an electromagnetic field inside a hollow, cylindrical section surrounded by electromagnetic within the flowmeter (Young and Pearson, 1995; Paillet, 2000). The EM flowmeter has no moving parts and a large dynamic range that can measure velocities ranging from <0.1 to 82 m/min (Newhouse et al., 2005). Pumped and unpumped well-bore flow data were collected in the downward direction at three trolling speeds, approximately 1.5, 3, 4.5 m/min (5, 10, and 15 ft/min) within each well. A temporary submersible pump, having a capacity of 6.3 liters per second (100 gallons per minute), was installed above the uppermost well screen for data collection under pumping conditions. Discharge from the temporary pumps measured at the surface using a sonic flowmeter was within 6% of discharge measured within the well using the EM flowmeter. Centralizers were used, but diverters (that would have interfered with passage of the EM tool around the temporary pumps) were not used. Field calibration of unpumped and pumped flow data is described in supporting information provided with the on-line version of this manuscript.

Depth-dependent water-quality samples were collected while water was pumped from the well using the temporary pump installed previously for pumped well-bore flow-log data collection. Sample depths within each well were determined on the basis of unpumped and pumped geophysical log data collected prior to sample collection. To obtain the large volumes of water required for radium isotopic analyses (200 L), samples were collected from a 5-cm diameter PVC pipe inside the well. The bottom (open end) of the PVC pipe was placed at the intended sample depth, and water was pumped from the pipe at land surface using a 4-cm diameter, positive-displacement sample pump. Samples were collected after three casing volumes were pumped from the pipe and field parameters (temperature, pH, and specific conductance) stabilized. After sample collection, the bottom of the pipe was moved to the next sample depth, and sample collection was repeated until all depth-dependent samples were collected from within the well. In addition, composite samples were collected from the surface discharge of the temporary pump during depth-dependent sample collection after three casing volumes were pumped from the well and field parameters stabilized. Field parameters (pH, specific conductance, and temperature) were monitored using portable meters and thermometers from the discharge of the temporary pump and the sample pump within the PVC pipe throughout depth-dependent sample collection.

The water quality and isotopic activity of water entering the well between sample depths was calculated on the basis of measured changes in flow (Q) and concentration (C) according to the following equation (Izbicki et al., 1999; and Izbicki, 2004):
C_a = [C_{Q_i} - C_i; (Q_{i+1})]/Q_a

Subscripts in the equations refer to sample depth; depth "i" is the first (top) sample/flow depth "i + 1" is the second sample/flow depth "a" is the interval (difference) between "i" and "i + 1". Q_a is calculated from measured flow data as:

Q_a = Q_i - Q_{i+1}

The mixture of two water sources with different δ^{53}Cr compositions follows a non-linear trend and can be calculated (Izbicki et al., 2008a) according to the following:

C_a = ((Q_i/ Q_a) + C_i + δ^{53}Cr_i + ((1 - (Q_i + 1/ Q_a))) + C_{i+1}

* δ^{53}Cr_{i+1}])/(C_i + (Q_i/ Q_a) - C_i + 1 - (Q_i - Q_{i+1})]

In addition to the depth-dependent samples, a composite water-quality sample was collected from well 410613 [105/5W-18M5].

After field parameters stabilized, dissolved oxygen was measured using the indigo-carmine method (CHEMetrics, Inc., Calverton, VA), and alkalinity was measured by titration with 0.016 N HCl on water filtered through 0.45 μm pore-sized filter. Water samples for selected anions, cations, uranium isotopes, and nutrients were filtered in the field though 0.45 μm pore-sized filters, placed in plastic bottles and chilled. Samples for analysis of stable oxygen and hydrogen isotope ratios, gross alpha, and gross beta were unfiltered and placed in glass bottles. Samples for cation analysis and uranium isotopes were preserved in the field using nitric acid. Samples for total Cr and Cr VI were field filtered through 0.45 μm pore-sized filters. Samples for Cr VI were speciated in the field using cation exchange resins to remove Cr III (Ball and McCleskey, 2003), preserved, and analyzed in the laboratory for total Cr. All chromium was presumed to be in the form of Cr VI in the field. Cr III was determined by difference from total Cr and field speciated Cr VI data. Samples for δ^{53}Cr were filtered, placed in 1-L containers, and shipped to the U.S. Geological Survey laboratory in Menlo Park for analyses.

Samples for ²²²Rn were collected by extracting exactly 10 ml of water from an overflow cup using a gas-tight syringe; the extracted water was then injected into glass scintillation vials pre-filled with 10 ml high-efficiency mineral oil (Smith and Swarzenski, 2012). Samples for radium isotopes were collected on a cation exchange chromatography (Ellis et al., 2002; Izbicki et al., 2008a and Izbicki et al., 2008b) to yield approximately 500 nanograms of Cr for analysis (Bullen, 2007), and minimize interference from organic compounds and SO₄ in the sample water. Sample processing also included the addition of a mixed ⁵⁰Cr–⁵⁴Cr “double spike” solution as an internal standard during analyses of the sample water (Bullen, 2007). Data are reported as δ^{53}Cr, the per mil difference between the ⁵³Cr/⁵²Cr ratio measured for the sample and that measured for the NIST979 Cr standard. Two samples were not analyzed. It was not possible to analyze all samples for δ^{53}Cr composition because of low chromium concentrations (<2 μg/L) in 2 samples and interference in the purification of chromium prior to isotopic analyses.

Not all data are discussed in this paper; however, data are available on-line from the U.S. Geological Survey’s computerized database National Water Information System (NWIS) at http://water-data.usgs.gov/nwis.

3. Results

3.1. Well-bore flow data

Well 410621, drilled to a depth of 75.6 m (248 ft) with a well screen from 42.7–54.9 m (140–180 ft) below land surface, is completed in marine deposits immediately underlying alluvium based on gamma and driller’s logs (Fig 3). Deeper deposits encountered during drilling were not screened and, based on driller’s log data, are probably the same older, less-permeable materials present at depth in well 41611. In September 2011, unpumped flow through well 410621 was upward from the bottom of the well to a depth of 45.7 m (150 ft) below land surface at rates as high as 0.2 liters per second (L/s) or 3 gallons per minute (gpm) (see supporting information)—consistent with groundwater discharge from marine deposits to the alluvium. Fluid temperature logs used to help identify flow into the borehole also showed slightly increased temperature in the lower deposits.

Specific capacity of well 410621, measured during collection of pumped flow log data, was 5.4 L/s per meter (26.5 gpm/ft) of drawdown. More than a quarter of the yield of the well was from the upper 0.9 m (3 ft), the screened interval above 4.42 m (145 ft) below land surface (Fig 3). If the alluvium were not present, the specific capacity of this well would have been less, about 4 L/s per meter (20 gpm/ft) of drawdown. Within the marine deposits, water entered the well from discrete intervals at depths of 46.3–47 m (152–154 ft), 49–50 m (161–163), and 54.3–54.9 m (178–180 ft) below land surface (Fig 3). Changes with depth in the gamma and temperature log further support this observation.

Well 41611, drilled to a depth of 86 m (282 ft) with openings from 22 to 85.1 m (72–279 ft) below land surface, is completed in alluvium and marine deposits based on gamma and driller’s logs. In June 2011, unpumped flow within the well was upward from a depth of about 64 m (210 ft) below land surface at a rate of about 0.1 L/s (2 gpm) (see supporting information). Upward flow through the well is consistent with data from well 41621 and groundwater...
discharge from the marine deposits to the alluvium. The fluid temperature log in well 41611 showed little difference in flow into the borehole.

The specific capacity of well 41611 measured during collection of pumped flow logs was 23.5 L/s per meter (92.5 gpm/ft) of drawdown. The pumped flow log from the well was comparatively uniform with depth (Fig. 4). However, little water was yielded to the well from deposits below 73 m (240 ft) and more than 80% of the well yield was from deposits above 64 m (210 ft). Driller's log data and increasing natural gamma data suggest geologic changes
that are consistent with older, less-permeable material at depth within the well. Changes in well diameter measured below 64 m (210 ft) using a caliper tool may reflect concretions formed within the well as water from different geologic units mixed within the well. Driller’s log data show the contact between alluvium and the underlying marine deposits about 49.3 m (162 ft) below land surface. Although there are small changes in the gamma and temperature logs at this depth (and in chemistry data discussed later in this paper), the contact is less obvious in the flow log data.

### 3.2. Chemistry and isotopic data

Water from the surface discharge and depth-dependent samples from the three sampled wells was alkaline, with pH ranging from 7.5 to 7.8. Dissolved oxygen concentrations ranged from 0.2 to 7.4 mg/L (Table S1). Dissolved oxygen concentrations were lowest in water from the surface discharge of well 410613 within alluvium in the Las Flores Creek watershed. Water was potable but had elevated dissolved solids concentrations ranging from 700 to 800 mg/L (Table S1). All samples exceeded the USEPA secondary MCL for dissolved solids of 500 mg/L (http://water.epa.gov/drink/contaminants/secondarystandards.cfm, accessed November 4, 2013), but did not exceed the California Upper Consumer Acceptance Level of 1,600 mg/L (http://www.cdph.ca.gov/certiic/dinkingwater/Documents/RecentlyAdoptedRegulations/R-21-03-finalregtext.pdf, accessed November 4, 2013). The major-ion composition of the water was a sodium/mixed bicarbonate-chloride type.

Unadjusted 72-h gross alpha activities in the surface discharge from wells 410621 and 41611 ranged from 15 to 25 pCi/L; unadjusted 30-day gross alpha activities were lower and ranged from 9.1 to 16 pCi/L (Table 1). Depth-dependent 72-h and 30-day unadjusted gross alpha activities were generally higher than the activities from the surface discharge of the well 410621 and lower than the surface discharge of well 41611 (Table 1). Differences between the 72-h and 30-day results indicate the presence of shorter-lived alpha-emitting radionuclides in groundwater. These shorter-lived alpha-emitting radionuclides are contributing a substantial amount (as much as 10 pCi/L) to the total alpha activity. 72-h gross beta activities in the surface discharge and depth-dependent samples collected from the three sampled wells ranged from 1.8 to 4.2 pCi/L and 30-day gross beta activities ranged from 3.5 to 8 pCi/L (Table 1). Increases in gross beta activity with sample holding time commonly occur as a result of in-growth of beta-emitting radioactive progeny with time (Thomas et al., 1993).

Uranium concentrations in the surface discharge and depth-dependent samples collected from the three sampled wells ranged from 5.8 to 22 μg/L, with the highest concentrations in well 410621 completed in the San Mateo Formation beneath the alluvium (Table 1). All uranium concentrations in the surface discharge and depth-dependent samples were below the MCL of 30 μg/L (20.1 pCi/L). When calculated as activities by summing the isotopes, uranium activities ranged from 3.7 to 12.9 pCi/L. 234U and 238U activities were similar, ranging from 1.9 to 6.5 pCi/L and 1.7 to 6.1 pCi/L, respectively; with 234U/238U activity ratios ranging from 1 to 1.16. 236U activities were about an order of magnitude lower. When corrected for uranium activity, 72-h adjusted gross alpha activities ranged from 7.1 to 15.9 pCi/L, and 30-day gross alpha activities ranged from 1.6 to 5.4 pCi/L. The 72-h adjusted gross alpha activities exceeded the MCL of 15 pCi/L in water from well 410621 collected at depths greater than 48.8 m below land surface. All adjusted 30-day gross alpha activities were below the adjusted gross alpha MCL of 15 pCi/L (http://water.epa.gov/drink/contaminants/index.cfm#Radionuclides, accessed November 4, 2013) (Table 1).

The combined activities of all four radium isotopes in the surface discharge and depth-dependent samples collected from the three sampled wells ranged from 1.2 to 4 pCi/L, neither 226Ra or 228Ra exceeded their combined MCL of 5 pCi/L. All four radium isotope activities were higher in well 410621. Unlike radon, radium isotope activity did not increase in the deeper part of well 410611. Overall 226Ra, the longest lived isotope of having a half-life of 1,601 years, was the most abundant isotope of radium, followed closely in almost equal proportions by 232Ra and 228Ra, having half-lives of 3.64 d and 5.6 years, respectively. 223Ra, part of the 223U decay chain and having a half-life of 11.4 d, was approximately an order of magnitude less abundant than the other three isotopes, consistent with the lower 235U activity. The ratio of the two longer lived isotopes 226Ra/228Ra ranged from 0.57 to 1.6 with a median of 1.2, consistent with data from Finland (Aiskainen, 1981) and the United States (Johnson, 1971; Kriege and Hahne, 1982; Michel and Moore, 1980) that show 226Ra/228Ra isotopic ratios near 1. Low radium activities in groundwater at the site are consistent with strong sorption of radium and relative insolubility of radium.

Chromium concentrations in the surface discharge and depth-dependent samples collected from the three sampled wells ranged from 360 to 2,080 pCi/L (Table 1). All radon concentrations are below the MCL of 4,000 pCi/L. Radon activities were higher in well 410621, and the deeper part of well 41611 below 48.8 m (160 ft) below land surface.

Chromium concentrations in the surface discharge and depth-dependent samples collected from the three sampled wells ranged from 0.25 to 3.8 μg/L and were less than the California MCL for Cr VI of 10 μg/L (Effective July 1, 2014) (http://www.cdph.ca.gov/certiic/dinkingwater/Pages/Chromium6.aspx, accessed November 4, 2013). Chromium concentrations were lowest in water from well 410613 that contained low dissolved oxygen concentrations. Although Cr VI was present in all samples, the reporting limit for this study of 2 μg/L prohibited quantification of Cr VI in some samples. δ53Cr values ranged from –0.23 to 1.47 per mil (Table 1). Near-zero δ53Cr values from fresh groundwater in the deeper parts of well 41611 are within the range reported for Cr VI associated with anthropogenic sources. However, some natural saline groundwaters have δ53Cr values near zero (Izbicki, 2008; Izbicki et al., 2008a,b, 2012).

### 4. Discussion

Well-bore flow and depth-dependent water-quality data were used to estimate the quality of water entering wells 410621 and 41611 under pumped conditions at depth. The purpose of these calculations was to understand how water quality differed with depth within the wells, and to determine the quality of water with respect to selected radioisotopes within marine and alluvial deposits penetrated by the wells.

Well 410621 is screened within the marine deposits, although increased yield near the upper part of the well may reflect contributions from the overlying alluvium. The unadjusted 72-h gross alpha activity in the surface discharge from the well was 25 pCi/L. The uranium activity was 12.3 pCi/L, and the 72-h adjusted (for uranium activity) gross alpha activity was 12.7 pCi/L. The adjusted gross alpha activity was less than the U.S. Environmental Protection Agency MCL of 15 pCi/L. At depth within well 410621, measured gross alpha, uranium, and adjusted gross alpha activities in water entering the well were as high as 28, 12.9 and 15.9 pCi/L, respectively; the gross alpha activities exceeded their respective MCLs (Fig. 5). Unadjusted and adjusted gross alpha activities were lower in the upper part of the well screen, possibly as a result of contributions of water from overlying older alluvium. 228Ra activities in groundwater were almost an order of magnitude lower...
Table 1
Gross alpha, gross beta, uranium, radium, radon, and chromium isotopic data from wells 41611, 410621, and 410613, MCB Camp Pendleton, southern California June and September, 2011.

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<th>Adjusted Gross alpha radio-activity, 30-day count in pCi/L</th>
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Date, in mm/dd/yy, month/day/year; Number in parenthesis is National Water Information System (NWIS) parameter code; MCL, Maximum Contaminant Level; MCL-US, Maximum Contaminant Level-US Environmental Protection Agency; MCL-CA, Maximum Contaminant Level-California; Number in bold equals or exceeds respective Maximum Contaminant Level; pCi/L, picocuries per liter; µg/L, micrograms per liter; per mil, parts per thousand.
than $^{238}$U and $^{234}$U activities, consistent with sorption of radium to aquifer materials and its removal from solution. $^{222}$Rn activities were high in well 410621 with the highest $^{222}$Rn activity of 2,230 pCi/L calculated at the depth interval between 42.5 and 48.6 m (140 and 160 ft) and decreased slightly in the underlying marine deposits reflecting changes in geology with depth. $^{222}$Rn activities were more than 2 orders of magnitude higher than $^{238}$U, $^{234}$U and $^{226}$Ra. Consequently, $^{222}$Rn activities are consistent with decay from radium (and uranium) sorbed onto the surface of aquifer materials. $^{224}$Ra activities, part of the $^{232}$Th decay-chain rather than the $^{238}$U decay-chain, were less than 1 pCi/L.

In contrast to well 410621, well 41611 is screened within alluvium and underlying marine deposits. Water from the surface discharge of the well is a mixture of water from alluvial and marine deposits. The unadjusted 72-h gross alpha activity in the surface discharge from well 41611 was 15 pCi/L. The uranium activity was 3.9 pCi/L and the 72-h adjusted gross alpha activity was 11.3 pCi/L and similar to the adjusted gross alpha activity of well 410621. Although the adjusted gross alpha activity from the surface discharge of the well was less than the U.S. Environmental Protection Agency MCL of 15 pCi/L, the adjusted gross alpha activity in water entering the well at depth between 21.9 and 30.5 m (72 and 100 ft) below land surface was 25.7 pCi/L (Fig. 6), which exceeds the MCL. This depth interval corresponds to recent alluvium encountered by the well. Uranium activities were relatively uniform at depth within well 41611 and lower than activities in well 410621. Calculated $^{224}$Ra activities, within the Thorium decay-chain, in well 41611 were as high as 1.5 pCi/L in water from the recent alluvium between 21.9 and 30.5 m (72 and 100 ft) below land surface. The data indicate high gross alpha activities at this depth are the result of alpha-emitting radionuclides within the Thorium decay-chain rather than radioisotopes within the Uranium decay-chain. These shorter-lived alpha-emitting radionuclides are contributing a substantial amount (as much as 10 pCi/L), to the total alpha activity, and should be included in any future analysis, especially $^{210}$Po. $^{222}$Rn activities increase with depth in well 41611 and activities are lower in the recent and older alluvium and higher in the underlying marine deposits reflecting changes in geology with depth.

Thorium is a naturally-occurring radionuclide, and is several times more abundant in the Earth’s crust than all uranium isotopes combined. In soil, thorium is present at average concentrations of 6 ppm (Reimann and de Caritat, 1998). Air-borne gamma-ray spectrometry surveys (Duval et al., 2005) show estimated thorium concentrations in the San Onofre Hills area of about 9 ppm, with lower concentrations along the coast of about 4.5 ppm. Elevated thorium abundance in recent alluvium within the Piedra de Lumbre watershed draining the higher altitudes of the San Onofre Hills is consistent with local geologic sources. In contrast, the larger Las Flores watershed includes a wider variety of geologic materials, which would be consistent with lower concentrations of thorium from the San Onofre Hills in the Los Flores alluvium.

The activity ratio (AR) of $^{234}$U/$^{238}$U in the surface discharge and depth-dependent samples collected within wells 410621 and 41611 ranges from 1.0 to 1.16. Calculated activity ratios of water entering the wells between sample depths (not shown in Figs. 5 and 6) range from 0.9 to 1.26. These values are near secular equilibrium and within the ranges reported for most groundwater (Osmond and Cowart, 2000). The values do not indicate large-scale enrichment of $^{234}$U through hydrologic and geochemical processes; however, most values are greater than 1 consistent with enrichment of $^{234}$U in ocean water and marine deposits (Henderson, 2000).

The AR of $^{234}$U and its progeny $^{226}$Ra ranged from 0.15 to 0.29, and are far from the AR of 1 for secular equilibrium. This is consistent with sorption of radium to metal-oxide coatings on aquifer solids and its subsequent removal from solution (Welch et al., 1997). Similarly, the AR for $^{226}$Ra and its progeny $^{222}$Rn range from about 650 to 5,000 and also are far from equilibrium, while $^{222}$Rn/$^{238}$U AR’s range from about 190 to 770. High activity of $^{222}$Rn compared to $^{226}$Ra and $^{234}$U activities in water are common and occur because of (1) the high mobility and solubility of radon,
Fig. 6. Flow, well construction, gross alpha, uranium, radium, and radon isotopic data collected within well 41611 under pumped conditions, June 2011. (Note: Geologic units [Qya, Qoa, QTsm, and Tso] are described in detail in Fig. 2. Dots are depth-dependent samples; lines are calculated activities between samples. Data in black and grey indicate gross alpha; data in red indicate isotopes in the uranium and actinium decay series; data in green indicate isotopes in the thorium decay series.)

Fig. 7. Flow, well construction, chromium, delta chromium-53 ($\delta^{53}$Cr), and iron data collected within well 41611 under pumped conditions (Note: Geologic units [Qya, Qoa, QTsm, and Tso] are described in detail in Fig. 2. Dots are depth-dependent samples; lines are calculated concentrations between samples.)
and (2) most radium and uranium are associated with metal-oxides on aquifer solids and are not present in solution (Welch et al., 1997). The lowest $^{222}$Rn activities, in water from the surface discharge of well 410613 and from alluvial deposits encountered by well 41611 reflect geologic differences in the source of alluvial deposits compared with marine deposits and the geologically younger age of the alluvium which has limited $^{226}$Ra sorption to sediments as water containing $^{234}$U discharged through the alluvium.

Chromium and Cr VI concentrations in water from the surface discharge of both wells were comparatively low. Although calculated chromium concentrations entering the well from the marine deposits tapped by well 41611 were as high as 5.5 μg/L, concentrations were lower than the recently proposed California MCL for Cr VI of 10 μg/L. Chromium concentrations vary inversely with iron concentrations (Fig. 7) suggesting that although water from the wells is oxic, some limited redox controls may be present. Isotopic data show comparatively low, near-zero δ53Cr values within the marine deposits tapped by well 41611. Near-zero δ53Cr values are consistent with anthropogenic sources of chromium, although recent work has shown that near-zero δ53Cr values occur naturally in saline groundwater (Izbicki et al., 2012) and saline unsaturated zones (Izbicki, 2008; Izbicki et al., 2008b). Additionally, chromium-bearing rocks and minerals (including serpentinite, actinolite, fuchsite, and glauconopate) are present in deposits in this area. According to base personnel, there are no known upgradient sources of chromium contamination. Thus, it is possible that the near-zero δ53Cr values within marine deposits extend the range of natural δ53Cr compositions. However, given the water purveyors desire to limit future water-quality issues associated with possible sources of contamination, it may be best to avoid this source if other sources are available.

5. Conclusions

Although water from existing wells in the Las Flores and Piedra de Lumbré watersheds is generally suitable for water supply, there is concern on the part of water resource managers that (1) new wells drilled in the area may exceed MCLs for alpha-emitting radioisotopes and chromium, and (2) future changes in MCLs for these constituents may limit use of the area for water supply. Data collected as part of this study suggest that alluvium from the Piedra de Lumbré watershed may exceed adjusted gross alpha MCL’s because of naturally-occurring thorium in the higher altitudes of the San Onofre Hills, which border the upper reaches of the catchment and contributed to the aquifer sediment provenance.

Data show that naturally-occurring uranium decay-chain isotopes, including radon, are present in underlying marine deposits. The combination of coupled well-bore flow and depth-dependent sample collection with analyses for a range of alpha-emitting radioisotopes within the uranium, actinium, and thorium decay-chains was useful in identifying the geologic source of high gross alpha activity in the study area. Future water supply development in alluvial deposits near current supply well 410613 within the Las Flores watershed, which drains a larger area and has low alpha activities and chromium, would help lessen water-quality concerns related to development in the area—although other constituents not analyzed as part of this study may be present.

The marine deposits also contain low concentrations of chromium. Although the δ53Cr isotopic composition of this chromium is near 0 per mil and within the range of anthropogenic chromium, the chromium is not known to be anthropogenic in origin. Alpha-emitting radionuclides and chromium are present at lower concentrations in alluvium within the Las Flores drainage which drains a larger area, having more diverse geologic source terrain compared to alluvium in the Piedra de Lumbré watershed. Reduced conditions within the aquifer further limit mobility of uranium series radionuclides.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.09.016.

References


