Natural Occurrence of Hexavalent Chromium in the Aromas Red Sands Aquifer, California

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To address increasing concerns of chromium contamination in the drinking water of Santa Cruz County, we designed a study to investigate the source(s) and spatial gradients of the chromium concentration and speciation in local aquifers. This study was catalyzed by a report (January 2001) by the Soquel Creek Water District of elevated hexavalent chromium concentrations ranging from 6 to 36 μg L^{-1}, approaching the state's maximum concentration limit of 50 μg L^{-1}, in the Aromas Red Sands aquifer. To test the accuracy of those preliminary measurements, we collected groundwater using trace metal clean techniques from 11 sites in Santa Cruz County, including 10 from the aquifer with reportedly elevated chromium concentrations and 1 from an adjacent aquifer, the Purisima, and analyzed them for total chromium using inductively couple plasma mass spectrometry. Nine of the reportedly 10 contaminated sites had total chromium concentrations ranging from 5 to 39 μg L^{-1}, while one from the control site was below the limit of detection (0.01 μg L^{-1}). We also measured the speciation of chromium at all sites using a solid supported membrane extraction coupled with graphite furnace atomic absorption spectrometry and determined that on average 84% of total chromium was Cr(VI). In addition to the groundwater analyses, a series of extractions were performed on sediment samples from both the Aromas Red Sands and Purisima aquifers. These tests were used to empirically characterize sediment trace metal (Cr, Fe, Mn) distributions in five phases providing information about the origin, availability, reactivity, and mobilization of these trace metals. Results from groundwater and sediment samples indicate that the chromium is naturally occurring in the Aromas Red Sands aquifer, possibly by Cr(III) mineral deposits being oxidized to Cr(VI) by manganese oxides in the aquifer.

Introduction

Trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), differ in both their geochemistry and effects on organisms. The former species, Cr(III), is an essential trace metal nutrient, and the latter species, Cr(VI), is a carcinogen (*1*). Under reducing conditions, Cr(III) is the more thermodynamically stable form, as cations (e.g., Cr^{3+}, $Cr(OH)^{2+}$, and $Cr(OH)^{4-}$) with high particle affinities and as precipitates [e.g., $Cr(OH)_3$ and $Fe,Cr(OH)_3$] at pH ranges commonly found in the environment (*2*−*4*). Under oxidizing conditions, Cr(VI) is thermodynamically favored and exists as relatively soluble oxyanions (e.g., CrO_4^{2-} and $HCrO_4^{-}$) (*5*, *6*). Consequently, Cr(VI) is more labile, as well as more toxic, than Cr(III) in most aquatic environments.

It is these differences in toxicity and solubility that are catalyzing revised criteria for measuring chromium in groundwater and drinking water, although evidence for aqueous Cr(VI) carcinogenicity has yet to be definitively established. For example, the California Department of Health Services previously required water agencies to measure total chromium in drinking water, but it began mandating tests for Cr(VI) as well as total chromium in 2001.

Those new water quality tests determined that 70−100% of total chromium in the Aromas Red Sands aquifer, in central California, was Cr(VI) (*7*). Moreover, total chromium concentrations in the aquifer ranged from 1.5 to 39 μg L^{-1} (*7*). This raised public health concerns because the higher levels approached the state's maximum concentration level (MCL) for chromium in drinking water (50 μg L^{-1}).

Consequently, this study was designed to determine (i) what factors accounted for the relatively high concentrations of chromium in the aquifer and (ii) whether the elevated Cr(VI) concentrations were due to natural processes or anthropogenic perturbations. The assessment included concurrent analyses of dissolved Cr(VI), total chromium, iron, and manganese in groundwater from both the Aromas Red Sands and Purisima aquifers. The latter aquifer, which is adjacent to the Aromas Red Sands aquifer and within the same drainage basin, was used as a control site because it has relatively low total chromium concentrations and no detectable Cr(VI) concentrations ($<$0.05 μg L^{-1}). Iron and manganese were included in our analyses because they are redox species whose redox chemistry is closely related and linked with that of chromium via the redox reactions among Fe(II)/Fe(III), Mn(II)/Mn(IV), and Cr(III)/Cr(VI).

In addition, sediment samples were collected from the Aromas Red Sands and Purisima aquifers to obtain qualitative information on particulate chromium, manganese, and iron speciation using a sequential extraction procedure based on the Tessier et al. (*8*) method. Their extractions operationally define five phases, which are dependent on the parent material and changes in environmental conditions (e.g., pH and redox potential), that yield information on the origin, availability, reactivity, mobilization, and transport of trace metals that may be used to determine whether the chromium in the aquifer is from a natural or anthropogenic source (*9*). As the following data show, results from both the sediment and water analyses indicate that the relatively high levels of chromium in the Aromas Red Sands aquifer are from natural processes that also favor the oxidation of Cr(III) to Cr(VI) in strata within that aquifer.

Geological Setting

The study area (Figure 1) is located in the Pajaro Valley and Santa Cruz Purisima Highlands Groundwater Basins (*10*). The Aromas Red Sands aquifer is one of two important water-bearing formations in Santa Cruz and Monterey Counties.

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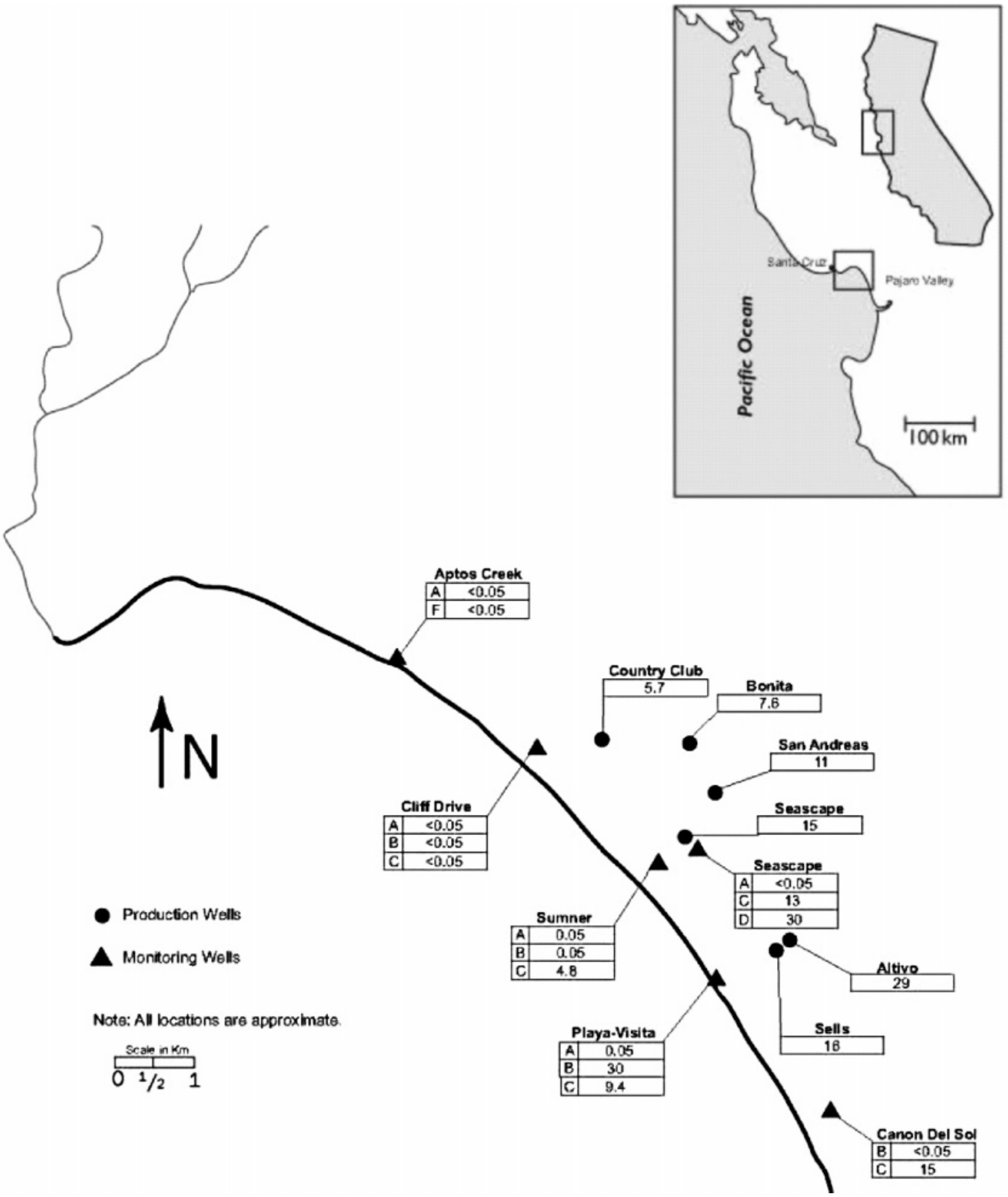

FIGURE 1. Location of monitoring and production wells in the Aromas Red Sands and Purisima aquifers. Cr(VI) concentrations (μg L^{-1}) in filtered (<0.45 μm) groundwater samples from the Aromas Red Sands and Purisima aquifers. Cr(VI) varied irregularly in monitoring wells, but not in production wells. In the latter, Cr(VI) steadily increased from the Country Club well toward the south to Sells well. For sample depths, please refer to Table 2.

It is mostly a confined aquifer of mid-Pleistocene age with a thickness ranging from 30 to 300 m and consists primarily of friable, quartzose sandstone, and well-sorted dark brown to red sands that have grain sizes ranging from sand to clay (*11*). The formation lies above the Purisima aquifer and other older formations and in most areas lies beneath unconsolidated quaternary alluvium and terrace deposits (*11*). The Aromas Red Sands aquifer dips toward the southeast, south, and west in Santa Cruz County (*12*). It discontinuously outcrops at the borders of the basin in parts of the Pajaro Valley and offshore on the continental shelf and Monterey submarine canyon (*12*, *13*). It continues toward the valley beneath younger unconsolidated deposits (*12*). Groundwater flow is primarily controlled by sedimentary texture that changes laterally through the aquifer. In general, permeability increases inland causing groundwater flow to go southeastward toward the Pajaro Valley (*12*, *14*). Due to fine grain deposits, flow may be vertically restrictive in the coastal subareas (*13*).

The Purisima aquifer is mostly of marine origin at the base and continental in the upper portions and is made up of poorly consolidated gravels, sands, silts, and clays (*11*, *15*). The thickness ranges from 300 to 600 m in the central portion of the Pajaro Valley down to ~1200 m between the San Andreas and Zayante−Vergales faults (*16*). Deposits of this formation can be found throughout most of the region northeast of the San Andreas Fault and lies above the Santa Lucia granite, Franciscan group, and Monterey group (*11*). Water-bearing units of the Purisima aquifer are mostly confined by clay layers that are thickest in the central portion of the Pajaro Valley and thin inland, eventually becoming thinly layered, discontinuous, or absent (*10*). In coastal areas (i.e., terrace areas) these clays are either thinly layered, discontinuous, or absent (*10*). Major recharge zones of the

TABLE 1. Sequential Extraction Scheme Used To Characterize Metal Concentrations in Aquifer Sediments Based on Methods Developed by Tessier et al. (*8*)

fraction	extracting agent	conditions	target phase
F1	1 M NaOAc, pH 8.2, 25 °C	8 mL, 1 h, continuous agitation	exchangeable
F2	1 M NaOAc, pH 5 (HOAc), 25 °C	8 mL, 1 h, continuous agitation	bound to carbonates
F3	0.04 M $NH_2OH{-}HCl$ in 25% (v/v) HOAc, 96 ± 3 °C	20 mL, 6 h, occasional agitation	reducible, bound to Fe−Mn oxides
F4	(a) 0.02 M HNO_3 + 30% H_2O_2, pH 2 (HNO_3), 85 ± 2 °C	3 mL + 5 mL, 2 h, occasional agitation	oxidizable, bound to organics and sulfides
	(b) 30% H_2O_2, pH 2 (HNO_3), 85 ± 2 °C	3 mL, 3 h, occasional agitation	
	(c) 3.2 M NH_4OAc in 20% (v/v) HNO_3	5 mL, 0.5 h, continuous agitation	
F5	(a) concd HNO_3, 100 °C	10 mL, near dryness	residual
	(b) concd HNO_3 + HF, 110 °C	5 mL + 2 mL, near dryness	
	(c) HNO_3, 120 °C	5 mL, dryness	

Purisima aquifer are north and east of the Pajaro Valley (*10*). Recharge occurs from percolation of precipitation and streamflow permeation. In general, groundwater flows southeastward toward the Pajaro Valley (*12*, *14*).

Materials and Methods

Groundwater Samples. Groundwater samples were collected on two separate occasions (August 2001 and January 2002) from existing wells in both the Aromas Red Sands and Purisima aquifers in Santa Cruz County, CA (Table 2). Two samples were collected at three different well depths from five sites in the Aromas Red Sands aquifer (Cliff Dr., Canon Del Sol, Seascape, Sumner, and Playa-Vista wells) as well as from two depths from the Aptos Creek well in the Purisima aquifer (Figure 1). Each well was constructed of PVC piping, and was installed in fine to coarse sands and clays. The wells were purged with air and sampled using nitrogen gas at low flow rates ranging from 6 to 20 L min^{-1}. In January 2002, production wells San Andreas, Seascape, Country Club, Altivo, Bonita, and Sells were sampled (Figure 1). Each production well was constructed of low carbon steel casing and stainless steel well screens with well screens located at three different depths, and each of them was equipped with their own pumping system with high flow rates ranging from 1600 to 3200 L min^{-1}. Because production wells were constructed to provide drinking water to the public, it was not possible to control the sampling flow rates in these wells.

Trace metal clean techniques, as delineated in Creasey and Flegal (*17*), were used for all sample preparation and sampling techniques, to the extent possible using existing wells and pumping systems. Duplicate water samples were collected after basic water parameters (i.e., pH, dissolved oxygen, conductivity, temperature, and turbidity) had stabilized. Water parameters were measure using a YSI Model 85 and Orion 250 SA multimeter. At a minimum, four casing volumes were purged from each well before collecting groundwater samples. Unfiltered and filtered (<0.45 μm) samples were collected from each site. Cr(VI) groundwater samples were field filtered (Osmonics polypropylene, 0.45 μm calyx filter cartridge), while unfiltered samples were collected for the analysis of total chromium, iron, and manganese. Trace metal samples were collected in acid-cleaned low-density polyethylene (LDPE) bottles. The bottles were rinsed (3×) with the groundwater before being filled and then were encased in two LDPE bags.

Groundwater Analyses. The Cr(VI) samples were not acidified and were analyzed within 48 h of collection. They were first put through a liquid membrane extraction in order to separate Cr(VI) from Cr(III) species (*18*, *19*). Samples were then analyzed on a Perkin-Elmer SIMAA 6000 graphite furnace atomic absorption spectrometer, fitted with a Zeeman background corrector and AS72 auto sampler. The limit of detection (LOD) for hexavalent chromium determination was 0.05 μg L^{-1}.

Total dissolved (<0.45 μm) chromium, iron, and manganese samples were filtered in the lab within a few hours of collection. Aliquots of 500 mL were acidified with 2 mL of 6 M high purity (Optima) HCl and were then stored until analysis. Total dissolved chromium concentrations, as well as those for manganese and iron, were determined with a Finnigan MAT ELEMENT high resolution magnetic sector inductively coupled plasma-mass spectrometer (HR-ICP-MS) using indium as an internal standard for each sample. National Institute of Standards and Technology (NIST) standard reference material (SRM) for trace elements in natural water (SRM 1640) were analyzed concurrently. Calculated LODs were 0.01 μg L^{-1} for total chromium, 0.02 μg L^{-1} for manganese, and 0.10 μg L^{-1} for iron. The average recovery for each element in the SRM was >96%.

Sediment Samples. Sediment samples from the Purisima and Aromas Red Sands aquifers were collected April−May 2000 and August 2002, respectively. Core samples from the Purisima aquifer were collected at one site by the United States Geological Survey (USGS) at selected depths between 250 and 530 m below ground surface (bgs) in Marina, Monterey County (*15*). Sediment samples from the Aromas Red Sands aquifer were collected at one site from fresh well tailings at five feet intervals from 15 m down to 152 m bgs in Santa Cruz County.

To minimize alterations of the natural state of the soil, all field samples were kept fresh, moist, and in the dark until processed (*20*). Then a small homogeneous portion of moist sediment was dried at 40 °C in an oven for 24 h. Organic matter (i.e., grass and twigs) introduced during the sampling of the Aromas Red Sands aquifer were picked out from the dried samples, which were then mixed to ensure homogeneity. From these homogenates, 1-g aliquots of sediment were added to trace metal clean 60-mL polypropylene copolymer centrifuge tubes for analyses. For quality-control purposes, a few randomly selected samples, NIST Buffalo River Sediment (SRM 2704), and blanks were analyzed in either duplicate or triplicate for every set of analyses.

Sediment Analyses. A sequential extraction procedure, based on methods developed by Tessier et al. (*8*), was used to empirically characterized sediment trace metal distributions in five fractions (Table 1). All extractions employed trace metal clean techniques. Between each extraction, separation of the extraction solution and sediment was obtained by centrifugation at an average and maximum relative centrifuge force of 19,360 and 28,660 for 45 min. The supernatant was decanted into LDPE bottles and stored at 4 °C until needed. The residue of each sample was washed with 8 mL of high-purity (18 Ω cm) water (Millipore Milli-Q water) and centrifuged at 16000 rpm for 45 min. The supernatant was decanted and discarded.

All extract solutions were analyzed for total chromium, manganese, and iron concentrations on a PerkinElmer Optima 4300 DV inductively coupled plasma-optical emission

TABLE 2. Total Dissolved (<0.45 μm) Trace Metals (Cr, Mn, and Fe) and Cr(VI) Concentrations in Groundwater from the Aromas Red Sands and Purisima Aquifers

sample ID	sample date	depth (m)	pH	total Cr (μg L^{-1})	Cr(VI) (μg L^{-1})	total Mn (μg L^{-1})	total Fe (μg L^{-1})
Cliff Dr.-A[a]	8/2001	150	7.0	<0.01[f]	<0.05[f]	52	230
Cliff Dr.-B[a]	8/2001	100	7.1	<0.01[f]	<0.05[f]	72	83
Cliff Dr.-D[a]	8/2001	34	6.7	0.2	<0.05[f]	5.0	83
Canon Del Sol-B[a]	8/2001	150	7.3	<0.01[f]	<0.05[f]	7.0	11
Canon Del Sol-C[a]	8/2001	98	7.1	18	15	0.06	<0.10[f]
Seascape-A[a]	8/2001	200	7.3	<0.01[f]	<0.05[f]	960	<0.10[f]
Seascape-C[a]	8/2001	110	7.3	14	13	1.0	0.3
Seascape-D[a]	8/2001	67	7.1	35	30	1.0	2.0
Aptos Creek-A[b]	8/2001	—[d]	8.9	<0.01[f]	<0.05[f]	0.7	20
Aptos Creek-F[b]	8/2001	—[d]	8.5	<0.01[f]	<0.05[f]	370	<0.10[f]
Sumner-A[a]	1/2002	140	7.2	<0.01[f]	0.05	530	2.4
Sumner-B[a]	1/2002	130	7.7	<0.01[f]	0.05	130	44
Sumner-C[a]	1/2002	46	7.4	4.1	4.8	0.8	0.5
Playa-Vista-A[a]	1/2002	91	7.0	0.3	0.05	160	4.0
Playa-Vista-B[a]	1/2002	76	6.5	39	30	0.8	52
Playa-Vista-C[a]	1/2002	41	7.4	10	9.4	0.1	7.1
San Andreas[c]	1/2002	—[d]	7.7	11	11	3.2	1.7
Seascape[c]	1/2002	—[d]	7.7	19	15	1.4	<0.10[f]
Country Club[c]	1/2002	—[d]	7.4	5.9	5.7	<0.02[f]	<0.10[f]
Altivo[c]	1/2002	—[d]	7.5	32	29	<0.02[f]	0.1
Bonita[c]	1/2002	—[d]	7.5	—[e]	7.6	—[e]	—[e]
Sells[c]	1/2002	—[d]	7.5	18	16	<0.02[f]	2.8

[a] Groundwater samples from monitoring wells in the Aromas Red Sands aquifer. [b] Groundwater samples from monitoring wells in the Purisima aquifer. [c] Groundwater samples from the production wells in the Aromas Red Sands aquifer. [d] Multiple well screens. [e] Analysis not conducted. [f] Analyte not detected above the limit of detection shown.

spectrometer (ICP-OES). To test for accuracy and precision, SRM 2704, spike solutions, and standards were run intermittently with each set of samples. Since only total metal concentrations are available for SRMs, values from each extraction were added and compared to the reported SRM metal values. These summed average SRM recoveries were 92% for chromium, 120% for manganese, and 107% for iron. The average recoveries for the spike solutions and standards were between 94% and 104% of the predicted value. The LODs for extractions 1 and 2 were 5.5 ng g^{-1} for chromium, 2 ng g^{-1} for manganese, and 13 ng g^{-1} for iron. LODs for extractions 3−5 were 1.06 ng g^{-1} for chromium, 2.5 ng g^{-1} for manganese, and 5.5 ng g^{-1} for iron.

Results and Discussion

Dissolved Trace Metal (Cr, Fe, Mn) Concentrations. Total dissolved (<0.45 μm) trace metal (Cr, Fe, Mn) concentrations (μg L^{-1}) of groundwater from the Aromas Red Sands and Purisima aquifers are listed in Table 2 and shown in Figure 1. It shows the metal concentrations varied inconsistently both horizontally and vertically in the aquifers, especially the Aromas Red Sands aquifer. It also shows that not all filtered groundwater samples from the Aromas Reds Sands aquifer had detectable levels (>0.01 μg L^{-1}) of dissolved chromium; 83%, on average, of the total measurable chromium in the aquifer was Cr(VI), and the correlation (r = 0.995, simple linear regression) between total chromium and Cr(VI) was highly significant (p <0.01). Therefore, the same processes appear to be influencing the solubility of chromium and its speciation throughout the Aromas Red Sands aquifer, even though they varied markedly within the aquifer.

Chromium Concentration Gradients. Total dissolved (<0.45 μm) chromium concentrations in the Aromas Red Sands aquifer exhibited two other trends at individual well sites. There was a vertical gradient in the Playa-Vista wells, where chromium concentrations increased at 76 m and then decreased below that, and there was a second vertical gradient in the Seascape, Canon Del Sol, and Sumner wells, where chromium concentrations decreased with depth (Figure 2). From a horizontal aspect, chromium concentrations varied irregularly in monitoring wells, but not in production wells, where chromium concentrations increased from north to south (Figure 1).

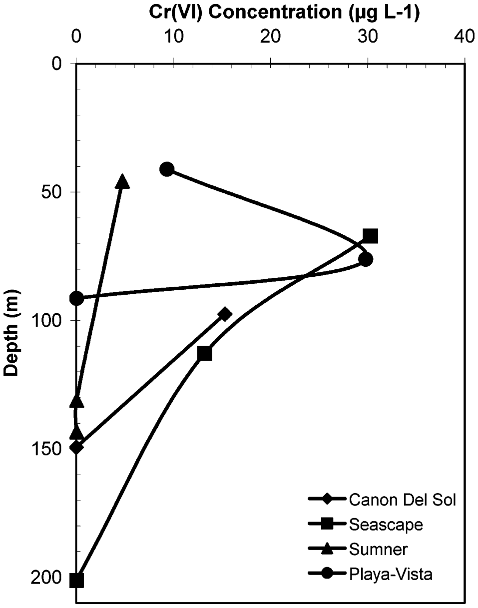

FIGURE 2. Cr(VI) concentration (μg L^{-1}) vs depth (m) in filtered (<0.45 μm) groundwater samples from the Aromas Red Sands aquifer.

The spatial variability of chromium concentrations in monitoring wells again indicates that the relatively elevated chromium concentrations in the Aromas Red Sands aquifer may be due to natural processes, rather than from industrial sources of contamination. With industrial contamination, previous research has shown that the highest chromium concentrations are at the source of contamination and steadily decrease downstream, while there are no signs of chromium contamination upstream from the source (*21−23*). Consequently, the apparently natural origin of chromium in the Aromas Red Sands aquifer is consistent

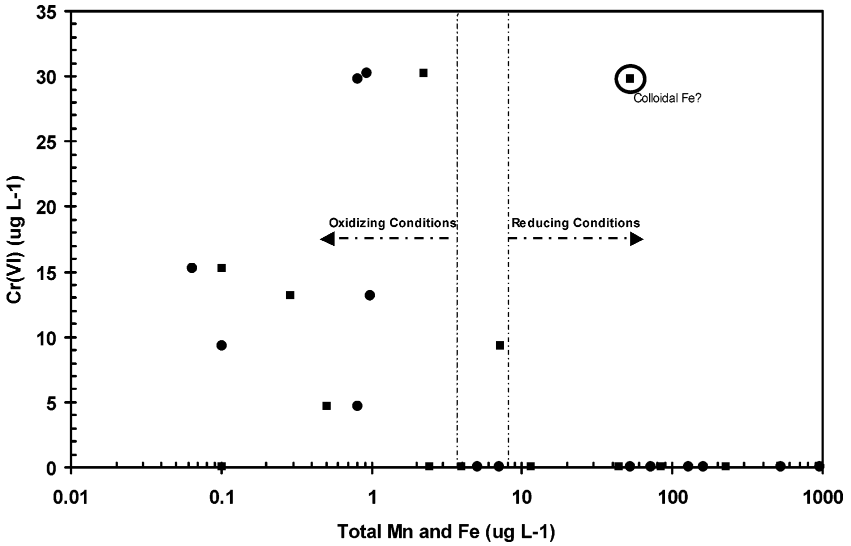

FIGURE 3. Total iron (■) and manganese (●) in log scale vs Cr(VI) concentrations (μg L^{-1}) in filtered (<0.45 μm) groundwater samples from monitoring wells in the Aromas Red Sands and Purisima aquifers. The circled data point is an outlier and is thought to have a high concentration of iron due to iron colloids passing through the filter.

with the results of a survey of its drainage basin, which determined that the majority of the area is primarily composed of residential communities and small businesses and that there was a relatively low risk for its contamination by industrial inputs (*7*).

Dissolved Iron and Cr(VI) Correlations. In most cases where Cr(VI) was found, little or no dissolved iron was found in either aquifer (Table 2). Although the oxidation states of iron were not identified in the groundwater samples, the trend between total iron and Cr(VI) suggests that the presence of Fe(II) limits the formation of Cr(VI). On the basis of the capabilities of Fe(II) to readily reduce Cr(VI) to Cr(III) in groundwater systems (*24*), dissolved concentrations of Fe(II) and Cr(VI) should be inversely correlated. Likewise, naturally occurring Cr(III) cannot be oxidized to Cr(VI) under reducing regions in the aquifers, tentatively attributed to the presence of Fe(II), derived from hematite, clay minerals, and ultramafic rocks; organic matter; and other electron donors (*4, 25*−*27*).

Figure 3 illustrates the inverse, albeit limited, relationship between total iron and dissolved Cr(VI) in the two aquifers. The distribution of the two is consistent with reports previously noted. Specifically, under reducing conditions, Cr(III) is thermodynamically stable and is strongly adsorbed by iron oxides and clay minerals (*5, 28*−*31*), but under oxidizing conditions, Cr(VI) is thermodynamically stable and soluble (*3*).

There is one outlier in Figure 3. It is a water sample from the Playa-Vista-B well in the Aromas Red Sands aquifer which had high total dissolved (<0.45 μm) concentrations (30 and 52 μg L^{-1}, respectively) of both Cr(VI) and iron. In contrast, all of the other water samples from that aquifer had relatively high dissolved Cr(VI) concentrations (≥4.8 μg L^{-1}) had low total dissolved iron concentrations (≤7 μg L^{-1}). Therefore, we tentatively attribute the anomalously high iron concentration in the one outlier to the presence of iron colloids suspended in the solution either naturally or by agitation during the sample collection process.

The inverse relationship between total iron and dissolved Cr(VI) concentrations in the Aromas Red Sands aquifer, as well as the spatial variability in those chromium concentrations, also suggests that there are regions within the aquifer that have negligible amounts of chromium-bearing minerals. This is consistent with the following analyses of the particulate phases in the aquifer, which exhibit inhomogeneous lithologies.

Dissolved Manganese and Cr(VI) Correlations. Similar to total iron, total manganese concentrations in groundwater samples showed an inverse relationship with Cr(VI) concentrations (Table 2). This negative correlation is consistent with reports that manganese oxides (MnO$_x$) strongly oxidize chromium in groundwater (*2*, *6*, *28*, *32*) and that MnO$_x$ is the most likely abiotic chromium oxidizer found naturally (*32*, *33*). Although the oxidation rates of manganese are relatively slow, the residence time of groundwater is considered long enough (i.e., thousands of years) so that kinetics is not a rate-limiting factor (*13*, *23*).

Although the speciation of total dissolved manganese was not determined, it is assumed that the predominant form in the aquifers is Mn(II) (*34*). This, again, is based on the inverse relationship between total dissolved Cr(VI) and manganese concentrations in the two aquifers (Table 2). Relatively high concentrations of total dissolved manganese, which are indicative of a reducing environment, can limit the oxidation of Cr(III), because the two compete for adsorption sites (*35*). Under oxidizing environments where Cr(VI) is detected, the most thermodynamically favorable oxidation state for manganese is Mn(IV) in the form of MnO$_2$. It quickly precipitates from solution and forms stable solids, typically as surface coatings on clays (*32*). Therefore, at sites with oxidizing environments, dissolved manganese concentrations should be relatively low (*34*).

Figure 3 shows that all sites with < 5 μg L^{-1} of total dissolved manganese have elevated levels (≥4.8 μg L^{-1}) of Cr(VI). On the basis of this trend, it may be possible to use manganese as a proxy to quickly survey for the possible presence of naturally high levels of Cr(VI) in an aquifer by simply measuring total dissolved manganese concentrations. If relatively high concentrations of manganese are detected in the groundwater sample, one can assume that most of that manganese is in the form of Mn(II) and there is a low risk of the site having high levels of Cr(VI). Conversely, if manganese concentrations are low, there can be relatively high concentrations of Cr(VI) naturally occurring in the aquifer.

The one sample that did not follow the major trends found in this study was from the Canon Del Sol-B well. It had low concentrations of total dissolved iron, manganese, and chromium, which may be due to the inhibition of chromium oxidation associated with the adsorption of Cr(III) to oxide surfaces at high pH (*36*). The anomalously low Cr(VI) concentrations may also be due to a high content of “free” iron and manganese oxide in the soil that may retard the migration of Cr(VI). Consequently, to fully understand the relationship of manganese and chromium in this environment, concurrent chromium and manganese speciation measurements are needed.

Particulate Chromium Distributions. Total chromium concentrations (dry weight) in sediments ranged from ~19 to 63 μg g^{-1} in the Purisima aquifer and from ~37 to 130 μg g^{-1} in the Aromas Red Sands aquifer (Table 3). These concentrations compare with those reported by Shacklette et al. (*37*), who found that the majority of soils in the United States contained total chromium between 25 and 85 μg g^{-1} (n = 863). Of the total chromium measured in sediment samples, 87−98% were from the residual phase in both the Aromas Red Sands and Purisima aquifers. The high percentage found in the residual phase indicates, again, the chromium in the aquifers was from a natural source, the sediments.

The relatively high concentrations of particulate chromium further indicate that the high levels of dissolved Cr(VI) in the aquifer are due to natural processes. Additionally, more of that chromium is potentially available to solubilize to Cr(VI) under oxidizing conditions, because the average concentration of chromium in the oxidizable phase of sediments in the Aromas Red Sands aquifer (2.6 μg g^{-1}) is higher than that in the Purisima aquifer (1.1 μg g^{-1}). Consequently, both the relatively high total and oxidizable concentrations of particulate chromium in sediments of the Aromas Red Sands aquifer are consistent with the relatively high total dissolved chromium and Cr(VI) concentrations in that aquifer.

Particulate Iron Distributions. Total iron concentrations in the sediments suggest that the oxidation of Cr(III) to Cr(VI) is more favorable in the Aromas Red Sands aquifer than in the Purisima aquifer (Table 3). Those concentrations (dry weight) ranged from ~18.6 to 55.6 mg g^{-1} in the Aromas Red Sands aquifer, and from ~5.6 to 23.9 mg g^{-1} in the Purisima aquifer. Up to 4% and 39% of the iron were extracted in the first four sequential extraction phases (Table 1) from the Aromas Red Sands and Purisima aquifers, respectively. Because the first four phases defined by the sequential extraction are the most likely phases to be involved in redox reactions occurring in these environments, quantifying the iron concentrations in each phase provides a measure of the redox potential of the two aquifers.

The comparison of the first four phases (Table 1) defined by the sequential extraction showed that sediments in the Aromas Red Sands aquifer had, on average, 800 μg g^{-1} of iron in the reducible phase and 250 μg g^{-1} in the oxidizable phase (i.e., 75% of the iron was associated with the reducible phase in the Aromas Red Sands aquifer). In contrast, sediments in the Purisima aquifer had, on average, 640 μg g^{-1} of iron in the reducible phase and 1000 μg g^{-1} in the oxidizable phase (i.e., 40% of the iron was associated with the reducible phase in the Purisima aquifer). The higher percentage of iron extracted in the reducible phase (i.e., bound to iron oxides) suggests that the Aromas Red Sands aquifer is under oxidizing conditions, while the Purisima aquifer is under reducing conditions.

Particulate Manganese Distributions. Total manganese concentrations in sediments from the two aquifers further suggest that the formation of Cr(VI) was favored in the Aromas Red Sands aquifer (Table 3). Those concentrations (dry weight) ranged from ~400 to 1200 μg g^{-1} in the Aromas Red Sands aquifer, with one exception (AOCI), and from ~80 to 400 μg g^{-1} in the Purisima aquifer. Moreover, while only ~30% of that manganese was in the residual phase of the Aromas Red Sand aquifer, ~70% of that manganese was in the residual phase of the Purisima aquifer. Consequently, both the relatively high total and relative oxidizable concentrations

TABLE 3. Summary of Metal Concentrations (μg g^{-1}) by Sequential Extraction Scheme as Delineated in Table 1

		fraction 1			fraction 2			fraction 3			fraction 4			fraction 5			total (fraction 1−5)		
sample ID	depth (m)	Cr	Mn	Fe	Cr	Mn	Fe	Cr	Mn	Fe	Cr	Mn	Fe	Cr	Mn	Fe	Cr	Mn	Fe
Aromas-55	16.8	< 0.055[a]	6.35E+01	< 0.013[a]	< 0.055[a]	2.51E+02	2.64E+01	1.85E+00	4.17E+02	1.04E+03	6.59E+00	2.51E+02	4.57E+02	1.01E+02	2.43E+02	3.11E+04	1.09E+02	1.23E+03	3.26E+04
Aromas-135	41.1	< 0.055[a]	1.06E+01	< 0.013[a]	< 0.055[a]	5.48E+01	6.07E−01	8.99E−01	1.30E+02	6.52E+02	1.98E+00	7.67E+01	1.84E+02	3.39E+01	1.26E+02	2.15E+04	3.68E+01	3.98E+02	2.23E+04
Aromas-285	86.9	< 0.055[a]	9.66E+00	< 0.013[a]	< 0.055[a]	2.84E+02	3.09E+00	1.07E+00	1.40E+02	5.10E+02	2.84E+00	1.36E+02	1.76E+02	1.04E+02	2.78E+02	4.48E+04	1.08E+02	8.49E+02	4.55E+04
Aromas-385	117.3	< 0.055[a]	1.29E+01	< 0.013[a]	< 0.055[a]	1.60E+02	1.33E+00	6.91E+00	2.05E+02	9.18E+02	4.89E+00	1.46E+02	1.53E+02	8.32E+01	2.47E+02	3.71E+04	9.50E+01	7.72E+02	3.81E+04
Aromas-435	132.6	< 0.055[a]	1.18E+01	< 0.013[a]	< 0.055[a]	2.25E+02	4.35E+00	2.27E+00	2.20E+02	1.07E+03	6.03E+00	2.13E+02	3.59E+02	1.19E+02	3.64E+02	5.42E+04	1.28E+02	1.04E+03	5.56E+04
Aromas-AOC1	0.9	< 0.055[a]	2.10E−01	1.65E+00	< 0.055[a]	2.34E+00	< 0.013[a]	2.74E+00	1.78E+01	5.76E+02	6.21E+00	7.08E+00	1.32E+02	7.09E+01	1.01E+02	1.79E+04	7.98E+01	1.29E+02	1.86E+04
Purisima-1040	250.0	< 0.055[a]	6.08E−01	< 0.013[a]	< 0.055[a]	2.69E+00	< 0.013[a]	1.17E+00	2.64E+01	2.69E+02	3.13E+00	2.17E+01	6.87E+01	2.83E+01	1.26E+02	1.42E+04	3.26E+01	1.78E+02	1.45E+04
Purisima-1217	317.0	< 0.055[a]	7.71E−01	< 0.013[a]	< 0.055[a]	6.29E+00	< 0.013[a]	2.63E+00	2.22E+01	5.14E+02	4.31E+00	2.91E+01	7.19E+01	5.51E+01	1.80E+02	2.33E+04	6.21E+01	2.38E+02	2.39E+04
Purisima-1310	370.9	< 0.055[a]	3.54E+01	5.32E+00	< 0.055[a]	6.09E+00	1.36E+02	6.12E−01	5.65E+00	2.12E+03	1.03E+00	8.76E+00	5.20E+02	6.17E+01	3.38E+02	1.65E+04	6.33E+01	3.94E+02	1.93E+04
Purisima-1700	399.3	< 0.055[a]	1.97E+01	3.23E−02	< 0.055[a]	3.24E+00	5.08E+01	2.74E−01	2.29E+00	4.64E+02	4.60E−01	1.55E+01	1.64E+03	1.82E+01	3.85E+01	3.46E+03	1.89E+01	7.92E+01	5.61E+03
Purisma-770	518.2	< 0.055[a]	2.78E+00	5.97E+00	< 0.055[a]	3.08E+01	3.56E−01	5.70E−01	2.82E+01	4.64E+02	6.94E−01	2.72E+01	3.78E+03	2.05E+01	1.79E+02	1.16E+04	2.18E+01	2.68E+02	1.59E+04

[a] Analyte not detected above the limit of detection shown.

of particulate manganese in the Aromas Red Sand aquifer also evidence its greater capacity to form and solubilize Cr(VI) than that of the Purisima aquifer.

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Literature Cited

(1) IARC. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Chromium, Nickel, and Welding;* International Agency for Research on Cancer, World Health Organization, 1990.

(2) Eary, L. E.; Rai, D. Kinetics of chromium(III) oxidation to chromium(VI) by reaction with manganese-dioxide. *Environ. Sci. Technol.* **1987**, *21* (12), 1187−1193.

(3) Sass, B. M.; Rai, D. Solubility of amorphous chromium(III)−iron(III) hydroxide solid-solutions. *Inorg. Chem.* **1987**, *26* (14), 2228−2232.

(4) Eary, L. E.; Rai, D. Kinetics of chromate reduction by ferrous-ions derived from hematite and biotite at 25-degrees-C. *Am. J. Sci.* **1989**, *289* (2), 180−213.

(5) Richard, F. C.; Bourg, A. C. M. Aqueous geochemistry of chromium—a review. *Water Res.* **1991**, *25* (7), 807−816.

(6) Rai, D.; Eary, L. E.; Zachara, J. M. Environmental chemistry of chromium. *Sci. Total Environ.* **1989**, *86* (1−2), 15−23.

(7) Todd Engineers. *Source Water Assessment of Soquel Creek Water District Aromas Red Sands Aquifer Wells*; Todd Engineers, Inc., 2002.

(8) Tessier, A.; Campbell, P. G. C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace-metals. *Anal-.Chem.* **1979**, *51* (7), 844−851.

(9) Gouws, K.; Coetzee, P. P. Determination and partitioning of heavy metals in sediments of the Vaal Dam system by sequential extraction. *Water Sci.* **1997**, *23* (3), 217−226.

(10) DWR. *California's Groundwater Bulletin 118*; Department of Water Resources, 2003.

(11) Allen, J. E. *Geology of the San Juan Bautista Quadrangle California*; Division of Mines Bulletin 133, 1946, 112 pp.

(12) H. Esmail & Associates. *Nonpoint sources of groundwater pollution in Santa Cruz and Monterey Counties, California*; H. Esmail & Associates Inc., 1978.

(13) Hanson, R. T. *Geohydrological Framework of recharge and seawater intrusion in the Pajaro Valley, Santa Cruz and Monterey Countries, California;* U.S. Geological Survey, 2003.

(14) Muir, K. S.; Johnson, M. J. *Classification of ground-water recharge potential in three parts of Santa Cruz County, California*; U.S. Geological Survey, 1979.

(15) Hanson, R. T.; Everett, R. R.; Newhouse, M. W.; Crawford, S. M. *Geohydrology of a deep-aquifer system monitoring-well site at Marina, Monterey County, California;* Geological Survey, 2002.

(16) Clark, J. C. *Preliminary geologic and gravity maps of the Santa Cruz-San Juan Bautista area, Santa Cruz, Santa Clara, Monterey, and San Benito Counties, California*; U.S. Geological Survey, 1970.

(17) Creasey, C. L.; Flegal, A. R. Elemental analyses of goundwater: demonstrated advantage of low-flow sampling and trace-metal clean techniques over standard techniques. *Hydrogeol. J.* **1999**, 7 (2), 161−167.

(18) Djane, N. K.; Ndung'u, K.; Johnsson, C.; Sartz, H.; Tornstrom, T.; Mathiasson, L. Chromium speciation in natural waters using serially connected supported liquid membranes. *Talanta* **1999**, *48* (5), 1121−1132.

(19) Ndung'u, K.; Djane, N. K.; Malcus, F.; Mathiasson, L. Ultrasonic extraction of hexavalent chromium in solid samples followed by automated analysis using a combination of supported liquid membrane extraction and UV detection in a flow system. *Analyst* **1999**, *124* (9), 1367−1372.

(20) Bartlett, R. J. Chromium cycling in soils and water—links, gaps, and methods. *Environ. Health Perspect.* **1991**, *92*, 17−24.

(21) Henderson, T. Geochemical reduction of hexavalent chromium in the Trinity Sand aquifer. *Ground Water* **1994**, *32* (3), 477−486.

(22) Loyaux-Lawniczak, S.; Lecomte, P.; Ehrhardt, J. J. Behavior of hexavalent chromium in a polluted groundwater: redox processes and immobilization in soils. *Environ. Sci. Technol.* **2001**, *35* (7), 1350−1357.

(23) Fetter, C. W. *Applied Hydrology*; Prentice-Hall: Upper Saddle River, NJ, 2001.

(24) Sedlak, D. L.; Chan, P. G. Reduction of hexavalent chromium by ferrous iron. *Geochim. Cosmochim. Acta* **1997**, *61* (11), 2185−2192.

(25) James, B. R.; Bartlett, R. J. Behavior of chromium in soils. 6. Interactions between oxidation−reduction and organic complexation. *J. Environ. Qual.* **1983**, *12* (2), 173−176.

(26) James, B. R.; Bartlett, R. J. Behavior of chromium in soils. 7. Adsorption and reduction of hexavalent forms. *J. Environ. Qual.* **1983**, *12* (2), 177−181.

(27) Kozuh, N.; Stupar, J.; Gorenc, B. Reduction and oxidation processes of chromium in soils. *Environ. Sci. Technol.* **2000**, *34* (1), 112−119.

(28) Schroeder, D. C.; Lee, G. F. Potential transformations of chromium in natural-waters. *Water, Air, Soil Pollut.* **1975**, *4* (3−4), 355−365.

(29) Dreiss, S. J. Chromium migration through sludge-treated soils. *Ground Water* **1986**, *24* (3), 312−321.

(30) Bartlett, R. J.; Kimble, J. M. Behavior of chromium in soils. 1. Trivalent forms. *J. Environ. Qual.* **1976**, *5* (4), 379−383.

(31) Bartlett, R. J.; Kimble, J. M. Behavior of chromium in soils. 2. Hexavalent forms. *J. Environ. Qual.* **1976**, *5* (4), 383−386.

(32) Bartlett, R.; James, B. Behavior of chromium in soils. 3. Oxidation. *J. Environ. Qual.* **1979**, *8* (1) 31−35.

(33) Adriano, D. C. *Trace Elements in the Terrestrial Environments*; Springer-Verlag: New York, 1986.

(34) Morgan, J. J.; Stumm, W. *Aquatic Chemistry*, 2 ed.; John Wiley & Sons, Inc.: NJ 1981.

(35) Amacher, M. C. Institute for Research on Land and Water Research, Redox reactions involving chromium, plutonium and manganese in soils. Pennsylvania State University, 1982.

(36) Fendorf, S. E.; Zasoski, R. J. Chromium(III) oxidation by δ-MnO_2. 1. Characterization. *Environ. Sci. Technol.* **1992**, *26* (1), 79−85.

(37) Shacklette, H. T., Hamilton, J. C., Boerngen, J. G., and Bowles, J. M Elemental composition of surficial materials in the United States Paper #574-D. U.S. Geological Survey, 1971.

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