Agenda Sacramento Suburban Water District **Government Affairs Committee**

3701 Marconi Avenue, Suite 100 Sacramento, CA 95821

Friday, August 21, 2015 $4:00$ p.m.

Public documents relating to any open session item listed on this agenda that are distributed to the Committee members less than 72 hours before the meeting are available for public inspection in the customer service area of the District's Administrative Office at the address listed above.

The public may address the Committee concerning any item of interest. Persons who wish to comment on either agenda or non-agenda items should fill out a Comment Card and give it to the General Manager. The Committee Chair will call for comments at the appropriate time. Comments will be subject to reasonable time limits (3 minutes).

In compliance with the Americans with Disabilities Act, if you have a disability, and you need a disability-related modification or accommodation to participate in this meeting, then please contact Sacramento Suburban Water District Human Resources at 679-3972. Requests must be made as early as possible and at least one-full business day before the start of the meeting.

Call to Order

Roll Call

Public Comment

This is an opportunity for the public to comment on non-agenda items within the subject matter jurisdiction of the Committee. Comments are limited to 3 minutes.

Items for Discussion and Action

1. Regional Water Authority Legislation Goals Receive written staff report.

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- 2. Hexavalent Chromium 6 Update Receive written staff report.
- 3. Development of Regulations to Implement the Sustainable Groundwater Management Act of 2014 (SGMA) and Potential 2015 Groundwater Legislation Receive written staff report.

Government Affairs Committee August 21, 2015 Page 2 of 2

Adjournment

Upcoming Meetings:

Friday, August 28, 2015 at 3:00 p.m., Finance and Audit Committee meeting Thursday, September 3, 2015 at 5:00 p.m., Facilities and Operations Committee Meeting Monday, September 21, 2015 at 6:30 p.m., Regular Board meeting

I certify that the foregoing agenda for the August 21, 2015, meeting of the Sacramento Suburban Water District Government Affairs Committee was posted by August 18, 2015 in a publiclyaccessible location at the Sacramento Suburban Water District office, 3701 Marconi Avenue, Suite 100, Sacramento, California, and was made freely available to the public.

> Robert S. Roscoe **General Manager/Secretary** Sacramento Suburban Water District

Government Affairs Committee

Agenda Item: 1

Date: August 18, 2015

Regional Water Authority Legislation Goals Subject:

Staff Contact: Dan York, Assistant General Manager

As previously reported the Sacramento Regional Water Alliance's contract lobbying effort with the Fernandez Government Solutions is being transitioned to a subscription program under the Regional Water Authority (RWA). The seven water purveyor members of the Program (the Cities of Sacramento, Roseville and Folsom, San Juan Water District, Carmichael Water District, Placer County Water Agency and SSWD) unanimously endorsed this transition.

The Program work commenced in January 2015 and will continue through December 2016, with the option to continue for a subsequent, but undefined duration. A new scope of work may be developed at least annually to guide the Program. Currently ten participants are submitting to the Program. The Program costs consist of monthly retainer payments to the Fernandez Government Solutions legislative advocacy and related services, plus reimbursement of approved expenses and miscellaneous ancillary work by other vendors.

The RWA developed a draft work plan for 2016, attached to this report as Exhibit 1. The members of the Program decided it would be beneficial to develop Regulatory and Policy Principles that would be included as part of RWA's Legislative Advocacy Program. A planning workshop was held on July 15, 2015. The workshop was very productive in developing Priority Issues and Policy Principles, which resulted in the following draft Priority Issues that were identified, also attached as Exhibit 2:

- Ensure a Diverse, Resilient, and Reliable Water Supply
- Promote Water Efficiency and Water Conservation
- Promote Balanced Statewide Water Management Solutions Beneficial to the Greater Sacramento Region
- Protect the Water Rights and Entitlements of RWA Member Agencies
- Maximize Funding Opportunities Beneficial to RWA Member Agencies \bullet
- Support Stewardship of the Regions Environmental Resources \bullet

The Priority Issues is still a work in progress and in particular, many of the "policy principles" still need refinement.

Regional Water Authority Legislation Goals August 18, 2015 Page 2 of 2

Strategic Plan Alignment

Leadership $-$ 5.A. Engage in legislative affairs on issues affecting the District.

Leadership $-$ 5.B. Engage in a leadership role with professional water industry groups to enhance proficiency in technical and policy matters.

Leadership - 5.C. Participate in regional, statewide and national water management partnerships.

Leadership – 5.D. Provide leadership within the community in a positive and progressive manner for the mutual benefit of the area (service groups, adjacent water purveyors, county/city/local government).

By participating in the subject Program, the District is able to assist in enhancing RWA's ability to advocate on behalf of its Members and the Sacramento Region on legislative and regulatory matters. This is a benefit to the District's customers based on the value of well-developed relationships with members of the state legislature and administration, active engagement on legislative and regulatory matters, development of a broad base of support, and the role of RWA as a regional representative to advance the region's interests in the water supplies, economic vitality, environmental sustainability, and quality of life of the greater Sacramento metropolitan area.

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EXHIBIT₁

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EXHIBIT 2

RWA Legislative and Regulatory Advocacy Program

Introduction

The Regional Water Authority (RWA) Legislative and Regulatory Advocacy Program (Advocacy Program) has been created as part of the commitment to regional collaboration and unity in pursuit of the region's common goals as acknowledged by the "RWA 2018+ Strategic Plan". The intent of the Advocacy Program is to positively influence legislative and regulatory actions to protect, preserve and financive the region's water supply reliability.

This advocacy effort takes on many forms including high level commitment to increasing the region's profile in California water politics; a focused and agreed upon set of priorities; a clear and resolute set of Policy Principles to guide advocacy positions and decisions; and fostering beneficial coalitions with allied organizations. The success of these advocacy efforts will be directly linked to maintaining the level of excellence this region has demonstrated in the stewardship of our water resources. This stewardship has resulted in the preservation and enhancement of our focal watersheds; protection of a federally designated Wild and Scenic River running through a metropolitan area of over 2 million people (the lower American River); and a reliable and diverse water supply supporting the growth of the local economy.

The Priority Issues and companion Policy Principles that are adopted by the RWA Board and included herein serve as the foundation for RWA's Advocacy Program. The Priority Issues are the long standing, foundational issues that are at the core of RWA's mission and stand the test of time. An examble of a Priority Issue adopted as part of the Advocacy Program is the "protection of the water rights and entitlements of RWA member agencies". Wigilant protection of these valuable, local assets will be a perpetual priority for RWA and its member agencies. The Policy Principles that support each of the Priority Issues are also long-term in nature though the RWA Advocacy Program should carefully consider and modify these on a regular basis to stay abreast of the ever-changing politics of california's water resources management.

Combined, the Priority Issues and Policy Principles adopted by the Board serve as the guidelines and road map for development of an annual legislative and regulatory advocacy platform. They allow RWA staff and member agencies to operate within an agreed upon set of guidelines when advocating for the region's common goals. (Currently, a contract lobbyist paid for by 10 RWA member agencies supports the Advocacy Program, and the program is staffed on a half-time basis. Consistent with the Strategic Plan, it is a goal of RWA to eventually support full-time staffing and expand participation in funding the lobbyist.)

Following the Priority Issues and Policy Principles are the guidelines the Advocacy Program will use for determining recommended positions and prioritizing legislation that is introduced as part of each legislative session.

RWA Legislative and Regulatory Advocacy Program

Finally, this document includes an overview of the California legislative process and calendar, as well as an overview of key state agencies in which we engage.

Priority Issues

Ensure a Diverse, Resilient, and Reliable Water Supply

Conjunctive use of surface and groundwater resources along with cost-effective investments in recycled water, stormwater capture, water efficiency, and water conservation can significantly drought proof the region's water supply, protect the region's water resources and environment, and assure the continued growth of the region's economy.

Policy Principles

- Promote legislative and regulatory measures that enhance local agencies ability to share regional water resources.
- Support and participate in Folsom Reservoir and Central Valley Project operational improvements to assure a reliable surface water supply to RWA agencies.
- Develop infrastructure necessary to access surface water entitlements.
- Advance efforts to streamline CEQA compliance for water resource projects that diversify or strengthen this regions water supply reliability.
- Promote and support amendments to SGMA and development of regulations that enhance water supply reliability and protect groundwater resources.
- Support measures that help expedite and cost-effectively integrate new water resources such as stormwater reuse and recycled water into the regions water supply portfolio.
- Continue to incréase conjunctive use capabilities within the region.
- Sponsorand/or support legislation that quarantees investments made in regional water supply reliability and drought resilience are available for their intended purposes.
- Support cost-effective surface water and groundwater storage projects.

Protect the Water Rights and Entitlements of RWA Member Agencies

Water rights issues are complex and contentious. This region's surface water rights and entitlements and long-standing management of groundwater resources have been critical in the shaping of the local economy and are vital for the future. Our reasonable use of water has and will continue to assure the region's water rights and entitlements provide the region with abundant. affordable and high quality water while maintaining and protecting the environmental resources of the Lower American River and the region's watersheds.

Policy Principles

- Support and defend the existing water rights priority system.
- Support enforcement of the existing water rights laws.
- Maintain area-of-origin protections.
- Oppose any unreasonable curtailments of our area's water rights that impact our beneficial use of water.
- Promote legislation that supports and clarifies the multiple beneficial uses of water.
- Support legislation and regulatory action that allows for retaining groundwater rights.
- Support new laws, policies, and regulations embracing the concept that recognize therent regional differences that drive water use efficiency and conservation?
- Ensure that water rights are preserved in the context of conserving water.
- Promote system operations that ensure delivery of water supplies based on water rights and contract obligations.
- Proactively engage with the SWRCB on the Delta tributary flow process.

Maximize Funding Opportunities Beneficial to RWA Member Agencies

The region is prepared to make and support investments that will improve water supply reliability and protect the environment, including the Lower American River. Large-scale infrastructure projects such as improvements at Folsom Reservoir, increased or new storage capacity, additional facilities on the Sacramento River, and expanded groundwater, recycled water, transmission and distribution facilities will help prepare the region for the future while protecting the environment and increasing water supply reliability.

Policy Principles

- Actively engage in legislative and regulatory initiatives that consider the development of a public goods charge.
	- o Develop RWA policy on public goods charges.
- Assure that any funding that is extracted from this region be returned to this region for the benefit of this region.
- Support policies that provide funding allocations based on merit of the project and the impact or benefit.
- Promote the statewide benefits that our actions provide due to our unique location within the State's water system.
- Support Proposition 218 reform that improves water agencies ability to fund programs that help diversify the region's water supply portfolio.
	- Develop RWA policy on Proposition 218 reforms.
- Promote statewide funding to increase flexibility for the CVP.
- \bullet Support legislation that provides funding for local and regional water resources infrastructure projects.
- Support funding for agencies to develop and utilize storm water capture projects.

Ensure state funding is available for state imposed mandates.

Promote Balanced Statewide Water Management Solutions Beneficial to the Greater Sacramento Region

RWA recognizes the need for a statewide water plan that assures a reliable water supply for all regions in the state. RWA supports a statewide solution, including protection of the Delta, that is balanced and beneficial to the

Sacramento region's water supply reliability.

Policy Principles

- Ensure improvements or modifications to the statewide water system are protective of this region's water supply.
- Support statewide water plans and policies that recognize and honor previous investments made to assure this region's water supply reliability.
- Promote a statewide drought action plan that acknowledges this region's investment in drought resiliency.
- Encourage revisions to policies and operations that streamline water transfers.
- Support statewide water stotage solutions that provide benefit or are neutral to the region's water supply reliability and flood protection.
- Encourage statewide water planning efforts that recognizes water management differs based on climate, population density, return flows, and other regional geographic and hydrologic factors.
- Promote modifications to state and federal operations that protect the region's ability to use regional resources.

Promote Water Efficiency and Water Conservation

Our region invests in water efficiency and water conservation that are locally cost effective, feasible, and improve the water supply reliability of the region. Water efficiency makes good business sense and is key to assuring we continue our reasonable use of water consistent with our water rights and contracts.

Policy Principles

- Unique factors such as climate, land use, and return flows must be taken into consideration when developing state wide laws and regulations.
- Promote policies that recognized the differences between water efficiency \bullet and water conservation.
- Promote a better understanding of water use efficiency based on local supplies and site-specific factors.
- Define appropriate water conservation requirements that consider local supplies.
- Develop partnerships with other local agencies on public affairs campaigns/messaging.
- Promote public-private partnerships with local businesses that lead to \bullet greater water efficiency and benefit the local economy.
- Support a state led effort to establish rate stabilization funds programs that are consistent with state laws.
- Assure that the region receives the benefit of its water conservation efforts.

Support Stewardship of the Region's Environmental Resources

The region's management of water resources is committed to the preservation of the Lower American River (LAR) and tributary watersheds as demonstrated by the historic Water Forum Agreement enacted in 2000. The LAR is a federally designated Wild and Scenic River running through a metropolitan area of over 2 million people that still supports one of the prime cold water fisheries in the State and is home to Chinook Salmon and threatened Central Valley Steelhead.

Policy Principles

- Support flow management standards that protect the ecosystem of the Lower American River, prevent dead pool conditions in Folsom Reservoir, and improve flood safety.
- Promote legislative and regulatory initiatives supporting conjunctive use that will make more surface water available for the Lower American River in dry years.
- Implement infrastructure projects that will improve temperature control and access to cold water at Folsom Reservoirs

RWA Legislative Analysis Process

Process for Adopting Positions on Introduced Legislation

The Priority Issues and Policy Principles will be adopted by the RWA Board and serve as the Legislative Platform, for which RWA works from in the legislative and regulatory arenas.

Each new legislative session, RWA staff and the contract lobbyist will screen newly introduced legislation using the adopted legislative platform as a guide. Bills that are relative to RWA's legislative platform or are otherwise considered noteworthy to RWA interests are presented to the Lobbyist Subscription Program (LSP) Committee for analysis and consideration.

Through this collaborative process, the LSP Committee determines a recommended position on each bill and then assigns a priority (see the list of formal positions and priorities below). During this process, bills may be removed from further consideration and additional bills may be added to RWA's list based on input from the LSP Committee or other factors. The Committee's

RWA Legislative Analysis Process (Continued)

recommendations are taken to the RWA Executive Committee for further discussion and approval, consistent with RWA Policy 100.5.

Many of these initial positions and priorities will change as bills are amended throughout the course of the legislative process. The LSP Committee will be routinely updated on the status of bills as they move through the legislative process and will decide upon changes in position and priority as the process dictates. In time sensitive situations, RWA staff may change a current position and/or priority with the approval of the RWA Executive Director and concurrence of general counsel. Such changes will be done using the adopted Legislative Platform as guidance. The LSP Committee will be updated of changes as soon as possible and the Executive Committee will be asked to ratify such changes at its first meeting following the changes.

Formal Positions

Support - A bill that would benefit RWA or one of more RWA members (without detriment to others), and/or is generally good public policy

Support if Amended - A bill that could benefit RWA, or one or more RWA members, if amended. This position implies that RWA is ready to offer specific amendments.

Oppose - A bill detrimental to RWA or one or more RWA members.

Oppose Unless Amended A bill that is detrimental to RWA or one or more RWA members, that could be amended to remove the detrimental provisions. This position implies that RWA is ready to offer specific amendments, and will move to a neutral position if accepted.

Watch - A bill of interest to RWA and its members that does not affect RWA directly, or for other reasons does not yet merit a position. May be a "spot" or "intent" bill that does not yet have meaningful language.

Neutral - Generally a bill from which we have removed an Oppose or Oppose Unless Amended position due to amendments or other factors.

RWA Legislative Analysis Process (Continued)

RWA Legislative and Regulatory Advocacy Program

Bill Priorities

High Priority - A bill of major significance with direct impact to RWA or a number of RWA members. RWA has a formal position and is actively lobbying, writing letters, offering amendments, testifying in committee, and taking other direct

actions as necessary. "Watch" bills can be considered high priority, especially early in the legislative process, depending on the topic, the author, or other factors that warrant heightened monitoring.

Medium Priority - A bill of interest but not anticipated to have major significance to RWA or more than a few of its members. RWA has a formal position but is not actively lobbying legislators. RWA and/or RWA members may submit letters, provide testimony or take other actions as part of other groups of coalition or, in some situations, directly. Individual RWA members may be more active depending on the topic of the bill.

Low Priority - A bill in an area of interest to RWA but with little potential impact. RWA will only have a Watch position on such bills. No immediate action is planned but these bills will be monitored to assure they don't evolve into a high priority status. Individual RWA members may be more active depending on the nature of the bill.

The California Legislative Process Calendar

January - February

- Bills are introduced in their houses of origin. Most bills first go to the \bullet Legislative Counsel's Office where they are drafted into formal legislative language.
- Deadline for introducing bills to be heard that year is the end of the third week of February.
- Bill is given a "first reading" in its house of origin.

March - April

- Bills are heard in their respective policy committees. \bullet
	- \circ Bills with a fiscal impact must be outby the beginning of May.
	- Bills without fiscal impact must be out by the beginning of the second week of May

May

- Fiscal committees in house of origin hear bills
- Bills go to the "floor" for vote by full house be last week of May. \bullet

June - August

- Process is repeated in the other house.
	- o June through mid- August in policy committees
	- Second half of August considered by fiscal committees. \circ

September

- Floor sessions held in both houses,
- All bills must be out of the legislature and to the Governor's desk by end of second week of September.
- Governor has until the end of September to act on bills.

RWA Legislative and Regulatory Advocacy Program

State Regulatory Agencies and Processes

State Water Resources Control Board

- \circ Water Rights
- o Water Conservation
- o Drinking Water Program
- \circ Grants
- Discharge Programs (through the Regional Water Quality Control Boards)

Department of Water Resources

- o Sustainable Groundwater Management Act Regulations
- o Water Efficiency
- o State Water Project
- o Grants IRWM

Government Affairs Committee

Agenda Item: 2

August 18, 2015 Date:

Subject: Hexavalent Chromium 6 Update

Staff Contact: Dan York, Assistant General Manager

Background

As previously reported, the State Water Resources Control Board, formerly the California Department of Public Health, established the first ever drinking water maximum contaminant level (MCL) for Hexavalent Chromium (HC) at 10 parts per billion (ppb). Implementation of this new drinking water standard for HC began on July 1, 2014.

Due to the new regulation, water purveyors statewide, including Sacramento Suburban Water District (District), began analyzing groundwater sources for HC. This new wave of data has allowed water purveyors, as well as regional authorities such as the Sacramento Groundwater Authority (SGA), to gain a better understanding of the concentrations of HC in groundwater throughout the region. Results from samples analyzed in November 2013 and April 2014 indicate the HC concentration in the majority of District wells is less than 5.0 ppb. However, eighteen District wells have concentrations between 5.0 ppb and 8.5 ppb, and seven wells exceeded the new MCL of 10 ppb, with the highest at 17 ppb.

Discussion

There are water purveyors statewide that have a large percentage of their water supplies that exceed the new MCL for HC, including Rio Linda/Elverta Community Water District (RLECWD). As a result, RLECWD contracted with Wood Rodgers to conduct a study of the occurrence of HC in Northern Sacramento County. Wood Rodgers discovered an increase in the HC concentration in wells that are in close proximity to the former McClellan Air Force Base (McClellan). These findings were reported to the SGA by Wood Rodgers.

It is well known that historical activities at McClellan have resulted in contamination of the groundwater sources in the area. Efforts to remediate this contamination included extraction and treatment of the groundwater to remove volatile organic compounds. It should be noted that all 7 District wells with HC concentrations above the MCL are in close proximity to McClellan.

Hexavalent Chromium 6 Update August 18, 2015 Page 2 of 3

The Central Valley Regional Water Control Board (CVRWCB) issued a letter stating they communicated their concerns to the Air Force in comments in the McClellan Five-Year Report that was completed prior to the rule making process of HC. The Air Force has informed the CVRWCB that they will update the human health risk assessment and conduct an evaluation and report findings by fall of 2015.

On August 13, 2015, Assemblymember Kevin McCarty held a Safe Drinking Water Town Hall meeting in Rio Linda to inform the public of the new HC standard and had panel members participate in the discussions. The panel members consisted of staff from RLECWD, State Water Board, U.S. EPA and California EPA Department of Toxic Substance Control.

Rob Swartz, SGA, has provided staff with an update on information that he recently received related to the occurrence of HC in the region. He was provided two articles, attached as Exhibit 1 & 2. The first article by Jean Morrison et al was published in 2009 and presents the results of a soil geochemical survey of chromium and nickel in soils in our region. The second article, by Andrew Manning et al, is in press at this time. It looks at the occurrence and controls of HC in the Sacramento Valley and hypothesizes that HC in our region is naturally occurring. While these articles do not eliminate the possibility that contamination from McClellan is showing up in some production wells, they do offer a plausible alternative that elevated HC in this region could be naturally occurring.

SGA is continuing to coordinate with the RWQCB to ensure that the extent of HC associated with known activities at McClellan is fully characterized. It is encouraging that the RWQCB is requiring McClellan to resample the wells that were used to determine background about a decade ago. If the HC is naturally occurring, concentrations should not have changed much. If they were from the releases at McClellan, the sampling results may show change through time.

Public water systems are committed to meeting the standard, which is the first of its kind in the nation, but the timeline provided for compliance does not recognize the complex steps that some water systems must take to achieve the standard. The steps involved, from designing appropriate treatment systems to securing financing to building and testing new treatment facilities, can take up to five years or more and cost millions of dollars. To address this challenge, Senator Ben Hueso introduced SB 385, which would establish a carefully monitored process for public water systems to work toward and achieve compliance with the new HC standard. SB 385 was passed unanimously by the Assembly Appropriations Committee on July 15, 2015.

The only significant change to this bill is the original date set for compliance. The bill originally stated an approved compliance plan would extend to January 1, 2020. The bill now states comments may include requiring the public water system's compliance with the primary drinking water standard for HC if the earliest feasible date, based on review of the compliance plan and based on the public water system's specific circumstances identified in the plan, is prior to January 1, 2020.

Hexavalent Chromium 6 Update August 18, 2015 Page 3 of 3

On July 31, 2015, a Request for Proposal for a HC Management Study was sent to eight consulting firms soliciting services to provide technical, mitigation and management strategies for complying with the HC standard.

Strategic Plan Alignment

1. Water Supply (D) – Manage the District's water supplies to ensure their quality and quantity.

Adequate supplies of uncontaminated groundwater are crucial to the health of District customers.

EXHIBIT 1

Applied Geochemistry 24 (2009) 1500-1511

A regional-scale study of chromium and nickel in soils of northern California, USA

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ARTICLE INFO

Available online 3 May 2009

Article history:

ABSTRACT

A soil geochemical survey was conducted in a 27,000-km² study area of northern California that includes the Sierra Nevada Mountains, the Sacramento Valley, and the northern Coast Range. The results show that soil geochemistry in the Sacramento Valley is controlled primarily by the transport and weathering of parent material from the Coast Range to the west and the Sierra Nevada to the east, Chemically and mineralogically distinctive ultramafic (UM) rocks (e.g. serpentinite) outcrop extensively in the Coast Range and Sierra Nevada. These rocks and the soils derived from them have elevated concentrations of Cr and Ni. Surface soil samples derived from UM rocks of the Sierra Nevada and Coast Range contain 1700-10,000 mg/kg Cr and 1300-3900 mg/kg Ni. Valley soils west of the Sacramento River contain 80-1420 mg/kg Cr and 65-224 mg/kg Ni, reflecting significant contributions from UM sources in the Coast Range. Valley soils on the east side contain 30-370 mg/kg Cr and 16-110 mg/kg Ni. Lower Cr and Ni concentrations on the east side of the valley are the result of greater dilution by granitic sources of the Sierra Nevada.

Chromium occurs naturally in the Cr(III) and Cr(VI) oxidation states. Trivalent Cr is a non-toxic micronutrient, but Cr(VI) is a highly soluble toxin and carcinogen. X-ray diffraction and scanning electron microscopy of soils with an UM parent show Cr primarily occurs within chromite and other mixed-composition spinels (Al, Mg, Fe, Cr). Chromite contains Cr(III) and is highly refractory with respect to weathering. Comparison of a 4-acid digestion (HNO₃, HCl, HF, HClO₄), which only partially dissolves chromite, and total digestion by lithium metaborate (LiBO₃) fusion, indicates a lower proportion of chromite-bound Cr in valley soils relative to UM source soils. Groundwater on the west side of the Sacramento Valley has particularly high concentrations of dissolved Cr ranging up to 50 μ g L⁻¹ and averaging 16.4 μ g L⁻¹. This suggests redistribution of Cr during weathering and oxidation of Cr(III)-bearing minerals. It is concluded that regional-scale transport and weathering of ultramafic-derived constituents have resulted in enrichment of Cr and Ni in the Sacramento Valley and a partial change in the residence of Cr.

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1. Introduction

Serpentinites are compositionally ultramafic rocks formed through the subduction and alteration of peridotite and pyroxenite along convergent plate margins (Coleman and Jove, 1992; O'Handley, 1996; Oze et al., 2004b). Although serpentinites (and serpentine soils) comprise less than 1% of the earth's total exposed surface, they are relatively common along the western coast of North America (Oze et al., 2004b). Serpentinites cover approximately 2860 km², 1170 km², and 520 km² of the exposed land surface in California, Oregon and Washington, respectively (Kruckeberg, 1984) and potentially impact the geochemistry of much greater areas through transport and weathering. This study focuses on two major geological occurrences of serpentinites in

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California; those associated with the Coast Range Ophiolite (CRO) and those associated with the Western Metamorphic Belt (WMB) located in the western foothills of the Sierra Nevada (Fig. 1).

The process of serpentinization occurs as peridotite and pyroxenite rocks, which contain the Fe- and Mg-rich silicate minerals olivine $((Mg_1Fe^{2+})_2[Si_2O_4])$ and pyroxene $(XY(Si, Al)_2O_6)$, are altered by hydrothermal fluids as they are detached from the subduction block and incorporated into subduction mélanges (Coleman, 1967; Gough et al., 1989; O'Handley, 1996; Oze et al., 2004b). Hydration of pyroxene and olivine forms the serpentine group minerals; lizardite $(Mg_3Si_2O_5(OH)_4)$, chrysotile $(Mg_3Si_2O_5(OH)_4)$ and antigorite $((Mg, Fe^{2+})_3Si_2O_5(OH)_4)$. Other minerals commonly associated with serpentinites are magnetite ($Fe^{2+}Fe^{3+}_{2}O_{4}$), Cr-rich magnetite ($Fe^{2+}(Fe^{3+}, Cr)_{2}O_{4}$), chromite ($FeCr_{2}O_{4}$), and other mixed-composition spinels, talc (Mg₃Si₄O₁₀(OH)₂), chlorite $((Mg, Fe)_5Al[(OH)_8|AlSi_3O_{10}])$, tremolite $([Ca_2][Mg_5]](OH)_2[Si_8O_{22}])$, and brucite $(Mg(OH)_2)$ (Oze et al., 2004b).

E-mail address: jmorrison@usgs.gov (J.M. Morrison).

Fig. 1. Maps illustrating (a) the major physiographic provinces of California, with the study area outlined by the box, (b) shaded areas showing the extent of mapped ultramafic rocks in California, with outlines of counties for reference, and (c) close-up of study area showing lakes and rivers.

Serpentinite rocks are enriched in Cr and Ni, which have potential to adversely impact environmental and human health once they are mobilized by weathering into soil, water and dust. Nickel and Cr(III) can substitute for Mg or Fe in the octahedral sheet in olivine and pyroxene in peridotites, and in serpentine minerals (Oze et al., 2004b). Since pyroxene and olivine in peridotite weather more quickly than serpentine minerals (Alexander, 2004), the lability of Ni and Cr in rocks and soils derived from ultramafic sources in the study area may be a function of the degree of serpentinization. Chromium is mostly found in spinel minerals as chromian magnetite, chromite, and other mixed-composition spinels containing Al, Cr, Mg, and Fe (Oze et al., 2004b). Chromium may also be substituted into serpentine minerals in trace amount.

Although Cr associated with the mineral chromite is generally quite recalcitrant, studies have shown that a fraction of the total Cr can be found in the potentially more soluble hexavalent form (Becquer et al., 2003; Gough et al., 1989; Oze et al., 2004a, 2007; Robertson, 1975). Chromium and Ni are both micronutrients for plants and animals, but they are biological toxins at higher concentrations and are considered carcinogens primarily through the respiratory pathway (Goyer, 1996). Nickel occurs as Ni(II) in the environment; however, Cr commonly exists in the Cr(III) and Cr(VI) oxidation states. The dominant naturally-occurring form under reducing conditions is Cr(III), which in circum-neutral pH solutions occurs as various hydroxy-complexes; $CrOH²⁺$, $Cr(OH)⁺$ and Cr(OH)₃. Trivalent Cr has a relatively low solubility at circum-neutral pH and is readily sorbed onto Fe oxides. At higher concentrations, it can form oxide (Cr_2O_3) and hydroxide $(Cr(OH)_3)$ solids in natural environments. In contrast, Cr(VI) typically exists as a soluble oxyanion, $(CrO₄²$ or HCrO₄), and is thus more mobile in soils. The occurrence of Cr(VI) in soil is of concern because it is the chromate ion that is toxic and carcinogenic (Goyer, 1996; Katz and Salem, 1993; Kortenkamp et al., 1996). Previous studies have shown elevated Cr(VI) concentrations in groundwater within proximity of rocks and soils containing naturally-occurring Cr indicating that there is potential for redox cycling to occur in Cr(III)-dominated systems (Ball and Izbicki, 2004; Fantoni et al., 2002; Robertson, 1975; Robles-Camacho and Armienta, 2000).

Manganese oxides are thought to be the only environmentally relevant oxidizers of Cr(III), whereas S, Fe and organic matter are known Cr(VI) reducers (Bartlett and James, 1979; Eary and Rai, 1987; Fendorf, 1995; Negra et al., 2005). It is likely that any Cr(VI) generated as a result of reactions with Mn oxides would be soluble in groundwater or be re-reduced to Cr(III) and precipitated or adsorbed onto hydroxides/clays. Such sorbed Cr(III) is likely more reactive in oxidized systems than Cr(III) in more stable spinel minerals. Therefore, understanding the potential redox cycling of Cr during weathering and transport of ultramafic materials is important in determining the potential health risks associated with Crrich rocks and soils.

The purpose of this study was to understand chemical and mineralogical controls on the weathering of Cr and Ni from ultramafic rocks and the subsequent lability of Cr and Ni in sediments, soils and groundwaters as ultramafic materials are transported to the Sacramento Valley. Although previous studies have characterized individual ultramafic/serpentine units in California (Lee et al., 2003; Oze et al., 2004a, 2003), this study investigated the influence of serpentine-bearing sources on regional-scale soil geochemistry in the Sacramento Valley.

2. Study area

A soil geochemical survey was conducted across a 27,000-km² study area in northern California including the western Sierra Nevada, the Great Valley (specifically the Sacramento Valley), and the Coast Range (Fig. 1). The ultramafic rocks within the study area outcrop extensively in the Coast Range and the western foothills of the Sierra Nevada (Figs. 1 and 2). Ultramafic rocks in the Coast Range are part of a serpentinized Mesozoic ophiolite suite. The ophiolite structurally overlies the Franciscan Complex, a thick sequence of marine sediments tectonically emplaced during the subduction of the Farallon Plate along the continental margin. The Great Valley Sequence consists of a Cretaceous submarine fan that was shed off the ancestral Sierra Nevada and deposited into the forearc basin on top of oceanic crust, that is now the Coast Range Ophiolite (Carlson, 1984). In the Sierra Nevada foothills, serpentinites are associated with Mesozoic sedimentary and volcanic rocks in the western metamorphic belt that occurs along the western foothills of the Sierra Nevada (Kruckeberg, 1984).

Serpentine soils, a generic term used for soils derived from ultramafic source material, characteristically have low concentrations of essential plant nutrients (N, P and K) and low Ca: Mg ratios. The soils support sparse, unique vegetation termed serpentine chaparral that consists primarily of scrub oak and grasses (Gough et al., 1989; Oze et al., 2004b). Serpentine soils within the study area are Entisols, poorly developed, shallow and rocky (NRCS, 2004). Mean annual precipitation in upland areas containing serpentine soils is 500-1000 mm with precipitation generally greater in the Sierra Nevada foothills than the Coast Range. The Sacramento Valley receives 380-500 mm/a of precipitation (PRISM, 2007).

3. Methodology

3.1. Sample collection and preparation

Two sets of archived soil samples exist within the study area. One set consists of 1293 samples collected as part of the US Department of Energy's National Uranium Resource Evaluation (NURE) Program in the 1970s and early 1980s. These soils were specifically collected in 1979-1980 as part of the Hydrogeochemical and Stream Sediment Reconnaissance (HSSR) Program on a 1km grid spacing in the 1:250,000-scale Sacramento Quadrangle (Smith, 1997). At each site, the top 5 cm of plant material and soil were scraped off and a 10-15 cm depth sample was collected with a hand spade. Soil samples from at least 10 locations at least 3 m apart were combined as composite samples and sieved into two fractions; 40-18 mesh (400-1000 μ m) and <40 mesh (Price and Jones, 1979). Splits of the sieved soil samples were stored in plastic jars at the US Geological Survey in Denver, CO. For the present study all archived <40 mesh NURE soils collected in the Sacramento Quadrangle (Fig. 2a) were submitted for chemical analysis.

The second soil archive (Fig. 2a) was collected as part of the US Department of Agriculture Soil Conservation Service (now Natural Resources Conservation Service, NRCS) survey of benchmark soil pedons. The soils were collected by soil horizon and the <2-mm size fraction was archived in plastic vials in a warehouse at the University of California - Davis. Splits of the archived samples from 98 soil profiles were taken for chemical analysis as described below (Fig. 2). For comparison with NURE soil samples, only results for the surface soil samples (uppermost A horizon) are reported in this study.

New samples were collected (2004-2007) from serpentine soils in the Coast Range and Sierra Nevada foothills, along Cache Creek on the western side of the valley, and within the Sacramento Valley (Fig. 2). Samples were collected by soil horizon; however, for comparison with the two archived datasets, only data for the surface soils (uppermost A horizon) are reported in this study. Most samples were sieved to <2 mm in the field using stainless steel sieves. Some indurated clay-rich soils were collected as bulk samples and later disaggregated using an agate mortar and pestle and sieved to <2 mm in the lab. A comparison study of duplicate field- and laboratory-sieved samples showed no significant difference in bulk chemistry. Samples were air dried and ground for chemical analysis (Smith et al., 2005). Additionally, rock samples were collected from Coast Range and Sierra Nevada serpentinite and Great Valley Sequence rocks to compare parent material to soil samples.

3.2. Analyses

Chemical analysis of rock and soil samples, both those sieved to <2 mm and ground and those sieved to <40 mesh (0.4 mm) and ground, was determined by a 4-acid digestion (HNO₃, HCl, HF, HClO₄) followed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) (Briggs and Meier, 2002). The analyses were done by the USGS contract lab, SGS Minerals in Toronto, Ontario, Canada. Standard reference materials (SRMs) SRM 2709 (NIST) and DGPM-1 (USGS) as well as four USGS-produced SRMs were used to monitor the digestion procedure. Smith et al. (2009) describes in detail the quality assurance/quality control methods used for USGS contract lab chemistry. Standards were analyzed at the rate of one SRM for every 10 samples. Sample duplicates were submitted at a rate of one for every 20 samples and analytical duplicate samples were analyzed at the frequency of one duplicate for every 20 samples. The accuracy was deemed acceptable if recovery was within the range 85-115% at five times the lower limit of detection and the calculated relative standard deviation of duplicate samples was no greater than 15%.

Previous studies have shown that acid digestions are not sufficient at reporting true totals for elements associated with refractory minerals-zircon, chromite and rutile. Therefore, additional analysis for 16 elements that included some of the more refractory elements was completed using a lithium metaborate fusion followed by ICP-AES at the USGS contract laboratory. The procedure fused 100 mg of ground soil/rock with lithium metaborate in a graphite crucible, followed by dissolution in HNO₃. The solutions were aspirated into the ICP-AES through a high-solids nebulizer and the elemental emission signal was measured simultaneously for all 16 elements (SGS Mineral Services). The SRMs listed for the 4-acid digestion/ICP-MS method were also used to monitor this procedure and the same acceptance criteria were applied for accuracy as well as the same ratio of sample and analytical duplicates. Lithium metaborate fusion/ICP-AES data is used when reporting total Cr values throughout this manuscript. Only a subset of the NURE soils was analyzed using lithium metaborate fusion, thus a smaller dataset exists for total Cr relative to total Ni and acid-soluble Cr.

Mineralogy was determined for subsets of rock samples and <2mm fraction of soil samples collected between 2004 and 2006 using X-ray diffraction (XRD) and scanning electron microscopy (SEM). In order to obtain semi-quantitative mineralogical analyses, samples were hand ground, spiked with a 10% ZnO standard, and micronized (Eberl, 2002). A Siemens Diffraktometer D500 at the

Fig. 2. Maps showing study area with simplified geologic units and soil sample locations. Ultramafic rocks are shown in dark green and alluvium is shown in two shades of yellow. The graduated symbols show the location of soil samples, with size indicating (a) Ni concentrations in mg/kg and (b) Cr concentrations in mg/kg. Red symbols show NURE soils, green show Davis Archive soils and purple symbols represent samples collected as part of this study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

US Geological Survey (Denver, CO) was used to generate X-ray patterns between 5.0° and 65.0° with a generator potential of 40 kV and current of 30 mA with Cu K-alpha radiation. Mineral identification was obtained using Materials Data Inc. JADE software. Scanning electron microscopy was also used to identify mineral phases in the soil.

4. Results and discussion

Surface soil samples from the three datasets (the NURE and Davis archives and newly-collected samples) were grouped by associated parent material or region including: the serpentine soils of the Coast Range Ophiolite (CRO) and western metamorphic belt (WMB), soils associated with the Great Valley Sequence (GV), and soils located with the western and eastern Sacramento Valley alluvium (WSV and ESV, respectively). Serpentine soils from the archived datasets were identified as samples that were located within 1 km of mapped ultramafic rocks in the WMB (Fig. 2). No archived soils existed within the proximity of CRO, Valley soils were identified as those that were located within the mapped alluvium in the valley. For newly-collected samples, the authors collected rocks and soils from CRO and WMB serpentinite, the Great Valley Sequence, and Sacramento Valley soils. The Sacramento River is the boundary between WSV and ESV samples.

The Davis archive and newly collected soil samples consisted of the <2-mm size fraction, whereas the NURE soil archive consisted of the <0.4-mm fraction. Comparison of NURE samples to soils of a larger size fraction has the potential to introduce bias in the chemical data. Table 1 summarizes the range, mean, standard deviation, and median for Cr and Ni concentrations in rocks and soils by region (Morrison et al., 2008). The CRO and Great Valley groups were outside the extent of the NURE data, therefore no comparisons were made in those groups. However, NURE data was included for WSV, ESV and WMB soil groups. Nonparametric rank-sum tests were used to determine if there was a statistically-significant difference in the concentrations of total Cr, acid-soluble Cr, and Ni between the datasets (NEW, NURE, DAVIS) in each region (WSV, ESV, WMB). Those tests revealed that significant differences (significance level α < 0.05) between the sample groups exist for total Cr in the WSV, and for 4-acid digestible Cr and total Ni in the WMB. In the WSV, total Cr concentrations in the NURE samples are significantly higher (α < 0.05) than total Cr concentrations in both the NEW and Davis sample sets (Fig. 3). It is not yet evident if this is a function of grain size effect or another unidentified variable. In

Table 1

Statistical summary of rock and soil data by dataset for: Coast Range Ophiolite (CRO), Great Valley Sequence (GV), western Sacramento Valley (WSV), Eastern Sacramento Valley (ESV), and the western metamorphic belt (WMB). Datasets include: the NURE archive, the University of California, Davis archive, and newly-collected samples. The mean values were calculated as arithmetic means and Std Dev represents the standard deviation of the mean. Rows in bold lettering show the data used to classify groups presented in Figs. 4 and 7.

Group	Nickel (mg/kg)					Total chromium (mg/kg)					Acid-soluble chromium (mg/kg)				
	Number of samples	Range	Mean	Std Dev	Median [®]	Number of samples	Range	Mean	Std Dev	Median	Number of samples	Range	Mean	Std Dev	Median
CRO ⁻	G.	$235 -$	1600	1031	1752	6	1400-	2262	826	1910	6	$106 -$	434	291	341
rock		2841					3400					926			
CRO soil	12	512- 4060	2505	1139	2785	12	1200- 11,670	4464	3164	3860	12	$488 -$ 2610	1365	684	1175
New	12	$512 -$	2505	1139	2785	12	$1200 -$	4464	3164	3860	12	$488 -$	1365	684	1175
		4060					11,670					2610			
NURE	$\mathbf{0}$					$\mathbf{0}$					$\mathbf{0}$				
Davis	$\boldsymbol{0}$					$\mathbf{0}$					$\mathbf{0}$				
GV rock	14	$31.4 -$ 127	64.2	23,4	59.3	14	53-391	117	83.1	94.0	14	$33 - 125$	78.5	24.6	73.5
GV soil	4	$47.9 -$ 183	93.5	60.9	71.5	4	84-318	254	113	307	4	69-193	130	54	129
New	4	$47.9 -$ 183	93.5	60.9	71.5	4	84-318	254	113	307	4	69-193	130	54	129
NURE	0					$\mathbf{0}$					$\mathbf{0}$				
Davis	$\mathbf{0}$					O					$\mathbf{0}$				
WSV.	323	$12.7 -$	118	60	120	50	76-1420	396	298	252	323	$27 - 296$	130	49.4	139
soil		295													
New	6.	$61.1 -$ 205	137	64	144	$\overline{6}$	95-419	242	-122	225	6°	73-169	131	38	145
NURE	299	$12.7 -$ 295	117	60	119	25	80-1420	570	325	560	299	$27 - 296$	130	50.1	138
Davis	-18	$23.9-$	131	60	134	18	76-455	214	111	184	18	40-191	139	41	146
		263													
ESV soil	502	$5.8 -$ 198	48.9	29.1	41.6	74	14-717	178	129	150	502	$8 - 311$	91.5	42.8	93.0
New	6	19.3–	52.3	31.7	54,5	6	40-520	172	182	-110	6.	$31 - 311$	116	104	95.0
		105													
NURE	457	$8.1 -$	48.0	27.6	41.4	29	70-690	197	115	170	457	$20 - 225$	90.3	40.0	93.0
		131													
Davis	39	$5.8 -$	58.6	42.7	45.5	39	$14 - 717$	165	132	141.	39	8-258	102	57.9	87.0
		198													
WMB	13	$1260 -$	2291	590	2290	13	990-	2685	1227	2700	-13	419-	1681	738	1790
rock		3920					5900					3110	1987	-1552	1820
WMB	22	$234 -$	1514	935	1363	15	1100-	5459	1974	3210	22	$207 -$			
		3950					9020					5910		1209	2610
New	7	1360-	2140	861	1940	7	2170-	3956	972	4270	7	$1850-$ 4880	3149		
		3950					4940	3024	2554	2465	15	$207 -$	1445	1414	1200
NURE	- 15	$234-$ 2890	1221	841	1032	3	$1100 -$ 9020					5910			
Davis	θ					$\mathbf{0}$					O				

Fig. 3. Box plots showing statistical analysis of concentrations of total Cr, acid-soluble Cr, and total Ni between datasets (Davis, New and NURE) in each region (WSV, ESV and WMB). All concentrations are in units of mg/kg. Vertical lines show the range in concentrations, the boxes are bounded by the 25th and 75th percentile values, and the bold line represents the median value.

the WMB, 4-acid digestible Cr and total Ni in the NURE samples are significantly lower (α < 0.05) than in the newly-collected samples (Fig. 3). This is likely attributed to the selection criteria of the NURE samples rather than a grain size effect. Some of the NURE soils included within the 1-km range of mapped ultramafic rocks may have had other parent material input compared to the samples collected by the authors where soils were identified as those derived directly from UM rocks.

4.1. Sources of Cr and Ni to Sacramento Valley Soils

Chromium and Ni are highly elevated throughout the study area relative to the geometric mean for these elements ($Cr = 37$ mg/kg; $Ni = 13$ mg/kg) in soils of the conterminous USA (Shacklette and Boerngen, 1984). Figs. 2 and 4 show that serpentine soil from both the Coast Range and the western metamorphic belt of the Sierra Nevada foothills were enriched in Cr and Ni relative to Sacramento Valley soils. Chromium and Ni concentrations also were elevated in the Sacramento Valley soils, reflecting the transport of these elements from their serpentine sources in the foothills; however, soils on the west side of the Sacramento River generally have higher concentrations of these elements than soils on the east side. The lower Cr and Ni concentrations in the Sacramento Valley soils, particularly east Sacramento Valley soils, are the result of variable dilution by the large volume of non-ultramafic material shed off the Coast Range and Sierra Nevada Mountains.

A Cr, Li and Ti ternary diagram (Fig. 5) can be used to describe the source of upland material contributing to Sacramento Valley soils. The Great Valley Sequence is elevated in Li relative to ultramafic rocks, diorite and granite, which is consistent with all marine sediments (Horstman, 1957). Titanium can be used as a semi-conservative element during weathering and transport of source materials (Taboada et al., 2006) and is typically associated with silicic igneous rocks and is highest in materials derived from the non-ultramafic rocks and soils in the Sierra Nevada. Chromium is highly insoluble and enriched in ultramafic rocks. Fig. 5a shows that rocks and soils derived from the Coast Range Ophiolite (CRO) in the western portion of the study area plot in the high Cr, low Li and Ti portion of the diagram, whereas rocks and soils derived from the Great Valley Sequence are grouped in the high Li and Ti and low Cr portion of the diagram. Soils from the western Sacramento Valley show a range of composition between the two sources with the majority grouping closer to the volumetrically more abundant Great Valley Sequence rocks. Serpentinites located in the Sierra Nevada foothills within the western metamorphic belt (WMB) are located in the high Cr, low Li and Ti portion of Fig. 5b. Rocks and soils from non-ultramafic (primarily granite and granodiorite) sources in the Sierra Nevada are located in a higher Ti and Li and low Cr portion of the diagram. Soils from the eastern Sacramento Valley primarily have a granitic chemical signature with little input from the volumetrically less significant serpentinite.

Fig. 4. Box plots showing (a) Cr and (b) Ni concentrations in rocks and soils grouped by location. Abbreviations on the x-axis are (from left); CRO - ultramafic rocks and soils associated with the Coast Range Ophiolite, GV - rocks and soils associated with the Great Valley Sequence in the Coast Range, WSV - soils that are located west of the Sacramento River and spatially located within Quaternary alluvium units, ESV - soils that are located cast of the Sacramento River that are located within the mapped Quaternary alluvium, WMB - soils and rocks that are associated with the Western Metamorphic Belt located in the western foothills of the Sierra Nevada. Values in parentheses indicate the number of samples within each group. The solid horizontal lines are the geometric mean for Cr (37 mg/kg) and Ni (13 mg/kg) in soils in the conterminous US (Shacklette and Boerngen, 1984) and the dashed horizontal lines are the EPA human health soil screening levels for Cr (210 mg/kg) and Ni (1600 mg/kg) (USEPA, 2007).

Ophiolite and serpentinite detritus was deposited locally along the base of the Great Valley Group due to deformation along the Franciscan subduction complex (Ingersoll, 1983; Linn et al., 1992). Chromium and Ni concentrations in Great Valley rocks are elevated compared to average soils, but are less than the western Sacramento Valley soils (Fig. 4a and b).

The largest ultramafic rock outcrops in the state of California, and in North America, are found in the Klamath-Siskiyou Mountains to the north of the study area (Kruckeberg, 1984). The movement of material from the north along the Sacramento River could contribute to the amount of Cr and Ni accumulating in valley soils. Deposition of material originating from the Klamath-Siskiyou

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Fig. 5. Ternary diagrams showing rocks and soils from the study area on the west (a) and east (b) sides of the Sacramento River. Abbreviations are as follows: Coast Range Ophiolite rocks and soils (CRO); western Sacramento Valley soils (WSV); eastern Sacramento Valley soils (ESV); ultramafic rocks and soils in the eastern part of the study area that are associated with the western metamorphic belt in the Sierra Nevada foothills (WMB); east side non-UM rocks and soils are samples derived from non-ultramafic sources (granite and granodorite) located in the Sierra Nevada foothills.

Fig. 6. SEM images of residual chromite and Cr-rich spinels after 4-acid digestion appear partially dissolved in serpentine soils from (a) CRO and (b) WMB. Typical magnetite grain found in CRO serpentine soils (c) and typical magnetite grain found in WMB serpentine soils (d).

region to the north is evident in the Sacramento Valley by elevated Cd, Cu and Zn concentrations in western Sacramento Valley soils (Goldhaber et al., 2009), which are not elevated in CRO or Great Valley Group rocks. Higher concentrations of Cd, Cu and Zn are not observed in eastern valley soils, which is likely the result of dilution from non-ultramafic Sierra Nevada sources. Previous studies have noted that ultramafic sources in the Klamath Mountains appear to be less serpentinized (Coleman, 1967; Kruckeberg,

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Cr Reactivity Index

Fig. 7. Box plot showing the Cr reactivity index, which is the ratio of Cr concentration reported for 4-acid/ICP-MES/MS method and LiBO3 fusion/ICP-MS method. Abbreviations on the x-axis are (from left) CRO - ultramafic rocks and soils associated with the Coast Range Ophiolite; GV - rocks and soils associated with the Great Valley Sequence in the Coast Range; WSV - soils that are located west of the Sacramento River and spatially located within Quaternary alluvium units; ESV - soils that are located east of the Sacramento River that are located within the mapped Quaternary alluvium; WMB - soils and rocks that are associated with the Western Metamorphic Belt located in the western foothills of the Sierra Nevada. Numbers in parenthesis indicate the number of samples within each group.

1984). Alexander (2004) observed that serpentine minerals are more stable relative to their unserpentinized counterparts, olivine and pyroxene. Therefore, olivine-hosted Ni in the Klamath region may be more soluble and mobile than Ni associated with their more serpentinized counterparts in the Coast Range and Sierra Nevada.

4.2. Mineralogical residence of Cr and Ni

Chromium concentrations obtained from the two digestion methods can be used to determine the fraction of total Cr residing in Cr-rich spinel versus the total amount of Cr in the soil. Reported Cr concentrations measured by lithium metaborate fusion-ICP-MS are up to an order of magnitude higher than 4-acid-soluble Cr concentrations for the same soil (Table 1). Scanning electron microscopy was used to observe the residue remaining after the 4-acid digestion on a subset of samples. Results showed that the primary mineral phases remaining were chromite and other Cr-rich mixedcomposition spinel minerals (Fig. 6a and b). Acid-soluble Cr is likely present in trace amounts in serpentine minerals, secondary silicate minerals resulting from hydrothermal alteration, clays and Fe oxides (Oze et al., 2004b). In addition, smaller, more weathered spinel grains of high surface area may also be acid-soluble. Results from the two digestion methods were used to calculate a Cr ratio (four acid-soluble Cr/total Cr), which is referred to as the Cr reactivity index. Chromium ratios closer to one indicate more potentially soluble sources of Cr. The Cr reactivity index values were markedly different between CRO and WMB serpentinite (Fig. 7). The acid-soluble fraction of Cr in the CRO is much less than in the WMB of the Sierra Nevada. Scanning electron microscopy of selected undigested soils showed a more euhedral appearance of magnetite and Cr-rich spinels in the Coast Range soils relative to their WMB counterparts (Fig. 6c and d). It has not yet been determined if this is a result of differences in primary mineralogy, extent of weathering, or a combination of the two. The Cr reactivity index was greater in soils relative to rocks in both the CRO and WMB. This suggests that Cr is becoming potentially more labile during pedogenesis. The acid-soluble fraction of Cr was low (0.2-0.48, mean = 0.32, $n = 13$) in Coast Range UM soils relative to valley soils $(0.2-0.99,$ mean = 0.50, $n = 50$). More acid-soluble Cr in valley soils may indicate a change in Cr residence related to extent of transport and weathering of primary Cr minerals,

Analysis by XRD showed that the primary minerals in soils derived from ultramafic rocks of the Coast Range and Sierra Nevada are serpentine and spinel with lesser amounts of quartz, clays and hematite. Scanning electron microscopy showed the spinel minerals to be primarily magnetite, Cr-magnetite and chromite as well as other mixed-composition spinels (Al, Cr, Mg, Fe). Primary mineral phases in Great Valley Sequence siltstone and the soils derived from them were quartz, feldspar, clay and plagioclase. XRD analysis on five western Sacramento Valley alluvial soils showed that quartz, feldspar, clay minerals and plagioclase were the primary mineral phases with minor amounts of serpentine evident in three of the five samples and spinel in one sample.

4.3. Cr and Ni mobility

Data from the USGS National Water Information System database (USGS, 2006) showed elevated dissolved Cr in groundwater of the Sacramento Valley (Fig. 8a). Dissolved Cr concentrations range up to 50 μ g L⁻¹, which is the maximum contaminant level (MCL) set by the State of California (ATSDR, 2000). The national MCL for Cr in drinking water established by the US EPA is $100 \mu g L^{-1}$ (ATSDR, 2000). Although total dissolved Cr concentrations were measured, the primary Cr species dissolved in groundwater is the oxidized and relatively soluble species Cr(VI) because

Fig. 8. Maps showing the study area including county boundaries, lakes and rivers. The graduated symbols show the location of groundwater samples with size indicating (a) Cr concentrations in µg/L and (b) Ni concentration

trivalent Cr is relatively insoluble (Hem, 1977). Regionally elevated Cr(VI) in Sacramento Valley groundwater indicates relatively abundant and/or chemically labile sources of Cr in the sediments and oxidation of Cr(III) to Cr(VI). Other studies have identified elevated

dissolved Cr(VI) in groundwater near Cr-enriched rocks and soils (Ball and Izbicki, 2004; Fantoni et al., 2002; Robertson, 1975; Robles-Camacho and Armienta, 2000). The most likely oxidant of Cr(III) to Cr(VI) is Mn oxides, which are ubiquitous in soil environments.

Dissolved Ni concentrations in Sacramento Valley groundwater samples are less than Cr concentrations, with many values below detection limits (Fig. 8b). Nickel does not undergo redox reactions and is strongly adsorbed onto Fe and Mn oxides in soils at neutral pH. Nickel is, therefore, unlikely to be soluble at the redox and pH conditions of regional California groundwater. It is possible for Ni to be mobilized in groundwater in isolated areas where pH is locally decreased. However, on a regional-scale, it is unlikely that Ni would become soluble in the groundwater of the Sacramento Valley.

5. Conclusions

This regional-scale geochemical study of Cr and Ni in soils of northern California shows that the geochemistry and mineralogy of soils in the Sacramento Valley are strongly influenced by the transport of weathered parent material from the Coast Ranges to the west and the Sierra Nevada Mountains to the east. Chromium and Ni in Sacramento Valley soils is primarily derived from serpentinite rocks of the Coast Range Ophiolite and, to a lesser extent, the western metamorphic belt in the Sierra Nevada foothills. The mineralogical source of Ni is serpentine minerals, which are more easily weathered than chromite and other Cr-bearing spinel minerals derived from the same parent material. Chemical analyses of total and acid-soluble Cr show that Cr in chromite and other Cr-rich spinels is recalcitrant, whereas Cr in Sacramento Valley soils contains a higher proportion of acid-soluble forms, which indicates increased mobilization of Cr during the transport and weathering of Cr-rich materials. Nickel is relatively strongly adsorbed onto mineral surfaces like Fe and Mn oxides, which are ubiquitous in most soils. Conversely, Cr is a redox sensitive element and its highly soluble oxidized form, Cr(VI), is classified as a carcinogen. The occurrence of soluble Cr in groundwater in the western Sacramento Valley suggests that naturally-occurring Cr(III) in soils is undergoing oxidation to Cr(VI). Understanding this redox mechanism on a regional-scale is important to determine the potential impact on ecological and human health in areas where high naturally-occurring Cr is present.

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

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ABSTRACT

Environmental tracers are useful for determining groundwater age and recharge source, yet their application in studies of geogenic Cr(VI) in groundwater has been limited. Environmental tracer data from 166 wells located in the Sacramento Valley, northern California, were interpreted and compared to Cr concentrations to determine the origin and age of groundwater with elevated Cr(VI), and better understand where Cr(VI) becomes mobilized and how it evolves along flowpaths. In addition to major ion and trace element concentrations, the dataset includes $\delta^{18}O$, δ^2H , 3H concentration, ^{14}C activity (of dissolved inorganic C), $\delta^{13}C$, ${}^{3}He/{}^{4}He$ ratio, and noble gas concentrations (He, Ne, Ar, Kr, Xe). Noble gas recharge temperatures (NGTs) were computed, and age-related tracers were interpreted in combination to constrain the age distribution in samples and sort them into six different age categories spanning from <60 yr old to >10,000 yr old. Nearly all measured Cr is in the form of Cr(IV). Concentrations range from <1 to 46 µg L⁻¹, with 10% exceeding the state of California's Cr(VI) maximum contaminant level of 10 μ g L⁻¹. Two groups with elevated Cr(VI) ($\ge 5 \mu g L^{-1}$) were identified. Group 1 samples are from the southern part of the valley and contain modern (<60 yr old) water, have elevated NO₃ concentrations (>3 mg L⁻¹), and commonly have 8¹⁸O values enriched relative to local precipitation. These samples likely contain irrigation water and are elevated due to accelerated mobilization of Cr(VI) in the unsaturated zone (UZ) in irrigated areas. Group 2 samples are from throughout the valley and typically contain water 1000-10,000 yr old, have $\delta^{18}O$ values consistent with local precipitation, and have unexpectedly warm NGTs. Chromium(VI) concentrations in Group 2 samples may be elevated for multiple reasons, but the hypothesis most consistent with all available data (notably, the warm NGTs) is a relatively long UZ residence time due to recharge through a deep UZ near the margin of the basin. A possible explanation for why Cr(VI) may be primarily mobilized in the UZ rather than farther along flowpaths in the oxic portion of the saturated zone is more dynamic cycling of Mn in the UZ due to transient moisture and redox conditions.

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1. Introduction

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

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

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Environmental tracers such as carbon isotopes, helium isotopes, and dissolved noble gases are powerful tools for determining groundwater age and recharge source (Cook and Herczeg, 2000). The application of environmental tracers in studies of $Cr(VI)$ in groundwater has been limited. Izbicki et al. (2008a) used stable isotopes of water (¹⁸O and ²H) to help identify a high-Cr industrial waste-water source, and used ¹⁴C activity of dissolved inorganic carbon to identify relationships between Cr(VI) and relative groundwater age. Lelli et al. (2014) employed δ^{18} O and ³H (along with $NO₃$) to distinguish recently recharged water from older water, and found different Cr(VI) concentrations in these two groups. These studies demonstrate the potential value of environmental tracer methods in groundwater Cr investigations, but in both cases the tracer data were presented for a modest number of samples, actual groundwater ages were not computed, and only two different tracers were utilized. Age and source determinations are considerably more robust when multiple types of tracer data are employed together, particularly in the case of constraining the age distribution in mixed-age samples from long-screened wells or springs (e.g., Manning et al., 2012).

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

In this study, environmental tracer data collected from 166 wells located throughout the Sacramento Valley were interpreted and compared to Cr concentrations in order to better understand the origin and age of groundwater with elevated geogenic Cr(VI). gain new insight into controlling factors, and focus future research efforts. The dataset was collected as part of the California Groundwater Ambient Monitoring and Assessment (GAMA) Program (Belitz et al., 2003), and is unusual in the number and diversity of tracer measurements. In addition to major and trace elements and Cr(VI), it includes stable isotopes of water (δ^{18} O, δ^2 H), carbon isotopes of dissolved inorganic carbon (¹⁴C activity, δ^{13} C), tritium (³H), helium isotope ratio (³He/⁴He), and dissolved noble gases (He, Ne, Ar, Kr, Xe). Apparent ³H/³He ages (applicable for waters <60 yr old) were computed from $3H$ concentrations, ³He/⁴He ratios, and noble gas concentrations. Unadjusted radiocarbon ages were computed from ^{14}C activities and $\delta^{13}C$. Computed ages along with other age indicators (mainly terrigenic ⁴He concentration) were used to sort samples into six different age categories spanning from <60 yr old to >10,000 yr old. Noble gas concentrations were also used to compute noble gas recharge temperature (NGT), the temperature at the water table at the recharge location. Noble gas recharge temperatures in combination with δ^{18} O values allow for the identification of the following types of recharge: high-elevation precipitation that recharges in the mountains and flows as groundwater to the valley (mountain-block recharge); high-elevation precipitation that becomes streamflow in the mountains, flows as surface water to the valley, then infiltrates as focused stream loss; low-elevation precipitation that recharges in a diffuse manner in the valley; and water that recharges through a relatively deep (>50 m) UZ. Comparison of these tracer results to Cr concentrations revealed which types of water were most likely to contain elevated Cr(VI), and pointed to likely controlling mechanisms.

2. Site description

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

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

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

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Fig. 1. Maps of study area showing relevant geology and sampled well locations (A), and water table elevation (B). Well locations are approximate, purposefully shown up to 2 km away from actual well locations to comply with the California Groundwater Ambient Monitoring and Assessment (GAMA) Program's policies regarding well-owner security. Elev = elevation, masl = meters above sea level.

dissected uplands along margins of the valley and in much the northern area. The younger Quaternary (mostly Holocene) sediments form alluvial fans and plains, stream-channels, and flood plains in the flatter, lower elevation areas (Olmsted and Davis, 1961). Morrison et al. (2009) measured total Cr concentrations in soil samples from the southern part of the valley and reported median values of 120 mg kg⁻¹ (maximum of 295 mg kg⁻¹) and 42 mg kg⁻¹ (maximum of 198 mg kg⁻¹) for samples collected on the western and eastern sides of the Sacramento River, respectively. Southern Sacramento Valley soil Cr concentrations thus commonly exceed the geometric mean for soils of the conterminous USA of 37 mg kg⁻¹ (Shacklette and Boerngen, 1984), and are generally higher on the west side than the east side. Goldhaber et al. (2009) performed a separate analysis of many of the same soil Cr data reported in Morrison et al. (2009) and found that median total Cr concentrations generally increased from the valley margin toward the Sacramento River, though maximum concentrations decreased or remained similar.

The valley aquifer is a heterogeneous mixture of unconsolidated to semi-consolidated gravel, sand, silt, and clay. Conditions at shallow depths and near the valley margins are generally unconfined, but typically become confined at greater depths (>100 m) toward the valley center due to numerous overlapping, discontinuous lenses of silt and clay (Williamson et al., 1989). The configuration of the water table (Fig. 1B) indicates that groundwater generally flows from the margins of the valley toward the Sacramento River, and from north to south. Significant groundwater development and diversion of surface water via canals for irrigation began in the 1930s (Faunt, 2009). Published pre- and post-development water budgets are available for the entire Central Valley, but not

for the Sacramento Valley, specifically. Under pre-development conditions, 75% of recharge to the Central Valley occurred as areal recharge from infiltration of precipitation on the valley floor ("areal recharge") and 25% as focused recharge from losing streams in the upper parts of the alluvial fans, where the major streams enter the valley ("stream loss"; Williamson et al., 1989; Thiros et al., 2010). Discharge occurred mainly to the Sacramento and San Joaquin Rivers and to evapotranspiration by vegetation in lowland areas where the water table was near land surface. Under current post-development conditions, areal recharge and stream loss together comprise only 31% of total recharge, the remaining 69% consisting of unconsumed irrigation water ("irrigation recharge") and other artificial sources (Faunt, 2009; Thiros et al., 2010). Discharge to rivers and lowland evapotranspiration comprise only 36% of total discharge, the remaining 64% being well extractions, Under both pre- and post-development conditions, areal recharge rates are likely higher farther north in the valley and closer to the valley margins, where precipitation is greater. Stream loss is likely greater on the eastern side of the valley, where surface-water inflows are larger. Direct groundwater inflow from adjacent mountains (mountain-block recharge) to the Central Valley is believed to be negligible, but data do not exist to directly test this hypothesis. Although the types of recharge sources in the Sacramento Valley are likely the same as those for the rest of the Central Valley, their relative contributions to total recharge could deviate substantially from the Central Valley averages due to large differences in climate and agriculture between the southern and northern ends of the valley. However, Criss and Davisson (1996) presented groundwater isotopic data from the southern Sacramento Valley that are generally consistent with the Central

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Valley recharge estimates; model ^{14}C ages and $\delta^{18}O$ values revealed the same three recharge components (areal recharge, stream loss, and irrigation recharge), and suggested that irrigation recharge composes up to half of shallow groundwater in parts of the southwest area.

3. Methods

All data were taken directly from published GAMA Program reports (Dawson et al., 2008; Schmitt et al. 2008; Bennett et al., 2009, 2011) and are presented in Table S1 (Supplementary material). These reports divide the Sacramento Valley into southern, middle, and northern study units based on variations in climate, geology, and land-use. These divisions are maintained here, and are referred to as the south, middle, and north zones (Fig. 1A). The data set includes a total of 235 samples (one per well) collected from 2005 to 2008. Of these, Cr and/or environmental tracer measurements (beyond $\delta^{18}O$) are available for 197 samples. The types of tracer data available for the samples with Cr data $(n = 166)$ differ from well to well, but most have multiple associated tracer measurements (Table S1). Samples were collected from production wells (85%) and monitoring wells (15%; Fig. 1A), most having a total depth of 25-250 m. Median mid-screen depths are 87, 67, and 75 m for the south, middle, and north zones, respectively, and median screen lengths are 31, 30, and 21m, respectively.

Both total Cr (Cr_T) and Cr(VI) concentrations are available for middle and north zone samples, but only Cr_T concentrations are available for south zone samples. All south zone samples containing detectable Cr_T (>0.8 µg L⁻¹) have a pH of 7.0 to 8.6, except one. In this pH range, it is expected that nearly all Cr will occur in the form of Cr(VI) (Rai et al., 1989; Richard and Bourg, 1991; Saputro et al., 2014; see Supplementary material). Generally low concentrations of Cr(III) in the Sacramento Valley aquifer are supported by a comparison of Cr_T and $Cr(VI)$ concentrations for middle and north zone samples, where geochemical conditions are similar to the south zone (Fig. S1). These data plot near the 1:1 line, with Cr_T exceeding $Cr(VI)$ by $\leq 2 \mu g L^{-1}$ for all but 3 samples (maximum discrepancy of 5 μ g L⁻¹). Further, Cr_T concentrations are low for clearly anoxic samples, in which all Cr should be in the form of $Cr(HI)$ (Fig. S2). Measured south zone Cr_T concentrations therefore probably closely approximate Cr(VI) concentrations, and we thus assume the two to be equal herein.

Details regarding sample collection and analytical methods can be found in the GAMA Program reports cited above. The following is a summary of methods used to interpret the tracer data. Details beyond the information below are provided in the Supplementary material. Bennett et al. (2011) computed NGTs, apparent ³H/³He ages, and unadjusted radiocarbon ages for this dataset. However, inadequate information was provided to fully understand how these values were calculated and to assess their reliability, necessitating their re-calculation.

Concentrations of Ne, Ar, Kr, and Xe dissolved in groundwater can be used to compute the temperature at the water table at the recharge location (NGT) due to the temperature-dependence of gas solubility and the non-reactive character of noble gases (Kipfer et al., 2002). NGTs were computed for 173 samples using a computer code that employs a Newton inversion method to minimize the error-weighted misfit (χ^2) between measured and modeled Ne, Ar, Kr, and Xe concentrations (Aeschbach-Hertig et al., 1999; Manning and Solomon, 2003). The closed-system equilibrium (CE) model of excess air formation was assumed (Aeschbach-Heritg et al., 2000), and the air pressure at the water table in the recharge location was assumed equal to the atmospheric pressure at the elevation of the sampled well. Computed

NGTs were not reported for 7% (13 of 173) of samples for which data were unreliable as indicated by either unreasonably high excess air concentrations (Δ Ne > 500%), unacceptably high χ^2 values indicating poor model fits (probability < 0.005), or both. Such samples were likely affected by gas stripping or bubble entrapment during sampling or analysis. Model fits were generally good for the remaining samples, with only 7% (11 of 160) having χ^2 values indicating a probability of <0.05. Uncertainties in modeled NGTs (1 σ) generally range from 0.5 to 1.5 °C.

Tritium, He, and the 3 He/ 4 He ratio were used in combination with modeled recharge parameters (NGT and excess air) to: (1) compute terrigenic He concentrations; (2) sort samples into modern (M), mixed-modern (MM), and pre-modern (PM) age categories; and (3) compute apparent ${}^{3}H/{}^{3}He$ ages for M and MM samples (Solomon, 2000; Solomon and Cook, 2000). Terrigenic He (He_{terr}) is produced in the subsurface primarily by radioactive decay of U and Th in minerals within and below the aquifer, and can place constraints on the age of older groundwater. Here, the He_{terr} concentration is expressed as a percentage of the total measured He concentration (%He_{terr}). Modern recharge is recharge that occurred after 1953, when ³H concentrations in precipitation began to increase in response to open-air nuclear weapons testing. In this study, M samples likely contain >80% modern recharge, PM samples likely contain <20% modern recharge, and MM samples likely contain 20–80% modern recharge. A precipitation ³H record was estimated for the field area using measured precipitation ³H records from Menlo Park, California and Portland, Oregon (closest available; International Atomic Energy Agency's Global Network of Isotopes in Precipitation, http://www-naweb.iaea.org/napc/ih/ IHS₋resources_{-gnip}.html). The precipitation 3 H record was used to calculate a minimum $3H$ concentration of 0.5 Tritium Units (TU) for M and MM samples. Samples with a ${}^{3}H$ concentration <0.5 TU were thus designated as PM. Apparent 3 H/ 3 He ages were only computed for M and MM samples because computed ages are highly uncertain for PM samples. For MM samples, computed ages represent the approximate age of the modern fraction. Uncertainties in apparent ages (1 σ) are generally 1-5 yr. Apparent ages were not computed for samples with: (1) unreliable recharge parameters (probability <0.005 or ΔNe >500%); (2) unacceptably low He concentrations (measured concentration <92% of modeled concentration), indicative of He being stripped; or (3) elevated He_{terr} concentrations (%He_{terr} >25%). Apparent ages computed for such samples would have uncertainties >5 yr (potentially >5 yr), and would thus be of limited value. Modern samples were distinguished from MM samples utilizing computed initial 3 H concentrations (3 H concentration at the time of recharge), defined as the sum of measured ³H and modeled tritiogenic ³He (in TU; Aeschbach-Hertig et al., 1998; Manning and Solomon, 2005). The initial ³H concentration for each sample was compared to the precipitation ³H concentration for its apparent recharge year, and those having initial ${}^{3}H$ > 80% of precipitation ${}^{3}H$ were designated as M samples (Fig. S3). The remaining samples likely have lower initial ³H concentrations because they contain a sizable component (>20%) of low-³H PM water, and were thus designated as MM, Samples with a 3 H concentration >0.5 TU and a%He_{terr} >25% were designated as MM because they likely contain a Heter component larger than about 20 µcc kg $^{-1}$, the maximum expected for modern, shallow-circulating waters (Solomon et al., 1996; Solomon, 2000).

Unadjusted radiocarbon ages were computed from the ${}^{14}C$ activity of dissolved inorganic carbon for 144 samples using the conventional ¹⁴C modern half-life of 5730 yr, with ages being prior to 1950 (Kalin, 2000). Carbon-14 activity at the water table in the recharge area (initial 14 C activity, or A_0) was estimate for each zone by examining the lower end of the range of ^{14}C activities for M samples and the upper end of the range of ¹⁴C activities for PM

samples. The overlap between these two ranges was relatively narrow (2-14 pmC; Fig. S4), and the mean 14 C activity of samples within this overlap was taken as A_0 . Estimated A_0 values for south, middle, and north zones are 92, 90, and 80 pmC, respectively. The likelihood of significant introduction of dead carbon in the saturated zone by water-rock interaction with carbonate minerals is low, given the scarcity of carbonate source rocks in the surrounding mountains. Further, the high end of the range of $\delta^{13}C$ values for the considerable majority of samples with <90 pmC (-12%) is similar to that for samples with >90 pmC (-13‰), consistent with only minor introduction of dead carbon by reaction with calcite minerals or mixing with deeply circulating fluids high in CO₂ (Fig. S5). Unadjusted ¹⁴C ages for the seven samples with $\delta^{13}C$ values >-12% were not used in the interpretation of Cr(VI) data. Uncertainties in computed radiocarbon ages are still considerable because geochemical modeling was not performed to account for all carbon mass transfers, such as likely reactions involving dissolved organic carbon. Uncertainties are probably up to 20% (minimum of 1000 yr), and computed ages are more likely to be erroneously old rather than erroneously young (Bennett et al., 2011; Manning, 2009).

Samples were sorted into the following age categories using all available age information: M; MM1, containing a mixture of M water and PM water dominantly <1000 yr old; MM2, containing a mixture of M water and PM water dominantly >1000 yr old; PM1, containing dominantly PM water <1000 yr old; PM2, containing dominantly PM water 1000-10,000 yr old; and PM3, containing dominantly PM water >10,000 yr old. These age categories provide a more reliable indication of the range of ages within each sample than a specific apparent age computed from any single age-tracer. For mixed-age samples (as these likely are, given median well screen lengths of 21-31 m), computed apparent ages can be substantially different from the actual mean age of the sample and provide no information on how broad the age distribution may be (e.g., how much water >1000 yr old may be in a sample with an apparent ${}^{3}H/{}^{3}He$ age of 25 yr). Mixed-modern and PM samples were subdivided into MM1, MM2, PM1, PM2, and PM3 categories based on the unadjusted ¹⁴C age, if available. For samples without carbon isotope data in the south and middle zones, secondary (less direct) age indicators were utilized, including %He_{terr}, δ¹⁸O, and NGT (see Supplementary material). These indicators exhibit some age-dependence but have other major controlling factors as well. Relationships between the secondary age indicators and unadjusted ¹⁴C age were identified and then used to apply age constraints to samples lacking carbon isotope data,

4. Results and discussion

4.1. General groundwater chemistry

Samples shown in the Piper diagram in Fig. 2 are from the south zone only, but are representative of the whole valley (Fig. S7). Sample age categories suggest that groundwater generally evolves from mixed-cation/Ca + HCO₃ type to Na + K/Ca + HCO₃ type along flowpaths. Sodium concentration is correlated with ¹⁴C activity $(r^2 = 0.42$; Fig. 3A), whereas other major cations show no such correlation, indicating that increasing Na⁺ concentrations are mainly responsible for this evolution. Increasing Na⁺ concentrations are probably due to the dissolution of sodic plagioclase, and cation exchange with Ca^{2+} and Mg²⁺. The Piper diagram provides some indication that Cl⁻ concentrations also generally increase with groundwater age, suggesting that mixing with deep-circulating saline groundwater and/or halite dissolution could be partly responsible for increasing Na⁺ concentrations. However, the correlation between Cl^- concentration and ^{14}C activity is weak

 $(r^2 = 0.13)$, and Na⁺/Cl⁻ molar ratios are generally well above unity (median of 3.3), suggesting only minor Na⁺ contributions from these sources. Groundwater in the Sacramento Valley is p H-neutral to slightly alkaline (median = 7.6) and p H generally increases with decreasing ¹⁴C activity (r^2 = 0.47; Fig. 3B). Increasing pH is likely due to progressive silicate weathering along flowpaths (consuming H⁺). Groundwater is generally oxic, with 78% of samples having a dissolved oxygen concentration (DO) >0.5 mg L⁻¹ (Fig. 3C). The high end of the range of DO values decreases with decreasing ¹⁴C activity, and the oldest samples with ¹⁴C activities <20 pmC have a DO ≤ 0.5 mg L⁻¹. This indicates that DO is progressively consumed along flowpaths, probably by oxidation of organic matter.

4.2. Environmental tracers

Computed groundwater ages in the valley range from 0 to about 40,000 yr (Table S1, Fig. 4). The distribution of samples among the different age categories is 20% M, 35% MM, 10% PM1, 25% PM2, and 10% PM3. Groundwater age generally increases with depth in the aquifer, as expected (Fig. S8). Groundwater ages are also generally greater farther south in the valley and farther from the mountain fronts (Figs. 5A, S9A), consistent with the general direction of groundwater flow (Fig. 1B). On average, ages are younger on the east side of the valley compared to the west side, consistent with higher surface water inflows and associated recharge on the east side.

Plots of $\delta^{18}O$ and NGT versus unadjusted ¹⁴C age (Fig. 4) were used to identify different sources of recharge for sampled waters. The vertical line on these plots indicates the boundary between Pleistocene and Holocene epochs at 11,700 yr BP (Walker et al., 2009), the end of a period of climate warming following the end of the last glacial maximum around 20,000 yr BP. On the δ^{18} O plots (Fig. 4A–C), horizontal lines indicate the range of local valley precipitation in the current (Holocene) climate regime; -7 to -8% in the south zone, -8 to $-9.5%$ in the middle zone, and -9 to -10% in the north zone (Criss and Davisson, 1996; Ingraham and Taylor, 1991). Most Holocene samples plot within this range, consistent with most pre-development Holocene recharge being areal recharge of valley precipitation. Holocene samples plotting above this range (enriched) underwent evaporation prior to recharge. Excess irrigation water that becomes irrigation recharge is commonly enriched (e.g., Chen et al., 2006). Enriched samples with a 14 C age near 0 yr and an age category of M or MM (considerable majority) therefore likely contain irrigation recharge. Holocene samples plotting below the valley precipitation range (depleted) contain precipitation that fell at higher elevations in surrounding mountains. These samples likely contain either recharge from stream loss or mountain-block recharge. Pleistocene samples are generally depleted, as expected given that they recharged in a cooler climate.

On the NGT plots (Fig. 4D-F), horizontal lines indicate the expected range of NGTs for Holocene samples recharged in the valley. Water table temperatures, and thus NGTs, are typically 0-3 °C above the mean annual surface air temperature (MAAT; Domenico and Schwartz, 1990; Lee and Hahn, 2006; Cey, 2009). For each zone, MAAT was determined from three different National Oceanic and Atmospheric Administration Cooperative meteorological stations (Western Regional Climate Center, http://www.wrcc.dri.edu/climatedata/climsum/) spread throughout the zone and having a temperature record extending back prior to 1950. Based on these computed MAATs, expected Holocene NGTs are 15.2-18.2 °C, 16.2-19.2 °C, and 17.1-20.1 °C for the south, middle, and north zones, respectively. Holocene samples plotting above the expected range (warm) were either recharged where the water table is >50 m deep (e.g., Manning, 2009) or during the summer

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Fig. 2. Piper diagram showing south zone samples. Age categories (M, MM1, etc.) are defined in text. Circles are samples from the east side of the valley, squares are from the west side.

as rapidly infiltrating, focused recharge where the water table is shallow (<5 m deep; Cey et al., 2009). Possible sources for the latter include irrigation recharge and stream loss, Several of the warm-NGT samples have ¹⁴C ages <100 yr (and are M or MM type), and thus may contain irrigation recharge. However, most (68%) are PM-type. Available hydrographs for streams entering the valley (U.S. Geological Survey, http://waterdata.usgs.gov/ca/nwis/rt) generally indicate that <20% of annual flow occurs from June to October, so summer stream loss is probably minor. Therefore, the PM-type warm-NGT samples likely contain water recharged where the water table is deep. Predevelopment water table depths were computed from the initial-state water table elevation distribution in a recently published numerical model of groundwater flow in the Central Valley (Faunt, 2009), based mainly on water level measurements from the early 1900s (Williamson et al., 1989; Fig. 5B). Computed water table depths are commonly 40-60 m or more near the margins of the basin where land-surface elevations are higher and topography is more irregular. The warm-NGT samples compose a large fraction (51%) of all Holocene samples, suggesting that much of the water in the aquifer recharged through a relatively thick UZ.

Holocene samples plotting below the expected NGT range (cool) contain either mountain-block recharge from mid to high elevation, or cool-season stream loss that infiltrated rapidly where the water table is shallow $(5 \text{ m}$ deep). Most of these Holocene cool-NGT samples (80%) also have depleted δ^{18} O values, as expected. Stream loss typically should not have cool NGTs because most probably occurs closer to the mountain front where the water table depth is generally >>5 m. The Holocene cool-NGT samples are therefore more likely to contain mountain-block recharge than stream loss, with the possible exception of young samples from the region where the Sacramento River enters the valley in the north zone. Regardless, the small number of Holocene samples with cool-NGTs (9%) suggests that mountain-block recharge from mid to high elevations is relatively minor, consistent with existing recharge estimates. Pleistocene samples in the south zone mostly have cool NGTs, consistent with recharge in a cooler climate. This is not the case for Pleistocene samples in the middle and north zones, but these samples are generally cooler than most of the Holocene predevelopment samples which is also consistent with recharge in a cooler climate.

The spatial distributions of δ^{18} O class (enriched, depleted, and same as local precipitation) and NGT class (cool, expected, and warm) are shown in Fig. S9. Although some subtle and/or local trends are apparent, well-defined regional trends that cannot be attributed to the age distribution are lacking.

4.3. Chromium(VI)

Chromium(VI) concentrations for middle and north zone samples ($n = 124$) and Cr_T concentrations for south zone samples $(n=42)$ are shown in Fig. 6. In the following discussion, it is assumed that measured Cr_T in the south zone is all in the form of Cr(VI) based on rationale presented above in Section 3 (also see Supplementary material). Seventeen of 166 samples (10%) have concentrations $\ge 10 \mu g L^{-1}$, the state of California's MCL for Cr(VI) (Table S1). Thirty-seven samples (22%) have concentrations \geqslant 5 µg L⁻¹, and are referred to herein as "elevated". Roughly half of the samples (45%) have concentrations below the reporting limit of $1 \mu g L^{-1}$. The south zone has both the largest fraction of elevated samples (36%) and the highest measured concentration

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Fig. 3. Sodium concentration (A), pH (B), and dissolved oxygen concentration (C) versus ¹⁴C activity of dissolved inorganic carbon. Linear regression lines also shown in (A) and (B) , $DO =$ dissolved oxygen.

 $(46 \mu g L^{-1})$. In the remainder of the valley, 18% of the samples are elevated and the maximum concentration is 31 μ g L⁻¹.

The areal distribution of Cr concentrations (Fig. 6) suggests that proximity of exposed ultramafic rocks to the valley margin may be a first-order control on groundwater Cr levels. Concentrations are consistently low in the northeastern part of the middle zone and in the eastern and northern parts of the north zone, where ultramafic rocks in adjacent mountains are either non-existent or far from the mountain front $($ >30 km; Fig. 6). The lack of ultramafic sources, or long transport distances from these sources to the valley, would presumably result in a relatively low abundance of Cr-rich minerals in valley sediments in these areas, Concentrations are mixed in the remainder of the valley, where ultramafic rocks crop out closer to the valley margin. The occurrence of samples of varying concentration in these areas suggests that, when sources of Cr-rich sediments are close to the valley, other factors (e.g., hydrology or anthropogenic influences) become important in controlling groundwater Cr levels. Concentrations are also generally lower on the eastern side of the valley than the western side, suggesting a possible positive correlation between groundwater Cr levels and groundwater age (Fig. 5A and Fig. 6).

All but two samples with $Cr(VI)$ (middle and north zones) or Cr_T (south zone) concentrations >1 μ g L⁻¹ have a pH \ge 7.0 and a DO concentration ≥ 1 mg L⁻¹ (Fig. 7). Samples with a pH < 7 probably have low Cr(VI) concentrations due to high levels of adsorption onto Fe and Al oxides or clays in acidic waters, resulting in low mobility (Rai et al., 1989). Low Cr(VI) concentrations in low DO samples are likely due to the reduction of Cr(VI) to Cr(III) and its removal from solution when oxygen becomes sufficiently depleted along flow pathways (81% of these samples have a 14 C activity <60 pmC; Fig. 3C). Low Cr(VI) concentrations in samples with a $pH > 8.3$ are probably due to many of these samples having a low DO (Fig. 7A); most of these higher pH samples are relatively old, and groundwater generally increases in pH and decreases in DO with increasing age (Fig. 3). Similar relationships between Cr(VI) and pH and DO have been observed in other aquifers containing elevated geogenic Cr concentrations (e.g., Izbicki et al., 2008a; Bertolo et al., 2011).

4.4. Relationships between $Cr(Vl)$, nitrate, and environmental tracers

Total Cr concentration is positively correlated with NO₃ concentration (as N) in the south zone (Fig. 8A). Mills et al. (2011) suggested that elevated Cr concentrations in the south zone are caused by processes related to irrigation recharge. Davisson and Criss (1993) found that most groundwater samples from the western part of the south zone with NO₃ concentrations above a typical background level of 2 mg L⁻¹ (as N; Mueller and Helsel, 1996) were also isotopically enriched ($\delta^{18}O \ge -7$), and concluded that these samples contained irrigation recharge. The GAMA data are consistent with these findings; many of the south zone samples with elevated NO₃ concentrations also have enriched δ^{18} O values (60%), and nearly all samples with elevated NO₃ are either M or MM type (irrigation recharge must be <100 yr old; Fig. 8B). Nitrate concentrations in PM samples generally do not exceed 3 mg L^{-1} (Fig. 8B). Therefore, samples having both a $NO₃⁻$ concentration >3 mg L⁻¹ and an age category of M or MM likely contain an appreciable fraction of irrigation recharge and are defined here as "irrigation recharge samples".

In the south zone, five of six samples with Cr_T concentrations >15 µg L^{-1} are irrigation recharge samples, supporting a direct link between irrigation recharge and high Cr(VI) in groundwater. Some form of positive correlation between $Cr(VI)$ and $NO₃⁻$ has been observed in other aquifers as well and similarly attributed to irrigation recharge (Stamatis et al., 2011; Güler et al., 2012). Irrigation may substantially enhance recharge in locations that previously received little or none under natural conditions, mobilizing more geogenic Cr(VI) from UZ soils and accelerating its transport to the water table (Izbicki et al., 2008b; Mills et al., 2011). Both Chung et al. (2001) and Mills et al. (2011) showed that UZ material in the south zone contains Cr(VI) and is able to generate environmentally relevant amounts of Cr(VI) in groundwater on

Fig. 4. Delta ¹⁸O (A-C) and noble gas recharge temperature (D-F) versus unadjusted ¹⁴C age for south, middle, and north zones. Dashed line labels in (A) also apply to (B) and (C), and dashed line labels in (D) also apply to (E) and (F). Precip = precipitation, NGT = noble gas recharge temperature.

short time scales due to the presence of abundant Mn oxides. The presence of NO₃ itself may contribute to elevated Cr(VI) concentrations if the groundwater is suboxic or localized reduced zones occur in the UZ because $NO₃$ is a more thermodynamically favorable electron donor than Cr(VI), and thus may inhibit reduction of Cr(VI) to Cr(III) (Izbicki et al., 2008b). It is also possible that other dissolved constituents in the irrigation water such as fertilizer-derived NH⁺ could enhance the oxidation of Cr(III) to Cr(VI) (Mills and Golhaber, 2012). The microbially-mediated oxidation of NH $_4$ to NO₃ produces H⁺, which has been shown to increase the rate of Cr(VI) production in south zone UZ soils (Mills et al, 2011).

Chromium(VI) concentration in the middle and north zones is not positively correlated with NO₃ concentration (as N; Fig. 8C). To the contrary, few samples with elevated Cr(VI) concentrations have NO_3^- concentrations >3 mg L⁻¹, and vice versa, indicating a degree of negative correlation. Another factor unrelated to irrigation recharge clearly is causing elevated Cr(VI) concentrations in the middle and north zones. Some form of negative correlation between $Cr(VI)$ and $NO₃⁻$ has been observed in other aquifers with geogenic Cr contamination (Moraetis et al., 2012; Lelli et al., 2014). These studies suggest that the negative correlation may be due to older groundwater (deduced from well depths and limited ³H data) having higher $Cr(VI)$ concentrations than modern, high- $NO₃$ groundwater, Moraetis et al. (2012) hypothesized that older waters were recharged directly through Cr-rich ultramafic rocks and associated soils in neighboring foothills, whereas younger waters were recharged closer to the sampled well through soils with a lower Cr content and/or higher sorption rates. Note that in the south zone, few of the moderately elevated samples with Cr_T concentrations of $5-15 \mu g L^{-1}$ are irrigation recharge samples. The lack of correlation between Cr and $NO₃⁻$ for these samples suggests that a second factor unrelated to irrigation may be causing elevated Cr, perhaps the same as that acting in the middle and north zones.

Fig. 9 shows Cr(VI) (middle and north zones) and Cr_T (south zone) concentrations plotted versus age category (Fig. 9A-C), δ^{18} O (Fig. 9D-F), and NGT (Fig. 9G-I). The age category plots exclude MM2 samples because these contain water of such widely ranging age (modern to potentially >10,000 yr) as to be of limited value for discerning relationships between age and Cr(VI). In the south zone, many of the samples with elevated Cr concentrations $(\geq 5 \,\mu g \, L^{-1})$ are irrigation recharge samples, which by definition are M or MM type. However, a second group of elevated non-irrigation-recharge samples are PM type, most being PM2. Most elevated samples (and all samples $\geq 10 \text{ µg L}^{-1}$) in the middle and north zones are PM type, again dominantly PM2 (the elevated PM3 sample in the middle zone has a 14 C age of 11,200 yr and is thus borderline PM2). Only two of 18 PM3 samples are elevated in Cr (see also Fig. S10), probably because PM3 samples are generally low-DO, with all measured concentrations ≤ 0.5 mg L⁻¹. As expected, $\delta^{18}O$ values for irrigation recharge samples in the south zone are mostly enriched. However, most of the elevated non-irrigation-recharge samples have $\delta^{18}O$ values within the range of valley Holocene precipitation. In the middle and north zones, elevated samples also generally have $\delta^{18}O$ values within the range of valley Holocene precipitation. In the south zone, NGTs of irrigation recharge samples are mostly within the expected range. However, most of the elevated non-irrigation-recharge samples have warm NGTs, Similarly, in the middle and north zones, most elevated samples (and all samples $\geq 10 \mu g L^{-1}$) have warm NGTs. In summary, the environmental tracers define two different groups of samples with elevated Cr concentrations in the Sacramento

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Fig. 5. Maps showing distribution of age category (A) and predevelopment water table depth (B) computed from the predevelopment water table elevation distribution in Faunt (2009). Age categories (M, MM1, etc.) defined in text. Depths are in meters below ground surface.

Valley. Group 1 includes irrigation recharge samples from the south zone that are M or MM type, commonly have enriched δ^{18} O values, and typically have NGTs in the expected range. Group 2 includes a set of PM samples collected from all zones that are mostly PM2 type, have $\delta^{18}O$ values generally consistent with Holocene valley precipitation, and have warm NGTs.

4.5. Hypotheses for elevated Cr(VI) in Group 2 samples

The tracer data provide information that may help explain why Group 2 samples, and similar older waters in other aquifers, are elevated in Cr(VI). Excluding irrigation recharge samples and samples with a $DQ < 1$ mg L^{-1} , median Cr concentrations (Cr_T for south zone, Cr(VI) for middle and north zones) for M, MM1, PM1, and PM2 samples are <1 (non-detect), 1, 2, and 7 μ g L⁻¹, respectively. Also, samples with elevated Cr(VI) in the middle and north zones generally increase with increasing unadjusted ^{14}C age (Fig. S10). These relationships indicate a general positive correlation between groundwater age and Cr(VI) for oxic non-irrigation-recharge samples, which suggests that Cr(VI) concentrations may increase along flowpaths in the oxygenated portion of the saturated zone ("saturated zone hypothesis"). Izbicki et al. (2008a) found a similar general positive correlation between Cr(VI) and relative groundwater age (deduced from ¹⁴C activity) in oxic groundwater in an alluvial aquifer in the Mojave Desert, California. The authors hypothesized

that the correlation was caused by progressively increasing pH along flowpaths due to silicate weathering, and a resulting increase in the desorption and mobilization of Cr(VI) from exchange sites. Bertolo et al. (2011) observed an increase in both groundwater pH (due to cation exchange) and Cr(VI) concentration with increasing depth, and thus presumably age, in a sandstone aquifer in western Brazil, and attributed it to the same mechanism as Izbicki et al. (2008a). Given that pH generally increases with increasing groundwater age in the Sacramento Valley (Fig. 3B), this mechanism could also explain elevated Cr(VI) in Group 2 samples. Production of Cr(VI) from the oxidation of Cr(III) in aquifer solids along saturated-zone flowpaths is probably very slow due to the slow kinetics of oxidation by molecular oxygen (Schroeder and Lee, 1975; Namgung et al., 2014) and/or intransient Mn oxides (resulting from stable redox conditions) that may have developed relatively unreactive surfaces (Fendorf, 1995). However, residence times of Group 2 samples are sufficiently long that some contribution of Cr(VI) by ongoing production throughout oxic portions of the aquifer cannot be ruled out.

A significant shortcoming of the saturated zone hypothesis for Group 2 samples is that it does not explain the clear correlation between elevated Cr(VI) and warm NGTs (Fig. 9G-1). One possibility is that this correlation is simply the result of most PM2 samples having warm NGTs, and most Group 2 samples are PM2 type. If this were the case, the fraction of elevated-Cr PM2 samples having

 $10\,$

Fig. 6. Map showing distribution of Cr concentration. Location of ultramafic rocks are also shown. Cr_T = total Cr .

warm NGTs should be about the same as the fraction of all PM2 samples having warm NGTs. However, 82% (14 of 17) of the elevated-Cr PM2 samples have warm NGTs, compared to 65% (24 of 37) of all PM2 samples. The contrast is greatest for samples with higher Cr concentrations, particularly in the middle and north zones where 100% (8 of 8) of samples with $Cr(VI) \ge 10 \mu g L^{-1}$ have warm NGTs. Although the number of these samples is small, the probability of all eight having warm NGTs solely due to their age is only 0.05. These statistics support a direct link between warm NGT and elevated Cr(VI).

We propose a second hypothesis for the Group 2 samples in which they acquired their elevated Cr(VI) concentrations primarily in the UZ during recharge, and longer UZ residence times promote higher groundwater Cr(VI) concentrations ("UZ hypothesis"). The warm NGTs of Group 2 samples suggest that they recharged through a thick UZ, meaning that they may have experienced a longer UZ residence time than samples recharged where the water table is shallower. The general positive correlation between age and Cr(VI) could be primarily a result of the water table depth increasing with proximity to the mountain front (Fig. 5B); groundwater that recharged closer to the basin margin would tend to have both warmer NGTs and greater age (from following longer flowpaths) than groundwater recharged farther from the basin margin and closer to a sampled well. One reason why more Cr(VI) may be mobilized from the UZ versus the oxic portion of the saturated zone is the dynamic hydrologic nature of the UZ and associated high-frequency Mn redox cycling. Chromium(III) in soils and

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sediments is most likely to become oxidized to Cr(VI) by coming into contact with the surface of a Mn oxide particle (Rai et al., 1989; Fendorf and Zasoski, 1992). Chromium(III) is highly immobile at neutral to moderately alkaline pH, so its transport to Mn oxide surfaces is kinetically limited. The frequent reduction and re-precipitation of Mn oxides on or near solid phase Cr(III) could thus accelerate the formation of Cr(VI).

Precipitation in the Sacramento Valley is highly seasonal, with roughly 90% falling November--April, and regularly oscillates through multi-year wet and dry cycles. The moisture content of UZ soils is therefore probably highly variable both temporally and spatially. During periods of significant infiltration, parts of the UZ may approach saturation due to soil heterogeneities, temporary perching above fine-grained horizons, and relatively large rises in the water table. This saturation could promote localized reducing conditions and the reduction of Mn oxides. Mobilized Mn(II) might then migrate until it is re-oxidized, either when

Fig. 7. Chromium concentration versus sample pH (A) and dissolved oxygen (B), Dashed line in (A) indicates pH = 7.0, dashed line in (B) indicates $DO = 1$ mg L^{π} Cr_T = total Cr, DO = dissolved oxygen.

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Fig. 8. Total Cr (Cr_T) concentration versus $NO₃$ concentration for south zone samples (A), NO₃ concentration versus age category for all samples (B), and Cr(VI) concentration versus NO₃ concentration for middle and north zone samples (C). Dashed lines indicate $NO_3 = 3$ mg L⁻¹, considered maximum for natural background, and $Cr = 5 \mu g L^{-1}$, considered threshold for "elevated". Age categories (M, MM1, etc.) defined in text.

sufficient draining/drying brings a re-invasion of air, or when the next wet cycle brings another influx of oxygenated water.

In addition to increasing the likelihood of Mn oxide coming into contact with solid-phase Cr(III), the cyclical destruction and

re-formation of Mn oxide may also result in fresh, more reactive Mn oxides that are more capable of oxidizing Cr(III) (Fendorf, 1995; Tang, 2014). Furthermore, recent studies suggest that some fungi (primarily Ascomycetes and Basidiomycetes), in addition to bacteria, may play an important role in the formation of Mn oxides in soils (Hansel et al., 2012; Tang et al., 2013). The fact that these fungi cannot live in saturated sediments could lead to a typically higher Mn oxide content in the UZ compared to the saturated zone. promoting higher rates of Cr(VI) mobilization in the UZ. Given that the mobilization of Cr(VI) in groundwater systems is only partially understood, it is also possible that other transients in redox, pH, and microbial activity linked to transients in moisture and soil gas composition could cause enhanced Cr(VI) mobilization in the UZ via mechanisms that are currently unrecognized. Regardless of the mechanism, it is reasonable to suspect that longer UZ residence times may lead to higher Cr(VI) concentrations in groundwater if Cr(VI) is mainly mobilized in the UZ. It should also be recognized that the saturated zone hypothesis and UZ hypothesis are not mutually exclusive, and could both contribute to elevated Cr(VI) concentrations in the same aquifer.

The UZ hypothesis could help explain why irrigation recharge samples are typically elevated in Cr in the south zone, but not in the middle and north zones (Fig. 8A and C). In the middle and north zones, land used for agriculture is largely within areas where the water table is <5 m deep (Bennett et al., 2011; Fig. 5B). In the south zone, however, more agricultural land extends into areas where the water table is deeper, particularly in the southwest where the highest groundwater Cr concentrations were measured (Fig. 6). The potentially longer UZ residence times for irrigation recharge in the south zone could contribute to the higher Cr(VI) concentrations in irrigation recharge samples.

The Cr(VI) concentration in samples from wells near the mountain front that contain modern water (excluding irrigation recharge samples) provides a test of the UZ hypothesis. Elevated Cr(VI) in these samples would support the UZ hypothesis and conflict with the saturated zone hypothesis, and an absence of Cr(VI) in these samples would do the opposite. Unfortunately, the GAMA dataset includes only four such samples from locations where ultramafic rocks crop out relatively close to the valley margin and high-Cr sediments are expected (south zone, western middle zone, and western north zone). Three of the four samples have warm NGTs, as expected, and their $Cr(VI)$ concentrations are <1, 1, 3, and $6 \mu g L^{-1}$. Because these samples as a group are neither elevated in nor free of Cr(VI), and there are so few of them, they do not provide support for either hypothesis. Ball and Izbicki (2004) indicated that samples from mountain front (recharge zone) wells in the same Mojave Desert aquifer studied by Izbicki et al. (2008a) contained no detectable Cr(VI), consistent with the saturated zone hypothesis. It is possible that mobilization of Cr(VI) in the UZ may be unimportant in this more arid system, but the dataset also only contained 4-6 such wells along a roughly 100 km section of mountain front. Given the potentially high variability of mountain block lithology and Cr content in adjacent basin sediments over this distance, it is also possible that the sampled wells do not directly represent geochemical conditions in the recharge locations for the high-Cr groundwater sampled further down-gradient.

A third hypothesis for the Group 2 samples is that they recharged directly through ultramafic rock units and overlying serpentine soils within the foothills adjacent to the Sacramento Valley (foothills recharge hypothesis). These materials are generally an order of magnitude higher in Cr_T than valley alluvium (1000's compared to 100's of mg kg⁻¹; Morrison et al., 2009). Although the permeability of the fractured rocks composing the foothills is considerably lower than that of valley alluvium, it is sufficient to create an aquifer that supplies springs and numerous domestic

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Fig. 9. Chromium concentration versus age category (A-C), 8¹⁸O (D-F), and noble gas recharge temperature (G-I) for south, middle, and north zones. Horizontal lines indicate Cr = 5 µg L⁻¹, considered threshold for "elevated". Shaded symbols on south zone plots indicate irrigation recharge samples. Age categories (M, MM1, etc.) defined in text. NGT = noble gas recharge temperature.

wells. The foothills recharge location would explain the considerable age of Group 2 samples, since this water would have to flow farther to sampled wells than water recharged through the alluvium. Moraetis et al. (2012) found that soil and groundwater data, combined with laboratory sorption experiments and numerical reactive transport modeling, supported the foothills recharge hypothesis for high Cr(VI) groundwater samples in the Oropos plain, Greece. However, the reason why Group 2 samples would have warm recharge temperatures is not clear. Available data indicate that, although water table depths in crystalline-rock mountain areas can be >50 m under ridges, they are typically shallower and closely mimic the land surface topography (e.g., Bossong et al.,

2003). Further, total depths of domestic wells are generally <60 m in at least one area of the Sierra foothills east of the valley (Page et al., 1984), implying water table depths generally <50 m. The foothills recharge hypothesis is also inconsistent with a recently published broad survey of groundwater Cr in Greece (roughly 600 sites) which found that Cr(VI) concentrations in groundwater in fractured ultramafic rock were all <10 μ g L⁻¹, whereas concentrations in groundwater in surrounding sediments were considerably higher (Kaprara et al., 2015). Finally, Morrison et al. (2009) found a higher fraction of acid-soluble Cr (likely present in serpentine, secondary silicates, clays, and Fe oxides rather than spinels) in south zone soils than in adjacent mountain soils

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Environmental tracer data from the Sacramento Valley suggest that future research aimed at improving our understanding geogenic Cr(VI) in groundwater should prioritize data collection from the UZ in recharge areas. The GAMA dataset along with previous study results define three distinctly different hypotheses for where in the groundwater system most geogenic Cr(VI) becomes mobilized: (1) the UZ, (2) the oxic portion of the saturated zone, and (3) within ultramafic rocks and overlying serpentine soils in adjacent foothills. Determining with some level of confidence which of these hypotheses is correct for a particular aquifer will likely require a sampling program that targets a verified groundwater flowpath through Cr-rich sediments and/or rock, involving collection of soil/rock and water samples from the UZ in the recharge area, the immediately underlying saturated zone, and down-gradient oxic portion of the saturated zone.

5. Conclusions

Geogenic Cr(VI) occurs in groundwater throughout much of the Sacramento Valley. Thirty-seven (22%) of 166 groundwater samples contained elevated concentrations ($\geq 5 \mu g L^{-1}$), with 17 (10%) exceeding 10 μ g L⁻¹. The highest concentrations occur in the south zone. Proximity of ultramafic rocks in the mountains to the valley margin up-gradient of sampling locations appears to be a first-order control on Cr(VI) concentration; elevated samples were only found in parts of the valley where ultramafic rocks are exposed within about 30 km of the mountain front. Groundwater pH and dissolved oxygen also directly control Cr(VI) concentration, as observed in previous studies. Elevated Cr was found neither in samples with a pH < 7, likely due to high levels of adsorption, nor in samples with a dissolved oxygen concentration <1 mg L^{-1} , likely due to reduction of Cr(VI) to Cr(III).

The environmental tracer data, along with water chemistry, identify two different groups of samples with elevated Cr concentrations in the Sacramento Valley. Group 1 consists of samples from the south zone that contain modern (<60 yr old) water, have elevated NO₃ concentrations (>3 mg L⁻¹), commonly have $\delta^{18}O$ values enriched relative to local precipitation, and typically have noble gas recharge temperatures (NGTs) in the expected range for local Holocene recharge. These samples likely contain irrigation water and are elevated due to accelerated mobilization of Cr(VI) in the unsaturated zone in irrigated areas. Group 2 consists of samples from throughout the valley that are mostly 1000-10,000 yr old, have $\delta^{18}O$ values consistent with local precipitation, and have warm NGTs.

Elevated Cr(VI) in Group 2 samples is most likely the result of relatively long unsaturated zone residence times due to recharge through deep unsaturated zones near the margins of the basin, Other potential causes include long residence times in the oxic portion of the saturated zone (increasing pH and desorption of Cr(VI)), and recharge directly through high-Cr ultramafic rock and serpentine soils in adjacent foothills. However, these other hypotheses are inconsistent with some of the available data, particularly the uniformly warm NGTs of Group 2 samples. The reason Cr(VI) may be primarily mobilized in the UZ rather than the oxic portion of the saturated zone is not immediately evident, but one possibility is that Mn oxides are more dynamic (cyclically dissolving and re-precipitating), reactive, and abundant in the UZ due to transients in moisture and redox conditions and the enhancement of Mn(II) oxidation by fungi. Future research aimed at improving our understanding geogenic Cr(VI) in groundwater should prioritize data collection from the UZ in recharge areas, and include systematic sampling along verified groundwater flowpaths through Cr-rich sediments and/or rock.

Acknowledgements

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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.2015. 05.010.

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Government Affairs Committee

Agenda Item: 3

Date: August 17, 2015

Development of Regulations to Implement the Sustainable Groundwater Subject: Management Act of 2014 (SGMA) and Potential 2015 Groundwater Legislation

Staff Contact: Robert Roscoe, General Manager

Background:

In September 2014, Governor Jerry Brown signed into law an unprecedented three-bill legislative package, known as the Sustainable Groundwater Management Act of 2014 (SGMA). The SGMA provides a framework for sustainable management of groundwater supplies by local authorities, with a limited role for state intervention only if necessary to protect the resource. Implementation deadlines are attached as Exhibit 1.

The act requires the formation of local groundwater sustainability agencies (GSAs) that must assess conditions in their local water basins and adopt locally-based management plans. The act provides substantial time, 20 years, for GSAs to implement plans and achieve long-term groundwater sustainability. It protects existing surface water and groundwater rights and does not impact current drought response measures. The Department of Water Resources (DWR) has a draft list of critically overdrafted basins, attached to this report as Exhibit 2.

Discussion:

In February 2015, the Sacramento Groundwater Authority (SGA) directed their staff to move forward in preparations to become the GSA for the Sacramento County portion of the North American Subbasin of the Sacramento Valley Groundwater Basin. The SGA convened two workshops of those involved in groundwater management in three adjoining SGA in Placer, Sutter and Sacramento Counties.

GSA formation is governed by Section 10723 of the California Water Code. The process includes a public notice pursuant to Section 6066 of the Government Code, followed by a public hearing. If SGA elects to become the GSA for protection of the basin, the agency would notify the DWR, which posts the notice on its web site. At the August 13, 2015 SGA Board meeting, the Board directed staff to take actions necessary for SGA to become a GSA.

Development of Regulations to Implement the Sustainable Groundwater Management Act of 2014 (SGMA) and Potential 2015 Groundwater Legislation August 17, 2015 Page 2 of 2

The DWR has released a draft strategic plan for its Groundwater Sustainability Program describing DWR's responsibilities and outlining key actions it will take to support local agencies with implementation of the SGMA. The draft plan also describes current groundwater conditions in the state, identifies success factors in addressing key challenges, and presents an initial plan for DWR communication and outreach.

Under SGMA, DWR must complete multiple activities such as the adoption of regulations for local agency proposed revisions to groundwater basin boundaries, adoption of regulations for evaluating and implementing local agency prepared groundwater sustainability plans, updating the prioritization of basins, and conducting groundwater assessments.

Association of California Water Agencies
Leadership Advocacy
Information - Service

X **SUSTAINABLE GROUNDWATER** MANAGEMENT ACT OF 2014

EXHIBIT 1

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Implementation Deadlines

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Draft List of Critically Overdrafted Basins-August 6, 2015

