

# Factors Controlling the Regional Distribution of Vanadium in Groundwater

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## Abstract

Although the ingestion of vanadium (V) in drinking water may have possible adverse health effects, there have been relatively few studies of V in groundwater. Given the importance of groundwater as a source of drinking water in many areas of the world, this study examines the potential sources and geochemical processes that control the distribution of V in groundwater on a regional scale. Potential sources of V to groundwater include dissolution of V rich rocks, and waste streams from industrial processes. Geochemical processes such as adsorption/desorption, precipitation/dissolution, and chemical transformations control V concentrations in groundwater. Based on thermodynamic data and laboratory studies, V concentrations are expected to be highest in samples collected from oxic and alkaline groundwater. However, the extent to which thermodynamic data and laboratory results apply to the actual distribution of V in groundwater is not well understood. More than 8400 groundwater samples collected in California were used in this study. Of these samples, high ( $\geq 50$   $\mu\text{g/L}$ ) and moderate (25 to 49  $\mu\text{g/L}$ ) V concentrations were most frequently detected in regions where both source rock and favorable geochemical conditions occurred. The distribution of V concentrations in groundwater samples suggests that significant sources of V are mafic and andesitic rock. Anthropogenic activities do not appear to be a significant contributor of V to groundwater in this study. High V concentrations in groundwater samples analyzed in this study were almost always associated with oxic and alkaline groundwater conditions, which is consistent with predictions based on thermodynamic data.

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## Introduction

Concerns over the possible adverse health effects to humans from high concentrations of V in drinking water have led the U.S. Environmental Protection Agency to place V on its most recent contaminate candidate list (U.S. Environmental Protection Agency 2009). These same concerns also led the California Department of Public Health (CDPH) to establish a notification level (NL) of 50  $\mu\text{g/L}$  for V in drinking water (California Department

of Public Health 2007). Drinking water supplies in the United States (Hutson et al. 2004), and in many areas of the world, are dependent on groundwater. However, few groundwater studies have considered V as a constituent of interest. Consequently the significant sources, and behavior, of V in groundwater are not well understood.

The purpose of this paper is to provide an understanding of the factors that control V concentrations in groundwater at the regional scale. This is done by relating the location of potential sources and geochemical conditions (redox and pH) to the regional distribution of high ( $\geq 50$   $\mu\text{g/L}$ ) and moderate (25 to 49  $\mu\text{g/L}$ ) V concentrations in groundwater. Groundwater samples used in this study were collected across the state of California (Figure 1). Because of the vastness of the study area ( $\sim 410,000$   $\text{km}^2$ ), the areal distribution of V is examined in relation to the hydrogeologic provinces of California as defined by Belitz et al. (2003) (Figure 1). This will allow for easier

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**Figure 1. Map showing hydrogeologic provinces and geographical areas of interest.**

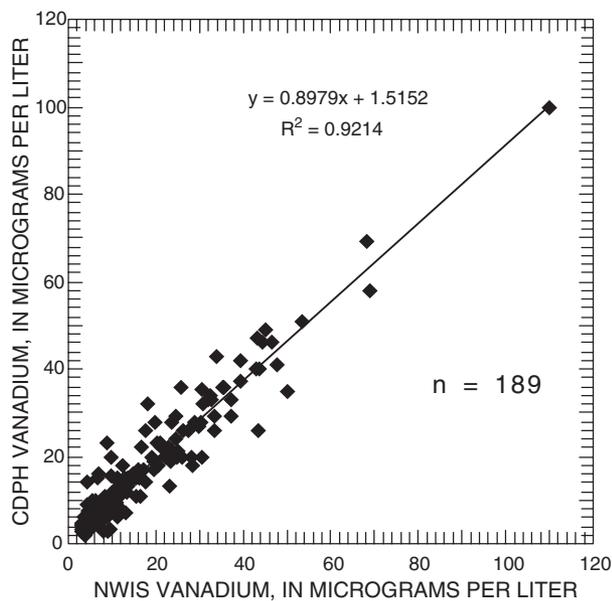
identification of areas where high concentrations of V most frequently occur at the regional scale. The hydrogeologic provinces (hereafter referred to as provinces) were delineated based on similarities in climate, geology, and hydrology. Because the state of California has a wide range of geologic and climatic regimes, aquifer and land use types, results from this study may be able to be extrapolated to other areas with similar conditions.

### Source of Water Quality Data and Statistical Methods

Groundwater quality data were compiled in 2008 from the U.S. Geological Survey's (USGS) National Water Information System (NWIS) and the CDPH water quality database. NWIS analyses are available for filtered (0.45 µm) samples, while CDPH analyses are available for unfiltered samples. Despite the differing methods of collection, a comparison of V concentrations for groundwater sampled by both the USGS and CDPH showed good agreement (Figure 2). For each sample point, the most recent V concentration, along with any associated water quality data (e.g., pH), from the previous

7 years of records was used. A 7-year period of record was used for two reasons: (1) comparisons between NWIS and CDPH V data during this time period showed good agreement; and (2) a 7-year time period provided a large number of samples (8470) affording a robust analysis of V in groundwater. Because the reporting levels for V are lower for NWIS data than for CDPH data, concentrations were screened at the higher CDPH reporting level of 3 µg/L. Nitrate (NO<sub>3</sub><sup>-</sup>), iron (Fe), and manganese (Mn) data were also used from both the NWIS and CDPH databases to infer the redox conditions of groundwater. A discussion of the comparison and use of this data can be found in the Section on "Redox and pH Conditions."

Nonparametric statistics were used to determine the significance of the relation between potential controlling factors and V concentrations in groundwater samples. The Wilcoxon rank sum test was used to compare two independent data groups (categories) to determine if one group contains larger values than the other (Helsel and Hirsch 1992). The results of the Wilcoxon rank sum statistical test is considered significant if the null hypothesis was rejected at least 95% of the time ( $p \leq 0.05$ ).



**Figure 2.** Comparison of vanadium concentrations analyzed by the U.S. Geological Survey's National Water Quality Laboratory (NWIS) and the California Department of Public Health (CDPH). NWIS analyzes filtered samples (0.45  $\mu\text{m}$ ) and the CDPH analyzes unfiltered samples. Trend line represents a linear regression of the data.  $n$  is the number of samples used for comparison.

## Potential Sources of V to Groundwater

### Natural Sources

Vanadium is a widely distributed minor element in the earth's crust, with an average crustal abundance of 120  $\mu\text{g/g}$  (Reimann et al. 1998). This makes V slightly more abundant than chromium (100  $\mu\text{g/g}$ ), and much more abundant than uranium (2.6  $\mu\text{g/g}$ ) and arsenic (1.8  $\mu\text{g/g}$ ). V is contained in a wide variety of minerals; with more than 80 V-containing minerals having been identified and described (Fleischer 1987; Clark 1990). Because of its affinity to substitute for Fe in minerals, V is more abundant in mafic rocks than in silicic rocks. Typical concentrations in basalts and gabbros range from 200 to 300  $\mu\text{g/g}$ , while concentrations in granites range from 5 to 80  $\mu\text{g/g}$  (Nriagu 1998). Somewhat curious is the relatively low enrichment of V in ultramafic rocks, which average 80  $\mu\text{g/g}$  (Reimann et al. 1998).

Shales can also be abundant in V, especially if they were formed in a marine environment, or are composed of a high percentage of organic carbon. Breit et al. (1991) attributed the higher V content of marine vs. lacustrine shale to the large mass of V circulating in ocean water compared to that in terrestrial runoff. Carbonaceous shale has been shown to contain V up to 16,000  $\mu\text{g/g}$  (Vine et al. 1970; McKelvey et al. 1986) compared to other shales that have an average V content of 130  $\mu\text{g/g}$  (Turekian et al. 1961).

### Anthropogenic Sources

The most important industrial process with respect to the use of V is the ferrous metallurgy industry

(World Health Organization 1988). Liquid waste and wash water from metallurgical plants may contain up to several hundred milligrams per liter of V. V may also be released into the environment via atmospheric emissions from smelting and foundry operations. Other industries possibly producing V-containing wastes include the following: the chemical and polymer industry, where V is an important component in a wide array of chemical syntheses and oxidation reactions (Nriagu 1998); and the mining industry where the processing of uranium and titanium ore produce V-containing effluents and leachates (Nriagu et al. 1988).

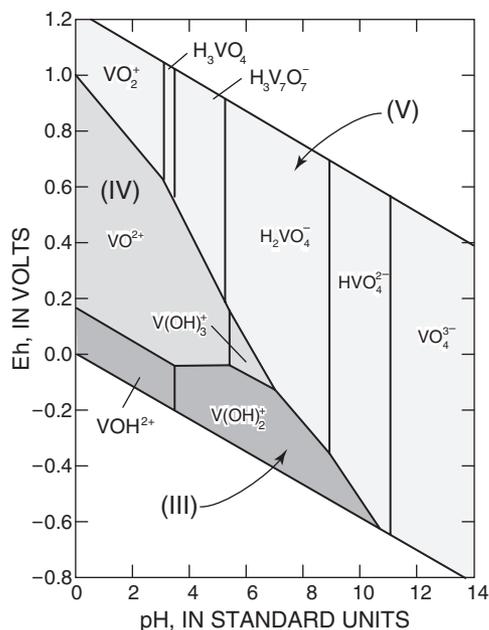
The combustion of V-enriched fossil fuels, primarily in the form of residual crude oil, is a significant source of anthropogenic V emissions to the atmosphere (Duce et al. 1976; Hope 1997). Reserves of crude oil range from relatively low concentrations of less than 1  $\mu\text{g/g}$  in oil mined in the United States to relatively high concentrations of 1400  $\mu\text{g/g}$  in oil mined in western Venezuela (National Academy of Sciences [NAS] 1974). Concentrations of V in the U.S. coal range from 15 to 34  $\mu\text{g/g}$ . Results of a study in Mexico indicated that atmospheric deposition of particulate V emitted from a thermoelectric plant was the source of increased V concentrations in local groundwater (Mejia et al. 2007). Conversely, an Italian study found that particulate V emitted from a large oil refinery was not a significant source of V to groundwater (Soldi et al. 1996). Other industrial processes may contribute emissions of anthropogenic V to the atmosphere, such processes include the following: mining of metals, smelting, and foundry operations.

## Geochemical Controls

The geochemistry of V is complex. This is because V participates in a wide range of chemical reactions due to its ability to form many different molecular arrangements (Crans et al. 1998). Because of its affinity for oxygen, V forms both stable oxyanions and oxycations. V is a redox sensitive element that exists in three oxidation states in the environment: V(III), V(IV), and V(V) (Figure 3). Thermodynamically speaking, the predominant oxidation state of V is dependent on the Eh and pH conditions of the aqueous system under consideration. V(V) and V(IV) are the most important species in natural water, with V(V) likely the most abundant under environmental conditions (Hem 1985). Important processes that control the concentration of V in groundwater include the precipitation/dissolution of V bearing mineral phases, adsorption/desorption, and chemical transformations (changes in oxidation state) under varying redox and pH conditions.

### Precipitation/Dissolution of Mineral Phases

The precipitation and dissolution of mineral phases can control trace element concentrations in solution. The stability of these mineral phases is dependent on the geochemical environment (Eh, pH, and concentrations of mineral forming ions) of aquifer systems. If the



**Figure 3. Stability diagram for vanadium with fixed total activities of vanadium =  $10^{-7}$ , sulfur =  $10^{-4}$ , and carbon =  $10^{-3}$  M at  $25^{\circ}\text{C}$  and 1 atm (adapted from Hem 1977).**

geochemical environment of an aquifer changes over time, due to such processes as declining water levels from pumping or the implementation of artificial storage, and recovery operations, V concentrations may increase or decrease due to shifts in equilibrium of mineral phases. Groups of V-containing minerals found in differing geochemical environments include the following: sulfides, sulfosalts (derived from the oxidation of sulfide bearing ores), silicates, and oxides (Nriagu 1998).

Co-precipitation of V in Fe minerals is likely an important process in governing the concentration of V in aquifer systems. V(V) has been speculated to be present in Fe minerals due to the precipitation of ferric-vanadate (Tenyakov 1965). Hem (1977) used thermodynamic data to suggest that a ferrous-vanadate compound may control the solubility of V in the environment. Structural similarities of Fe and V oxides suggest the substitution of V for Fe in Fe-oxides (Taylor et al. 1970). More recent studies have presented evidence that V(III) can substitute for Fe in Fe-oxides (Singh et al. 1992; Trolard et al. 1995; Schwertmann et al. 1996).

#### Adsorption/Desorption Processes

The mobility of V in groundwater is in part controlled by the adsorption/desorption processes on mineral surfaces (Wehrli et al. 1989; Northrop et al. 1990; Wanty et al. 1990, 1992; Breit 1995). These processes are in turn governed by the oxidation state of V, pH, and the presence of competing cations and anions for surface adsorption sites. V(V) and V(IV) are strongly adsorbed to mineral surfaces via inner-sphere complexation. The V(V) oxyanions,  $\text{H}_2\text{VO}_4^-$  and  $\text{HVO}_4^{2-}$  have been shown to adsorb to oxide surfaces (Micera

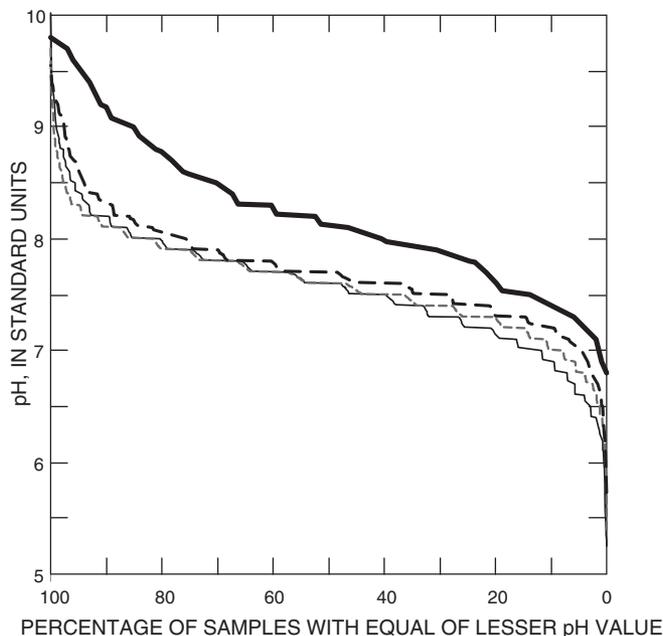
et al. 1988; Wehrli et al. 1989; Peacock et al. 2004), and to the clay mineral kaolinite (Breit et al. 1991). The V(IV) oxyanion  $\text{VO}_2^+$  adsorbs more strongly to oxides than do the V(V) oxyanions, although this complex has limited stability in oxidized environments (Wehrli et al. 1989). Studies performed under laboratory conditions have shown that V oxyanions and oxycations can adsorb to mineral surfaces over a wide range of pH despite electrostatic repulsion by charges on mineral surfaces (Wehrli et al. 1989; Peacock et al. 2004). However, the extent to which this behavior applies in the environment is not well understood. Dissolved V also adsorbs to organic compounds (Perrin 1979; Wehrli, 1987), with V(V) oxyanions forming relatively weak complexes compared to the V(IV) oxycation  $\text{VO}_2^+$ . Several studies have shown that organic compounds are capable of reducing adsorbed V(V) to V(IV) (Szalay et al. 1967; Goodman et al. 1975; Wilson et al. 1979).

In this study, a comparison of V concentration and pH from across California shows that 60% of the samples with high concentrations of V ( $\geq 50 \mu\text{g/L}$ ) occurred in groundwater with a pH of at least 8.0 (Figure 4). Conversely, only 20% of the samples that had either very low ( $< 3 \mu\text{g/L}$ ) or low V concentrations (3 to 24  $\mu\text{g/L}$ ) came from groundwater with a pH of 8.0 or above. The difference between pH values of samples with high V concentrations and those samples with moderate, low, and very low V concentrations was statistically significant ( $p < 0.05$ ). These results suggest that V is desorbed from particle surfaces in groundwater with an alkaline pH.

#### Redox and pH Conditions

Based on thermodynamic data, V should be most mobile in oxidized and alkaline groundwater (Figure 3). Under these conditions the formation of the V(V) oxyanions:  $\text{H}_2\text{VO}_4^-$  and  $\text{HVO}_4^{2-}$  are favored (Wehrli et al. 1989; Wanty et al. 1992). Under more reducing and acidic conditions, the V(IV) oxycations,  $\text{VO}_2^+$  and  $\text{V(OH)}_3^+$ , are thermodynamically predicted to be the dominant species. Studies have shown the presence of  $\text{VO}_2^+$  in marine shale (Ekstrom et al. 1983) and carbonaceous sediments (Premovic et al. 1986) where reducing environments are expected to predominate. Under certain environmental conditions V(IV) may be relatively insoluble, as indicated by a study of V mobility in evaporation pond sediments where the loss of V in solution was attributed to the precipitation of the V(IV) oxyhydroxide,  $\text{VO(OH)}_2$  (Amrhein et al. 1993). V(III) is thermodynamically stable over a wide pH range, but only under the most reducing environmental conditions. V(III) rapidly hydrolyzes in solution forming relatively insoluble oxyhydroxides (Wanty et al. 1992), and therefore is not likely an important species in the aqueous phase.

The redox condition of groundwater can be inferred by the presence and/or absence of redox indicator constituents. Microorganisms affect the redox conditions of groundwater by utilizing terminal electron acceptors during the degradation of organic carbon. The order of terminal electron acceptor utilization is  $\text{O}_2 > \text{NO}_3^- >$



**EXPLANATION**

- Vanadium concentrations by category vs pH—
- Very low (less than 3 micrograms per liter; n = 1883)
  - - - Low ( 3 to 24 micrograms per liter; n = 3993)
  - . - . Moderate ( 25 to 49 micrograms per liter; n = 554)
  - High (equal to or greater than 50 micrograms per liter; n = 102)

**Figure 4. Percentile of sample pH as a function of vanadium concentration by category.**

Mn(IV) > Fe(III) > SO<sub>4</sub><sup>2-</sup> > CO<sub>2</sub> (McMahon et al. 2008). With the successive utilization, and subsequent depletion, of terminal electron acceptors the redox condition of groundwater progresses from oxidizing (positive Eh values) to reducing (negative Eh values) (Figure 3). Therefore, assuming equality of sources, V concentrations should be higher in oxic groundwater where O<sub>2</sub> is the predominant terminal electron acceptor (O<sub>2</sub> is being reduced), and lower in anoxic groundwater where NO<sub>3</sub><sup>-</sup>, Mn(IV), and Fe(III) are predominant terminal electron acceptors (NO<sub>3</sub><sup>-</sup>, Mn(IV), and Fe(III) are being reduced).

In this study, the concentration of dissolved O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn [produced by the reduction of Mn(IV) to Mn(II)], and Fe [produced by the reduction of Fe(III) to Fe(II)] in samples were compared to thresholds to determine if a sample came from oxic groundwater or from anoxic groundwater (Table 1). This study uses both filtered (NWIS data) and unfiltered (CDPH data) samples to infer redox conditions of groundwater. For filtered samples concentration thresholds for all redox indicator constituents as outlined by McMahon et al. (2008) were used. However, because unfiltered samples can overestimate the concentration of dissolved constituents, a second set of raised concentration thresholds were used for CDPH data (Table 1). The difference in concentration between filtered NWIS samples and unfiltered CDPH samples collected at wells sampled by both methods was

**Table 1**  
**Concentration Thresholds in Milligrams per Liter for Dissolved Redox Indicator Constituents Used to Infer Redox Conditions in Groundwater**

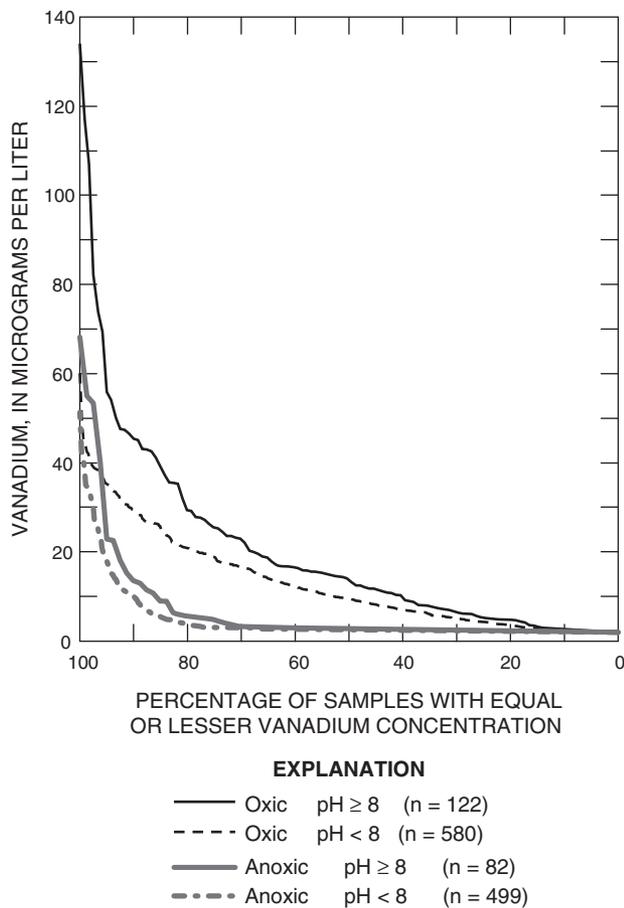
Redox Condition	O <sub>2</sub>	NO <sub>3</sub> <sup>-</sup> as N	Mn	Fe
Oxic	≥0.5	≥0.5 (0.6)	<0.05 (0.12)	<0.1 (0.23)
Oxic	≥0.5	<0.5 (0.6)	<0.05 (0.12)	<0.1 (0.23)
Anoxic	<0.5	<0.5 (0.6)	≥0.05 (0.12)	≥0.1 (0.23)
Anoxic	<0.5	<0.5 (0.6)	≥0.05 (0.12)	<0.1 (0.23)
Anoxic	<0.5	<0.5 (0.6)	<0.05 (0.12)	≥0.1 (0.23)
Anoxic	—	<0.5 (0.6)	≥0.05 (0.12)	≥0.1 (0.23)
Anoxic	—	<0.5 (0.6)	≥0.05 (0.12)	<0.1 (0.23)
Anoxic	—	<0.5 (0.6)	<0.05 (0.12)	≥0.1 (0.23)

Note: Numbers in parenthesis are raised thresholds used for unfiltered samples.  
 —, data not available.

used to create a raised threshold for unfiltered samples. The amount the thresholds were raised was calculated by taking the median value of the range of concentration differences between filtered and unfiltered samples and adding that value to the concentration threshold used for filtered samples. For example, the differences in concentration between filtered and unfiltered Mn samples collected at the same wells within 1 year of each other yielded a range in differences of 0.05 to 0.17 mg/L with a median value of 0.07 mg/L. Therefore, the raised threshold for unfiltered Mn is filtered threshold (0.05 mg/L) + median difference (0.07 mg/L) = raised threshold (0.12 mg/L). Available data did not allow for classifications to be made based on SO<sub>4</sub><sup>2-</sup> and CO<sub>2</sub> reducing conditions. Out of the 8470 wells with available V data used in this study, 1283 had sufficient data so that a redox classification could be made.

Samples were further classified based on whether the pH of the sample was below 8.0, or equal to, or greater than 8.0. A pH value of 8.0 was chosen on the basis that it is approximately the zero point of charge (zpc) for some iron oxide minerals (Stumm and Morgan 1996). The zpc of iron oxide minerals was chosen because these minerals are a ubiquitous sorbent in many aquifer systems (Stumm and Morgan 1996).

A comparison of V concentrations and redox conditions showed that samples collected from oxic groundwater had significantly higher V concentrations (*p* < 0.05) than samples collected from anoxic groundwater (Figure 5). Not taking into account pH, 18% of oxic samples had V concentrations ≥25 μg/L, and 1.6% had concentrations ≥50 μg/L. Conversely, only 3.6% of anoxic samples had V concentrations ≥25 μg/L and just 0.6% of the samples had concentrations that were ≥50 μg/L. Lower concentrations associated with anoxic conditions are consistent with the reduction of V(V) to V(IV and/or III), and subsequent precipitation of insoluble oxyhydroxides, and/or the formation of ferrous-vanadate compounds as predicted by Hem (1977).



**Figure 5. Percentile of vanadium concentration as a function of redox conditions (as inferred by redox indicator constituents) and pH.**

Under oxidic conditions, V concentrations were higher in alkaline samples ( $\text{pH} \geq 8.0$ ) than in more acidic samples ( $\text{pH} < 8.0$ ) (Figure 5). This result may be due to V(V) anions, which are predicted to be the predominant V species under oxidic and alkaline conditions, being desorbed from charged mineral surfaces that become increasingly negatively charged as the pH of groundwater increases. By contrast, under anoxic conditions pH does not appear to be as much of a factor in controlling V concentrations, which suggests that V may be precipitating as insoluble oxyhydroxides and/or that the reduced cationic forms of V (IV and III) are being strongly adsorbed to negatively charged mineral surfaces. Mineral surfaces are expected to be mostly negatively charged under the pH ranges found in the environment (Stumm and Morgan 1996). The relation between soluble V and redox conditions shown in this study indicate that V is most mobile in oxidized and alkaline groundwater, which is in agreement with predictions based on thermodynamic data.

### Areal Distribution of V in Groundwater

Because V concentrations used in this study come almost exclusively from the analysis of public supply well water the number and spatial distribution of V analyses

is not uniform across the provinces. In addition, because public supply wells tend to be located in or near populated areas, the distribution of V groundwater samples is not widely distributed within the provinces themselves. Therefore, care should be exercised when interpreting the results of the areal distribution of V presented in this study. V concentrations (filtered and unfiltered samples) in the following discussions are referenced using the categorical terms: very low ( $< 3 \mu\text{g/L}$ ), low (3 to  $24 \mu\text{g/L}$ ), moderate (25 to  $49 \mu\text{g/L}$ ), and high ( $\geq 50 \mu\text{g/L}$ ). These categories were defined in part based on the CDPH reporting level of  $3 \mu\text{g/L}$  for V, and the California NL for V in drinking water of  $50 \mu\text{g/L}$ .

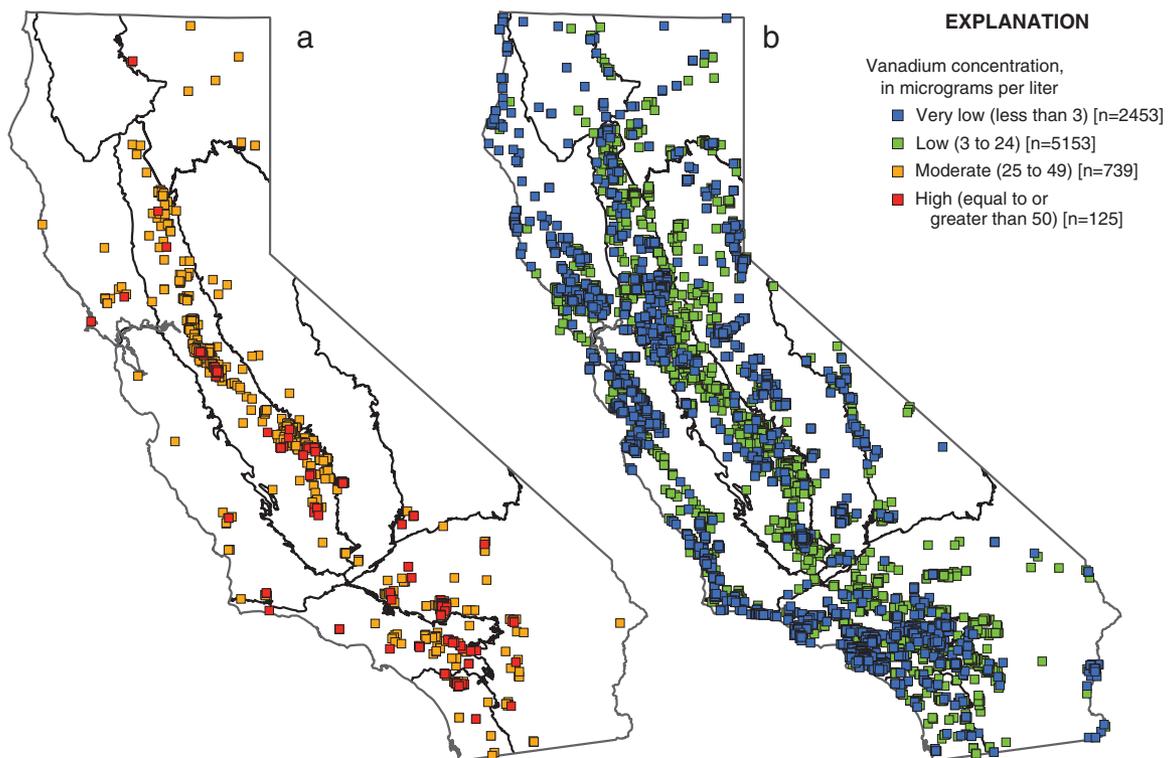
Of the 8400 V sample concentrations (filter and unfiltered samples) available statewide for this study, 90% of them ranged from very low to low (Table 2). This trend was also generally observed in each of the provinces where the majority of samples (80 to 100%) had concentrations that were either categorized as very low or low. Statewide, 8.5% of sample concentrations were classified as moderate and 1.5% of the sample concentrations were classified as high. High sample concentrations ranged from 50 to  $140 \mu\text{g/L}$ , and were detected in every province except for the Klamath Mountains (Figure 1; Table 2); absence of high concentrations in this province could be due to the low number of samples ( $n = 22$ ). Provinces where at least 1.5% of the samples were categorized as high include the San Diego Drainages, Desert, Sierra Nevada, and Central Valley. All of these provinces, except for the Sierra Nevada, also had median V concentrations that were higher than the statewide median of  $5 \mu\text{g/L}$  (Table 2). Based on Wilcoxon rank sum tests, concentrations tended to be highest in the Central Valley province, followed by the Desert and then the San Diego Drainages provinces; each of these provinces had significantly different V concentrations from one another ( $p < 0.05$ ). The rest of the provinces had lower concentrations than the top three and, statistically speaking, had the same sample concentration distribution as at least one other province in the study (Table 2).

Figures 1, 6a, and 6b show the geographical locations and areal distribution of V concentrations in the study area. Because of the scale of Figures 6a and 6b, caution should be used when interpreting the distribution of V concentrations within the provinces. Regional trends in the distribution of high V concentrations are discernable within provinces where high concentrations are frequently ( $\geq 1.5\%$ ) detected. In the Central Valley province, 96% of high concentrations were detected in the eastern San Joaquin Valley. In the Desert province, high concentrations were most frequently detected in samples collected in the western Mojave (85%), and of these high concentrations over half were detected in the Victor Valley. High concentrations in the San Diego Drainages province were almost exclusively (92%) detected in the Temecula Valley, which is located in the northern portion of the province. A similar trend was observed in the Sierra Nevada province where 100% of the samples with high concentrations were detected in the "Tule River Basin."

**Table 2**  
**The Distribution of V Concentrations (Filtered and Unfiltered Samples) Statewide and by Hydrogeologic Province**

Summary of Sample Concentrations					
Hydrogeologic Province (Total Samples)	Median (µg/L)	Percentage of Samples by Concentration Category			
		Very Low (<3 µg/L)	Low (3 to 24 µg/L)	Moderate (25 to 49 µg/L)	High (≥50 µg/L)
Statewide (8470)	5	30	60	8.5	1.5
Central Valley (2977) <sup>a</sup>	12	17.5	62.9	18.1	1.5
Desert (766) <sup>b</sup>	10.3	12.8	71.7	12	3.5
San Diego Drainages (203) <sup>c</sup>	8	24.1	60.6	8.9	6.4
Cascades and Modoc Plateau (124) <sup>d</sup>	6.5	31.4	61.3	6.4	0.9
Basin and range (150) <sup>d</sup>	4.2	32.7	64	2	1.3
South coast ranges (1039) <sup>e</sup>	4	33.5	65	1.2	0.3
Transverse and selected peninsular ranges (2054) <sup>e</sup>	3.7	38.8	58	2.1	1.1
North coast ranges (570) <sup>f</sup>	<3	43.5	54	2.1	0.4
Sierra Nevada (565) <sup>f</sup>	<3	50.6	45.1	2.5	1.8
Klamath Mountains (22) <sup>f</sup>	<3	54.5	45.5	0	0

Note: Hydrogeologic provinces with the same letter do not have significantly different concentration distributions based on the Wilcoxon rank sum test ( $p \leq 0.05$ ).



**Figure 6. Location of vanadium concentration by category. (a) Samples with moderate and high concentrations. (b) Samples with very low and low concentrations.**

### Distribution in Relation to Potential Sources

The distribution of groundwater samples with high V concentrations was examined in relation to land use to help determine if anthropogenic activities are a significant source of V in groundwater. Land use was based on the

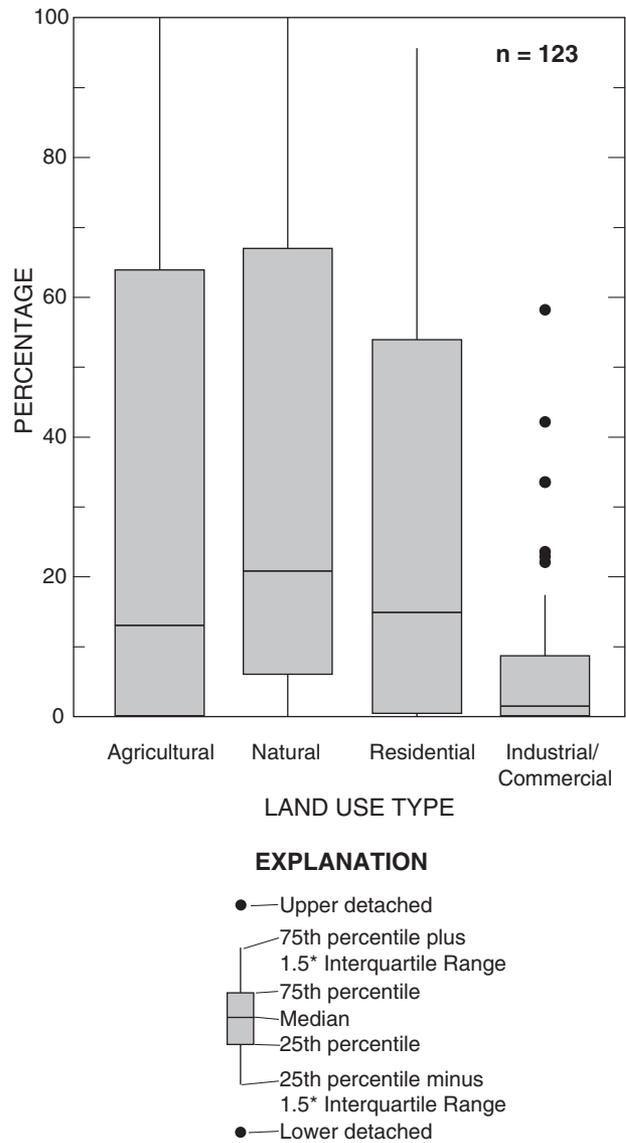
classification of the USGS National Land Cover Data (Vogelmann et al. 2001; Price et al. 2003), and each sample was attributed with land use by determining the percentage of land use type within 3 km of the well the sample was collected at. A radius of 3 km from the well was used because a previous study had indicated that the

effect of V contamination in groundwater due to emissions from a thermoelectric power plant was greatest within 3 km of the source (Mejia et al. 2007).

Anthropogenic sources of V are from industrial processes, so it seems reasonable to assume that samples having high concentrations of V due to anthropogenic activities would come from wells located in industrial and commercial areas. The distribution of groundwater samples with high concentrations in relation to industrial and commercial land use did not indicate that anthropogenic sources were a significant contributing factor to V in groundwater (Figure 7). When land use types were compared to one another, samples with high concentrations were significantly more likely ( $p = 0$ ) to be found in areas associated with agricultural, natural, or residential land use than in areas of industrial and/or commercial land use.

A qualitative assessment of the relation between V concentrations in groundwater samples and V-source rock was made to determine if the dissolution of V-source rocks was a potentially significant source of V in groundwater of California. A relation between V concentrations and V-source rocks was indicated if: (1) high and moderate concentrations were frequently detected in samples collected in groundwater basins where water-bearing formations consisting of V-source rocks, or materials derived from V-source rocks, are important sources of groundwater; and/or (2) high and moderate concentrations were frequently detected in samples collected in basins that are bounded by V-source rocks that may serve as recharge areas and/or as source material for basin deposits.

Samples with high and moderate V concentrations were most frequently detected in areas that are associated with mafic and intermediate rocks. In the northeastern San Joaquin and Sacramento Valleys high and moderate concentrations (Figures 1 and 6a) were primarily detected in groundwater samples from basins where water-bearing formations derived from andesitic and basaltic rocks are important sources of groundwater (Olmsted et al. 1961; Page 1986; Burow et al. 2004). Conversely in the southeastern San Joaquin and Temecula Valleys (Figures 1 and 6a) the main water-bearing formations in areas where samples with high and moderate concentrations were primarily detected are not described as being composed of sediment derived from mafic rocks (Croft 1972; Kennedy 1977). However, in the southeastern San Joaquin Valley high and moderate concentrations were detected in inter-fan areas that are bounded by meta-volcanic and gabbroic rocks of the Sierra Nevada foothills (Jennings et al. 1977) suggesting that some of the water-bearing deposits in these areas are indeed derived from mafic materials. A similar relation is also found in the Temecula Valley where Quaternary alluvium that is the main water-bearing unit is bounded by Tertiary basaltic and gabbroic rocks that constitute the southern California Peninsular Range (Kennedy 1977). Information was not readily available on water-bearing formations in the Tule River Basin; however, this basin is bounded on the west and



**Figure 7. Percentage of land use type within a 3 km radius of wells where samples with vanadium concentrations  $\geq 50 \mu\text{g/L}$  were collected.  $n$  is the total number of samples used for land use comparison.**

south by gabbroic rocks of the Sierra Nevada foothills (Jennings et al. 1977). In the western Mojave Desert high concentrations were detected predominately in samples collected in the Victor Valley and specifically on the Victorville fan (Figures 1 and 6a). The Victorville fan deposits contain abundant fragments of mafic rock, which contain minerals that have moderately high amounts of V (Izbicki et al. 2008a, b). The fan depositing themselves are unsaturated and thus are not a source of groundwater, but the concentration distribution in the area indicates that they are likely the source of high V concentrations in samples collected from the water-bearing formation that directly underlies these deposits.

The presence of V-source rocks was not uniformly predictive of the occurrence of high and moderate V concentrations in groundwater. This observation was most

notable in the Cascades and Modoc Plateau province where V concentrations were relatively low (Figures 1, 6a, and 6b) despite the fact that basaltic rock aquifers and basin fill aquifers, interlayered with basaltic flows, are important water-bearing formations (Planert et al. 1995; California Department of Water Resources 2003). Other provinces that have areas with V-source rock, but where concentrations were generally low include the Sonoma Volcanics in the North Coast Ranges province (Faye 1973; California Department of Water Resources 2003), and the Owens Valley in the Basin and Range province (Hollett et al. 1991). Factors contributing to the low V concentrations observed in these areas may include the following: (1) limited dissolution of low porosity basaltic flow rocks due to the low amount of water/rock interaction; (2) heterogeneity in the composition of volcanic rocks, and thus the content of V; (3) samples collected from wells not withdrawing groundwater that has interacted with V-source rock; and (4) geochemical conditions that do not favor V solubility (i.e., anoxic redox conditions).

### Distribution in Relation to Geochemical Conditions

Statewide results show (Figure 5) that V concentrations were significantly higher in oxic and alkaline groundwater samples than in anoxic samples regardless of their pH. At the regional scale, the concentration distributions in areas where samples with high concentrations were detected in a large percentage of samples also suggest that redox conditions and pH control V solubility in groundwater. For example, high concentrations in the eastern San Joaquin and Temecula Valleys were only detected in samples collected from oxic groundwater. Of the samples with very low V concentrations in the eastern San Joaquin Valley, 66% were collected from anoxic groundwater. Very low V concentrations in the northeastern San Joaquin were found most often in the trough of the valley where groundwater is frequently anoxic, while high concentrations were detected in samples collected more proximal to the Sierra Nevada (Figures 1, 6a, and 6b) where oxic redox conditions predominate. In addition to oxic redox conditions, high V concentrations in the Temecula and Victor Valleys were almost always detected in alkaline samples; of the 24 samples with high concentrations in these areas, 88% had a  $\text{pH} \geq 8.0$ .

Because of the presence of V-source rocks that serve as recharge areas and/or groundwater bearing deposits, high V concentrations might be expected to occur more frequently in areas of the Cascades and Modoc Plateau, Northern Coast Ranges, and Basin and Range provinces; however, low V concentrations were primarily detected in these areas (Figures 1, 6a, and 6b). In the Cascades and Modoc Plateau province and the Sonoma Volcanics area of the North Coast Ranges province, low V concentrations in groundwater may be partially due to the anoxic redox conditions found in these areas. However, due to the limited amount of redox indicator constituent data available in the Cascades and Modoc Plateau province

more data would be needed before a more solid conclusion could be made. In contrast to the anoxic redox conditions found in the Cascades and Modoc Plateau and Sonoma Volcanics of the Northern Coast Ranges province, samples collected in the Owens Valley of the Basin and Range province were primarily oxic and alkaline. The presence of oxic and alkaline conditions coupled with low V concentrations suggests that the volcanic rocks in the Owens Valley are not a significant contributing source of V to groundwater.

### Conclusions

The majority of groundwater samples assessed in this study contained V concentrations well below the California NL of 50  $\mu\text{g/L}$ ; 90% of sample concentrations in groundwater ranged from very low ( $< 3 \mu\text{g/L}$ ) to low (3 to 24  $\mu\text{g/L}$ ). Concentrations of V varied regionally, which is most likely due to a combination of the presence or absence of V-source rock, and redox and pH conditions of groundwater. Unlike the results of a previous study by Mejia et al. (2007), anthropogenic activities do not appear to be a significant contributing source to V concentrations in groundwater at the regional scale. High ( $\geq 50 \mu\text{g/L}$ ) and moderate (25 to 49  $\mu\text{g/L}$ ) V concentrations were most typically detected in samples collected from groundwater basins where water-bearing formations are derived from mafic rocks, and/or in basins that are bounded by mafic rocks. Additionally, intermediate rocks, such as andesite, and materials derived from these rocks are also likely contributors to high and/or moderate V concentrations in groundwater. However, not all samples collected in areas associated with V-source rocks have high and/or moderate V concentrations. In these areas, pH and redox conditions may not favor the solubility of V in groundwater, or there may be only limited dissolution of basaltic rocks. Groundwater samples collected from 8470 water wells distributed throughout the 410,000  $\text{km}^2$  study area show that V is most prevalent under oxidizing and alkaline conditions. Trends in V concentrations for samples collected in areas where high concentrations are frequently detected suggest that redox and pH conditions are important factors in controlling the solubility, and thus the distribution, of V in groundwater. These results are consistent with previous theoretical and laboratory study findings. However, further studies are needed to gain an understanding of the geochemical processes that are most important in governing the solubility of V in groundwater. Studies that would be helpful include the determination of V speciation (V, IV, and III) in groundwater under varying redox and pH conditions, and investigating the association between V compounds and mineral surfaces that are common in aquifer systems. Data could then be used in geochemical models to better predict conditions that favor precipitation and/or dissolution of V-containing minerals and the movement of V in the sub-surface.

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