



Assessing the solubility controls on vanadium in groundwater, northeastern San Joaquin Valley, CA



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ABSTRACT

The solubility controls on vanadium (V) in groundwater were studied due to concerns over possible harmful health effects of ingesting V in drinking water. Vanadium concentrations in the northeastern San Joaquin Valley ranged from <3 µg/L to 70 µg/L with a median of 21 µg/L. Concentrations of V were highest in samples collected from oxic groundwater (49% > 25 µg/L) and lowest in samples collected from anoxic groundwater (70% < 0.8 µg/L). In oxic groundwater, speciation modeling (SM) using PHREEQC predicted that V exists primarily as the oxyanion H₂VO₄⁻. Adsorption/desorption reactions with mineral surfaces and associated oxide coatings were indicated as the primary solubility control of V⁵⁺ oxyanions in groundwater. Environmental data showed that V concentrations in oxic groundwater generally increased with increasing groundwater pH. However, data from adsorption isotherm experiments indicated that small variations in pH (7.4–8.2) were not likely as an important factor as the inherent adsorption capacity of oxide assemblages coating the surface of mineral grains. In suboxic groundwater, accurate SM modeling was difficult since Eh measurements of source water were not measured in this study. Vanadium concentrations in suboxic groundwater decreased with increasing pH indicating that V may exist as an oxycationic species [e.g. V(OH)₃³⁺]. Vanadium may complex with dissolved inorganic and organic ligands under suboxic conditions, which could alter the adsorption behavior of V in groundwater. Speciation modeling did not predict the existence of V-inorganic ligand complexes and organic ligands were not collected as part of this study. More work is needed to determine processes governing V solubility under suboxic groundwater conditions. Under anoxic groundwater conditions, SM predicts that aqueous V exists as the uncharged V(OH)₃ molecule. However, exceedingly low V concentrations show that V is sparingly soluble in anoxic conditions. Results indicated that V may be precipitating as V³⁺- or mixed V³⁺/Fe³⁺-oxides in anoxic groundwater, which is consistent with results of a previous study. The fact that V appears insoluble in anoxic (Fe reducing) redox conditions indicates that the behavior of V is different than arsenic (As) in aquifer systems where the reductive dissolution of Fe-oxides with As adsorbed to the surface is a well-documented mechanism for increasing As concentrations in groundwater. This hypothesis is supported by the relation of V to As concentrations in oxic versus anoxic redox conditions.

Sequential extraction procedures (SEP) applied to aquifer material showed that the greatest amount of V was recovered by the nitric acid (HNO₃) extract (37–71%), followed by the oxalate-ascorbic acid extract (19–60%) and the oxalate extract (3–14%). These results indicate that V was not associated with the solid phase as an easily exchangeable fraction. Although the total amount of V recovered was greatest for the HNO₃ extract that targets V adsorbed to sorption sites of crystalline Al, Fe and Mn oxides, the greatest V saturation of sorption sites appeared to occur on the amorphous and poorly crystalline oxide solid phases targeted by the oxalate and oxalate-ascorbic acid extracts respectively. Adsorption isotherm experiments showed no correlation between V sorption and any of the fractions identified by the SEP. This lack of correlation indicates the application of an SEP alone is not adequate to estimate the sorption characteristics of V in an aquifer system.

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1. Introduction

Concern over the possible harmful health effects of ingesting vanadium (V) in drinking water has led the United States

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Environmental Protection Agency to list V on its Contaminant Candidate List 3 (U.S. Environmental Protection Agency, 2009). California's Department of Public Health (CDPH) has given V a notification level (CA-NL) of 50 $\mu\text{g/L}$ in drinking water (California Department of Public Health, 2010). The CA-NL means that CDPH recommends that water purveyors inform their customers and consumers about the presence of V > 50 $\mu\text{g/L}$ in drinking water and about the health concerns associated with exposure to it. A study by Wright and Belitz (2010) completed for the California State Water Resources Control Board's Groundwater Ambient Monitoring and Assessment Program Priority Basin Project (GAMA-PBP) showed that V in groundwater used for drinking water supply has been detected at concentrations above 50 $\mu\text{g/L}$ in several areas in the state of CA. The establishment of a health-based regulatory threshold for V in drinking water would likely result in adverse impacts to drinking water supplies through well abandonment and/or the installation of well head treatment operations.

The geochemistry of V is complex. This is because V participates in a wide range of chemical reactions and forms many different molecular arrangements (Crans et al., 1998). Because of its affinity for oxygen, V forms both stable oxyanions and oxycations (Fig. 1). Vanadium is a redox sensitive element that exists in three oxidation states in the environment: V^{5+} , V^{4+} and V^{3+} (Hem, 1985). Vanadium $^{5+}$ (V^{5+}) is the most thermodynamically stable oxidation state of V under oxygenated groundwater conditions and pH values typically found in aquifer systems. Under these conditions V likely exists in an oxyanionic form as either H_2VO_4^- or HVO_4^{2-} ions (Fig. 1). Polymeric species of V^{5+} can form, but only at V concentrations that are generally much higher than those found in natural water (Wanty and Goldhaber, 1992). The pH of systems under consideration will be an important factor in governing the solubility of

V^{5+} as the variable charge on mineral surfaces becomes more negatively charged with increases in pH (Stumm, 1992). At pH values below neutral the solubility of V^{5+} can be enhanced by forming complexes with dissolved organic matter (DOM) (Bartusek and Sustacek, 1983; Tracey et al., 1987). Vanadium $^{5+}$ complexed with DOM can be subsequently reduced to V^{4+} at pH values <6 (Lu et al., 1998).

Vanadium $^{4+}$ exists as an oxycation that is thermodynamically stable under moderately reducing conditions or at very low pH values (Fig. 1). The V^{4+} oxycation VO^{2+} adsorbs more strongly to oxides than do V^{5+} oxyanions, although this complex has limited stability in oxidized environments (Wehrli and Stumm, 1989). The stability field of VO^{2+} can be increased to include more alkaline and oxic conditions through complexes formed with organic and inorganic ligands (Breit and Wanty, 1991; Wanty and Goldhaber, 1992; Wehrli and Stumm, 1989). Several studies have indicated that complexation with DOM increases the mobility of V^{4+} in aqueous systems (Lu et al., 1998; Pourret et al., 2012; Szalay and Szilagyi, 1967).

Vanadium $^{3+}$ is thermodynamically stable over a wide pH range, but only under the most reducing environmental conditions (Fig. 1). Limited information is available regarding the complexation of V^{3+} with ligands. Because V^{3+} has a structure similar to Fe^{3+} (Kaur et al., 2009; Schwertmann and Pfab, 1996), it may form complexes with Cl^- and SO_4^{2-} , which could enhance the solubility of V^{3+} in groundwater. A study by Wanty and Goldhaber (1992) showed that V^{3+} rapidly hydrolyzed in solution forming relatively insoluble oxyhydroxides indicating that this oxidation state of V may not be an important species in the aqueous phase.

1.1. Purpose and scope

Because V is a potential health concern and because a limited number of studies have looked at the behavior of V in groundwater, the purpose of this study was to gain insight into the controls on V solubility in relation to geochemical conditions that occur in aquifer systems in northeastern San Joaquin Valley. The northeastern San Joaquin Valley was chosen as the study area due to the wide range of V concentrations and geochemical conditions present in the area. In addition, the large population base, a robust agricultural industry and numerous previous studies meant that there is existing infrastructure (public supply and monitoring wells) and water-quality data available to help achieve the goal of this study.

The scope of this study included examining the areal distribution of V concentrations in the study area. Geochemical modeling was done to determine the aqueous and solid phase speciation of V in groundwater. Geochemical modeling will determine if complexes of V with inorganic ligands are an important factor in controlling the solubility of V in groundwater. Comparison of the distribution of V concentrations among varying redox (oxic, suboxic and anoxic) and pH conditions were examined in conjunction with the modeled V speciation in an effort to understand the processes that are controlling V solubility under diverse geochemical conditions. A sequential extraction procedure (SEP) was applied to core material that was collected from the aquifer system in the study area in order to gain understanding of how V interacts with aquifer matrices. Adsorption isotherms for the most thermodynamically stable oxidation state V^{5+} typically found in potable aquifer systems were determined for the same core materials in order to gain a better understanding of potential V mobility in groundwater.

1.2. Study area description

The study area is in the northeastern San Joaquin Valley, which is located in the middle of the Central Valley of CA (Fig. 2). The

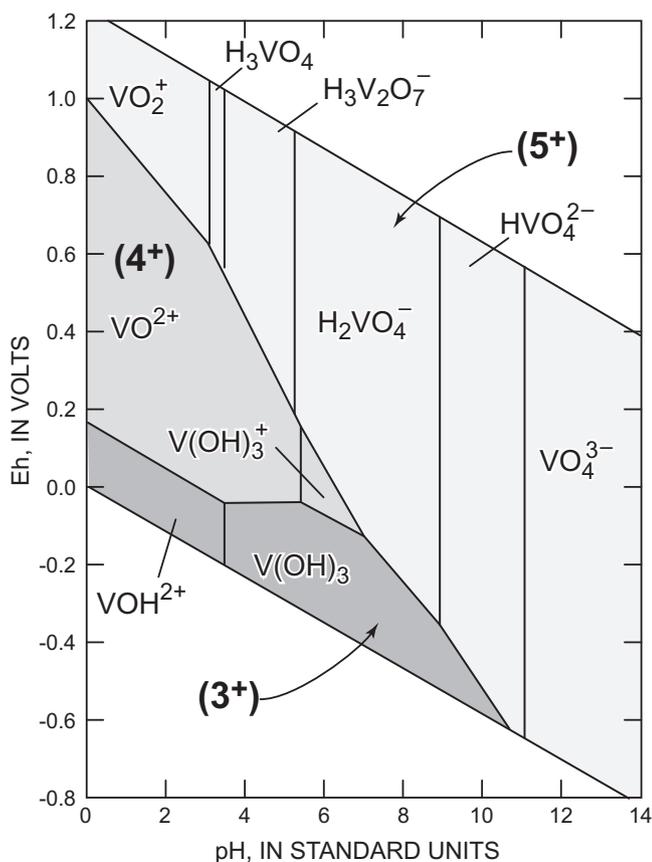


Fig. 1. Stability diagram for vanadium with fixed total activities of vanadium = 10^{-7} , sulfur = 10^{-4} , and carbon = 10^{-3} M at 25 °C and 1 atm (adapted from Hem, 1977).

study area is approximately bounded by the Cosumnes River to the north, the Sierra Nevada to the east, the Chowchilla River to the south and the San Joaquin River and Sacramento–San Joaquin Delta to the west. The study area is composed of five groundwater basins (GWB) as defined by the California Department of Water Resources: Cosumnes, Eastern San Joaquin, Modesto, Turlock and Merced (California Department of Water Resources, 2003).

The study area has a Mediterranean climate, with hot and dry summers, and winters that are cool and moist. Average rainfall across the study area ranges from 11 inches (in.) in the southern and western portions to 15 in. in the eastern to northeastern portions (Bennett et al., 2010; Landon et al., 2010). Numerous creeks and rivers drain the study area and most of the flow in the rivers is derived from runoff of the Sierra Nevada to the east. Each of these rivers ultimately drains into the San Joaquin River, which flows northwest and empties into the Sacramento–San Joaquin Delta.

Aquifer systems being tapped by wells in the study area consist of unconsolidated alluvial-fan deposits and deeper consolidated volcanoclastic deposits. Alluvial-fan deposits range in age from late-Pliocene to Quaternary and are composed of multiple sediment sequences linked to repeated episodes of glaciation in the Sierra Nevada (Burow et al., 2004; Davis and Hall, 1959; Weissmann et al., 2002, 2004, 2005). Alluvial-fan deposits contain interlayered lenses of gravel, sand, silt, and clay deposited by rivers draining the Sierra Nevada. A volcanoclastic deposit, the Mehrten Formation, separates overlying alluvial-fan deposits from deeper marine deposits that contain saline water in most parts of the study unit (Marchand and Allwardt, 1981; Page, 1986).

Groundwater conditions are unconfined, semi-confined, and confined in different zones of the aquifer system in the study area. The base of freshwater (TDS of about 2000 mg/L), where estimated, generally is more than 200 meters (m) below land surface (Page and Balding, 1973). Unconfined conditions are present in unconsolidated deposits above and east of the Corcoran Clay Member of the Turlock Lake Formation (Marchand and Allwardt, 1981), which underlies the southwestern half of the study area at depths ranging from 15 to 76 m (Burow et al., 2004; Davis and Hall, 1959; Page, 1986; Page and Balding, 1973). Confined conditions are present below the Corcoran Clay. Semi-confined conditions are present at depth east of the Corcoran Clay, because of many discontinuous clay lenses.

Primary sources of groundwater recharge are percolation of irrigation return waters, precipitation, seepage from reservoirs and rivers, and urban runoff return (Burow et al., 2004; Phillips et al., 2007). Primary sources of discharge are pumping withdrawals for irrigation and municipal water supply, evaporation from areas with a shallow depth to water, and discharge to streams. Agricultural irrigation supplied by surface water and groundwater accounts for about 95% of the total water use in the region (Burow et al., 2004).

2. Methods

2.1. Sample collection, analysis and compilation of existing water quality data

Data used to discuss the occurrence and distribution of V in groundwater in the study area come from wells sampled by the USGS and from sample measurements in the CDPH database. Measurements from wells sampled by USGS for the GAMA-PBP and other USGS studies are available to the public through the USGS online database NWIS Web. (U.S. Geological Survey, 2014, <http://waterdata.usgs.gov/ca/nwis/>). Measurements from the CDPH water quality database are available to the public through the GeoTracker database (California State Water Resources Control Board, 2009, website at <https://geotracker.waterboards.ca.gov/gama>).

Detailed sampling protocols for samples collected by the USGS for the GAMA-PBP are describe in Koterba et al. (1995), Bennett et al. (2006), Landon and Belitz (2008), and USGS National Field Manual (U.S. Geological Survey, variously dated); only brief descriptions are given here. Wells sampled by the USGS for the GAMA-PBP were pumped continuously to purge at least three casing-volumes of water from the well prior to sample collection. Sampling points were located as close to the well head as possible and were upstream from water-storage tanks and well-head treatment systems. Field measurements of dissolved oxygen, temperature, pH, and specific conductance were collected using a flow-through chamber fitted with a multi-probe meter that simultaneously measures all parameters. Field measurements were recorded at 5-minute (min) intervals for at least 20 min and when these values remained stable for four consecutive measurements samples were collected. If dissolved oxygen was <0.1 mg/L or an odor of sulfide detected, a sulfide measurement was done on-site using a portable colorimeter. Eh values were not measured in this study. Field blanks and sequential replicates were collected at approximately 10% of the well sites sampled in order to determine if contamination or errors in analysis were occurring. Constituent concentrations attributed to contamination are not used for any analyses (Supplemental Tables 1 and 2). Water quality data collected by other USGS programs that were used in this study were collected using the same or similar methods.

Samples for major ions, trace elements, and nutrients were analyzed at the U.S. Geological Survey's National Water Quality Laboratory (NWQL) in Denver, Colorado. Fe speciation samples were analyzed at the U.S. Geological Survey's National Research Program Trace Element Laboratory in Boulder, Co.

Groundwater V concentrations were also compiled from the California Department of Public Health's (CDPH) water quality database. CDPH data was not used for geochemical modeling or for comparisons of V distribution with respect to redox conditions because dissolved O₂ and Fe speciation data are not reported in the database. CDPH samples were only used to examine the areal distribution of V in groundwater of the study area. Vanadium data stored in the CDPH database come from unfiltered samples. However, a previous study by Wright and Belitz (2010) showed good agreement between unfiltered V concentrations reported in the CDPH database and filtered samples collected by the USGS.

2.2. Sequential extraction procedure

Selected trace elements were extracted from aquifer materials collected during the drilling of two monitoring wells (Jurgens et al., 2008) in the Modesto GWB (Fig. 2). These monitoring wells were located within 3 km of one another. After retrieval of core material from the borehole, core sleeves were capped and taped, placed in nitrogen filled bags and refrigerated (at approximately 4 °C) until use in this study. Prior to extraction the aquifer material was air-dried, placed in a plastic bag and gently crushed to break-up aggregates. The aquifer material was then sieved to <2.0 mm and homogenized to provide a consistent and unbiased matrix for analysis.

The sequential extraction procedure used in this study was modified from procedures described by Chao and Sanzalone (1989) and Wenzel et al. (2001), and was done at the U.S. Geological Survey Laboratory in San Diego, CA. Each step of the procedure is intended to extract trace elements from operationally-defined sorption sites on the surfaces of the mineral grains. For the first extraction, 20 g of sample was mixed with 100 ml of 0.25 mol/L KCl solution and shaken at approximately 20 °C for 4 h on a wrist-action shaker. Operationally, this step was intended to extract "non-specifically sorbed" trace elements associated with dissolved and water-soluble fractions within the sample. For the

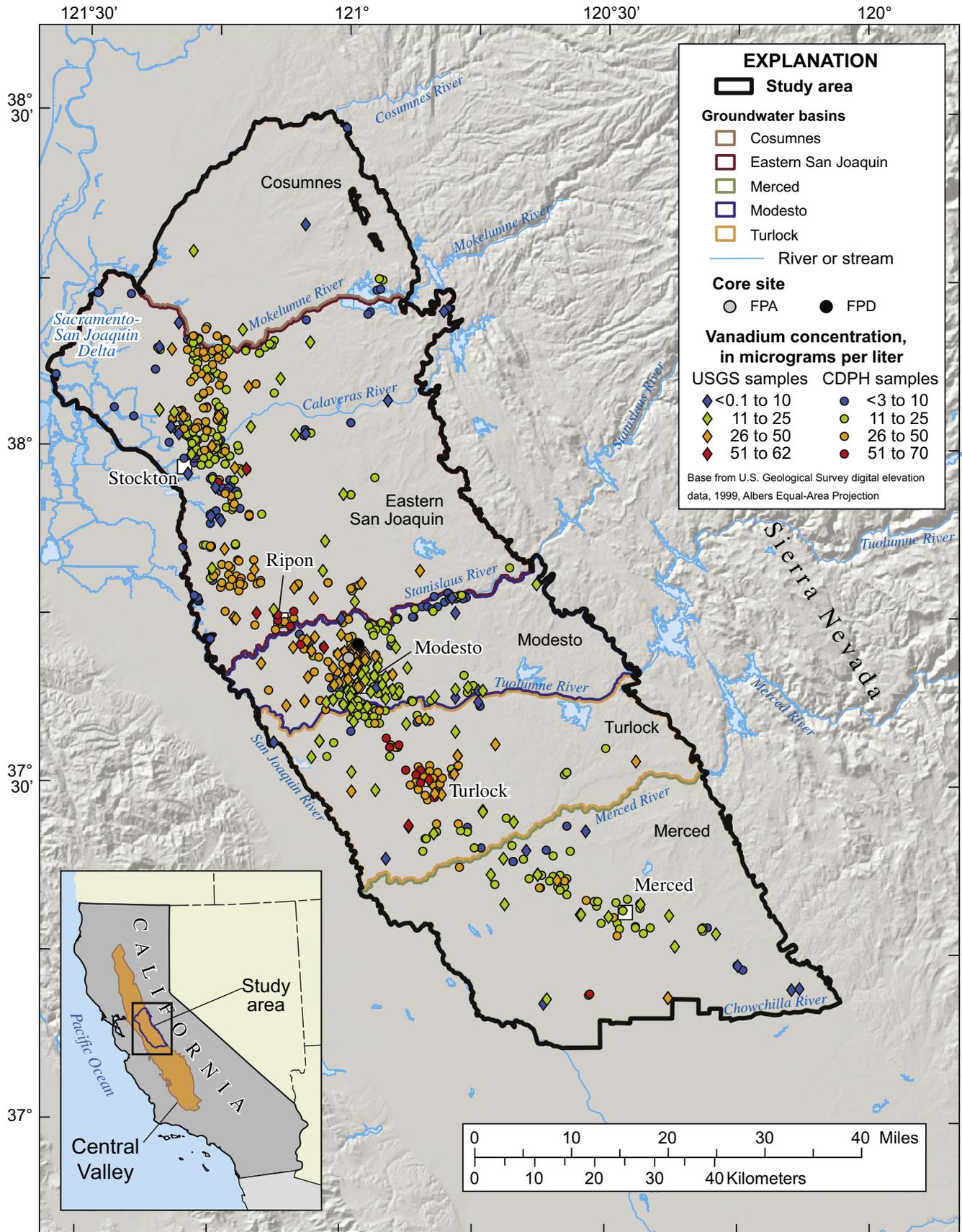


Fig. 2. Map of the study area boundaries, geographic features and distribution of vanadium concentrations.

second extraction, sample material recovered from the first extraction was mixed with 100 ml of 0.05 mol/L $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ solution and shaken at approximately 20 °C for 16 h. This step was intended to extract “specifically-adsorbed” trace elements that may be mobilized by changes in pH or by ligand exchange processes. For the third extraction, material recovered from the second extraction was mixed with 100 ml of 0.2 M ammonium-oxalate buffer $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ at pH 3.25 and 20 °C, and shaken for 4 h in the dark. This step was intended to extract trace elements associated with amorphous Fe, Mn, and Al oxides on the surfaces of mineral grains. For the fourth extraction, the material recovered from the third extraction was mixed with 50 ml of a 0.2 M NH_4^+ -oxalate buffer and 0.1 mol/L ascorbic acid $[\text{C}_6\text{H}_8\text{O}_6]$ solution at pH 3.25 and 96 °C, and shaken for 30 min. This step was intended to extract trace elements associated with poorly-crystallized and well-crystallized Fe, Mn and Al oxides on the surfaces of mineral grains. An additional extraction step using 100 ml of 4 mol/L HNO_3 (Chao and Sanzolone, 1989) was implemented to ensure the dissolution of all trace elements associated with Fe, Mn, and Al oxides. This extraction was incorporated into the procedure after a comparison with similar data determined (Izbicki et al., 2008) that the fourth extraction step (Wenzel et al., 2001) was not sufficiently vigorous to extract all the trace elements associated with highly-crystallized Fe, Mn, and Al oxides on mineral surfaces within the sample. More vigorous extractions (Chao and Sanzolone, 1989; Wenzel et al., 2001) to dissolve sulfides and silicate minerals were not done. Extractions specific to organic matter was also not done as the sediment samples had very low organic carbon content (Jurgens et al., 2008). The organic content of the sedimentary material ranged from below detection (<0.2 g/kg) to 0.3 g/kg. Assuming organic carbon composes 50% (by weight) of organic matter, the highest percentage of organic matter in the sedimentary material would be 0.06%. Therefore, the adsorption capacity of the sediment contributed by organic matter would be negligible compared to the adsorption capacity contributed by Al-, Fe- and Mn-oxides.

Sequential extractions were carried out using Teflon bottles to minimize trace element adsorption to the reaction vessel. Between each extraction, the slurry was centrifuged and the supernatant decanted to a syringe and filtered through a 0.45 μm pore-sized filter. The centrifuged sample material was then mixed with 20 ml of deionized water, put on the wrist-action shaker for 2 min and centrifuged. The rinse water was decanted to waste. Samples were then preserved with 7.7 mol/L HNO_3 and analyzed using ICP-MS (Fishman, 1993; Fishman and Friedman, 1989; Garbarino et al., 2006) at the U.S. Geological Survey National Water Quality (NWQL) in Denver, Colorado. A procedure blank was run concurrently with environmental samples to determine if any contamination was introduced while carrying out the SEP.

2.3. Adsorption isotherm experiments

Batch reactor experiments were used to determine adsorption isotherms for the aquifer material used in the sequential extraction procedure. Adsorption isotherms were also determined for aquifer material collected from two additional sites not included in the sequential extractions; these sites were also located in the Modesto GWB less than 3 km from the FPA and FPD sites (Fig. 2). Splits from these cores were shipped on ice to a USGS National Research Program laboratory in Denver, CO where the isotherm experiments were carried out. Aquifer material was air-dried and sieved to <2.0 mm. Experiments were conducted by combining 35 ml chemically modified deionized water with 2 g of sediment in 40 ml polypropylene centrifuge tubes and mixed continuously on an end rotating mixer at 2 rpm. An equilibration time of 3 days was used. It was determined in preliminary experiments that V adsorption was rapid with 90% occurring within a few hours, and

equilibrium within 2 days. Solutions were separated from sediment by centrifuging at 15,000 rpm for 15 min followed by filtering (0.2 μm). Use of a 0.8 $\mu\text{m}/0.2 \mu\text{m}$ filter cartridge is standard procedure in this laboratory. Separate experiments confirmed that there was no difference in element concentration between 0.2 μm and 0.45 μm filtrate.

Bicarbonate concentrations and pH for each solution were initially adjusted to simulate groundwater values associated with each aquifer material. Initial V^{5+} concentrations in each experiment ranged from 0 to 275 $\mu\text{g/L}$. Both initial and final V concentrations were measured by ICP-MS. The focus of these experiments was to determine the effect of sediment properties and pH on V^{5+} sorption; therefore, other inorganic constituents in groundwater were not included. Dissolved organic carbon was also excluded because of a lack of information on the composition of these compounds.

2.4. Geochemical modeling

The distribution of aqueous species in groundwater and the saturation state of groundwater relative to a set of minerals and amorphous phases was calculated in order to determine the effects of molecular configuration and mineral precipitation on the distribution of V in groundwater. PHREEQC (Parkhurst and Appelo, 1999), a computer program for simulating chemical reactions in natural or polluted water, was used to calculate aqueous species and saturation indices (SI). Thermodynamic data contained in the *MINTEQA4* database (U.S. Environmental Protection Agency, 1998) that is distributed with PHREEQC was used for speciation and SI calculations. Chemical constituents and water quality parameters used for modeling were: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , CO_3^{2-} , Cl^- , F^- , SO_4^{2-} , N^{3-} , N^{5+} , P^{5+} , Fe^{2+} , Fe^{3+} , U, V, dissolved O_2 , pH and temperature (Supplemental Table 1). Only USGS samples collected by the GAMA-PBP that had Fe redox couple data ($n = 59$) were speciated because these constituents are necessary to calculate the aqueous speciation and saturation indices of mineral phases for a redox sensitive element like V.

Data from adsorption isotherm experiments also were modeled using PHREEQC with the *MINTEQA4* database, which contains surface complexation reactions for V. Surface complexation site concentration was adjusted to give the best fit between model simulations and experimental data.

2.5. Statistical analysis

Nonparametric statistical methods were used to test the significance of correlations between water-quality variables and potential explanatory factors. Nonparametric statistics are robust techniques that generally are not affected by outliers and do not require that the data follow any particular distribution (Helsel and Hirsch, 2002). The significance level (p) used to test hypotheses for this report was compared to a threshold value (α) of 10% ($\alpha = 0.1$) to evaluate whether the relation was significant ($p < \alpha$). A low p -value gives greater confidence that the null hypothesis was not being falsely rejected. Correlations were investigated using Spearman's method to calculate the rank-order correlation coefficient (ρ) between continuous variables. The values of ρ can range from +1.0 (perfect positive correlation) to 0.0 (no correlation) to -1.0 (perfect negative correlation). The Wilcoxon rank-sum test was used to evaluate the correlation between water quality and redox conditions (oxic/suboxic or anoxic). The Wilcoxon rank-sum test can be used to compare two independent populations (data groups or categories) to determine whether one population contains larger values than the other (Helsel and Hirsch, 2002). The null hypothesis for the Wilcoxon rank sum test is that there

is no significant difference between the median values of the two independent data groups being tested.

3. Results and discussion

3.1. Areal distribution of vanadium in the study area

From 2001 to 2012, 758 samples with V analysis (200 USGS and 558 CDPH) were available in the study area. Only one sample per well was used. If a well had multiple sample sources or dates, USGS samples were given priority; otherwise the most recent sample was used. The one exception was for a well that changed in redox condition (oxic to suboxic) between sampling dates (site id: 373349121032302, [Supplemental Table 2](#)). The vast majority of sample analyses come from public supply wells which tend to be clustered in and around urban centers and thus do not have an even spatial distribution throughout the study area. For a statistical analysis of the spatial distribution of V concentrations in groundwater throughout the study area the reader is referred to [Bennett et al. \(2010\)](#) and [Landon et al. \(2010\)](#).

Vanadium concentrations in the study area ranged from non-detection to 70 µg/L ([Fig. 2](#)) with a median concentration of 21 µg/L. Samples with V concentrations greater than the California notification level (CA-NL) of 50 µg/L comprised nearly three percent of the samples analyzed and samples with concentrations greater than one half the CA-NL comprised 32% of the samples analyzed. Samples with the highest V concentrations (>50 µg/L) were found in all groundwater basins in the study area except for the Cosumnes. Vanadium concentrations >50 µg/L most frequently occurred in and around the city of Turlock and the city of Ripon, which are located in the Turlock and southern Eastern San Joaquin GWBs respectively. Samples with the lowest V concentrations (<10 µg/L) were frequently detected in samples collected from wells adjacent to surface water drainages near the Sierra Nevada Mountain front. Low V concentrations were also frequently detected in samples collected from wells located near the trough of the San Joaquin Valley where groundwater redox conditions were anoxic.

A previous study by [Wright and Belitz \(2010\)](#) indicated that high to moderate V concentrations (>25 µg/L) in groundwater of the northeastern San Joaquin Valley may be due to groundwater bearing deposits derived from volcanic (basaltic) and gabbroic rocks. This study also indicated that geochemical conditions are an important factor influencing the distribution of V concentrations in groundwater. High V concentrations were generally associated with oxic and alkaline groundwater while V concentrations in anoxic groundwater were generally low regardless of pH; this was not only found to be the case in the northeastern San Joaquin Valley, but across all areas of the state of California. The following results and discussion examine in much more detail the geochemical controls on V solubility in groundwater of the northeastern San Joaquin Valley.

3.2. Vanadium solubility under varying redox conditions

The concentrations of redox indicators, such as dissolved O₂ and Fe, are a useful tool for indicating the redox conditions of groundwater ([McMahon and Chapelle, 2008](#)). One hundred and fifty-two samples had sufficient data for redox classification ([Supplemental Table 2](#)); 59 of those samples had Fe speciation data (Fe²⁺/Fe³⁺). Samples were classified as oxic, suboxic or anoxic based on the criteria given in [Table 1](#). Samples with a mixed redox signal were not considered for analysis. One hundred and eighteen samples were classified as oxic, 17 as suboxic and 17 as anoxic. Oxic samples were collected from wells located throughout the study area. In contrast, samples classified as suboxic and anoxic were almost

Table 1
Classification scheme for redox conditions.

Redox class	Redox indicators		
	Dissolved O ₂ (mg/L) ^b	Fe ²⁺ (µg/L) ^c	Total Fe (µg/L) ^b
Oxic	>0.5	<2	<100
Suboxic	≤0.5	<2	<100
Anoxic ^a	≤0.5	≥2	≥100

^a Only one Fe criteria needs to be met.

^b Threshold based on [McMahon and Chapelle \(2008\)](#).

^c Threshold based on minimum reporting level for Fe²⁺.

exclusively collected from wells located on the western edge of the study area in the trough of the valley and near the Sacramento–San Joaquin Delta.

3.2.1. Oxic groundwater

In oxic samples V concentrations were significantly higher than concentrations detected in either suboxic (Wilcoxon rank-sum test, *p*-value = 0.01) or anoxic (Wilcoxon rank-sum test, *p*-value = 0) samples ([Fig. 3](#)). Three percent of the V concentrations in oxic groundwater samples were >50 µg/L and 50% were >25 µg/L. Speciation modeling predicts that in oxic groundwater V exists in an oxyanionic form as either H₂VO₄⁻ or HVO₄²⁻. However, concentrations of the HVO₄²⁻ were never predicted to consist of more than 33% of the total V in any sample. In an oxyanionic form the adsorption of V to organic matter should not occur to any great extent given that the pH values of groundwater in the study area generally ranged from above neutral to alkaline. Vanadium concentrations in oxic samples show no correlation (spearman's rho = -0.001, *p*-value = 0.99, *n* = 6) with DOC, which further indicates that V⁵⁺-DOM complexes are not an important factor in limiting V solubility. Based on SI calculations, V⁵⁺ containing minerals are not expected to precipitate in oxic groundwater. Therefore, the solubility of V in oxic groundwater may be primarily governed by adsorption/desorption reactions with solid phases such as Fe-oxide surfaces.

If adsorption/desorption reactions are the primary control on V solubility in oxic groundwater, then concentrations should

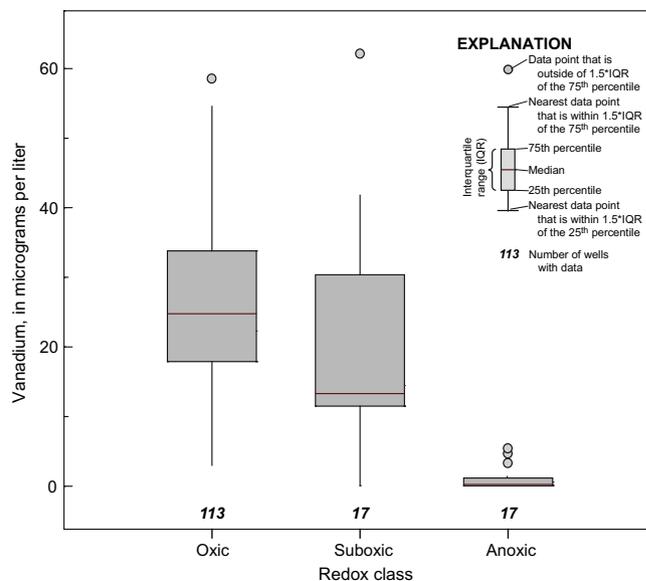


Fig. 3. The distribution of vanadium concentrations by redox classification. Wilcoxon rank sum test results show median values of redox classes are statistically different (*p*-value < 0.01 for all pairwise tests).

increase with increasing pH. As groundwater pH becomes increasingly more alkaline, surface complexation sites of oxide minerals, amorphous phases and clays will become increasingly more negatively charged (Stumm, 1992). Negatively charged surfaces will inhibit the adsorption and promote desorption of the negatively charged ions like H_2VO_4^- . At more near-neutral and acidic pH values negatively charged ions will be more likely to adsorb to surface complexation sites because of the relative abundance of positive charge on particle surfaces. Vanadium concentrations in oxic samples collected in this study show a significant positive correlation with pH (Fig. 4a), further indicating that V exists predominantly in an oxyanionic form in oxic and alkaline groundwater and that adsorption/desorption reactions are a limiting factor of V solubility. Scatter in the data presented in Fig. 4a are likely due in part to heterogeneity in V content of source material as well as heterogeneity in mineral assemblages that comprise the adsorbing surfaces of aquifer matrices. The effects of varying mineral assemblages comprising particle surface are illustrated in the discussion of the adsorption isotherm experiment presented below.

3.2.2. Suboxic groundwater

Suboxic samples had significantly higher V concentrations than anoxic samples (Wilcoxon rank-sum test, p -value = 0), but lower concentrations than oxic samples. Six percent (1/17) of suboxic samples had a V concentrations $>50 \mu\text{g/L}$ and 29% had concentrations $>25 \mu\text{g/L}$. Speciation modeling predicts that in suboxic conditions, like in oxic conditions, V exists predominately as H_2VO_4^- . However, unlike in oxic conditions, V concentrations in suboxic conditions have a significant negative correlation to pH (Fig. 4b). This relation between V concentration and pH indicates that SM may be giving inaccurate results and that V may be present in groundwater as a

cationic species where adsorption would be lower at near neutral pH values because of the higher density of positive charge on mineral surfaces.

The inaccurate prediction of V species by the geochemical model can reasonably be expected. Because the reduction of V^{5+} to V^{4+} in natural water occurs after the onset of Mn reduction, but before the onset Fe reduction (Wang, 2007), the Eh value (reduction potential) of groundwater needs to be measured in order to accurately speciate V in suboxic conditions. Unfortunately, these measurements were not done in this study. However, dissolved Mn concentrations in suboxic samples indicate that redox potentials were low enough to reduce V^{5+} to V^{4+} . Sixty-five percent of the samples classified as suboxic had Mn concentrations $\geq 15 \mu\text{g/L}$ (Supplemental Table 2). In contrast, less than 1% of the samples classified as oxic had Mn concentrations $\geq 15 \mu\text{g/L}$. The presence of Mn in solution in samples classified as suboxic indicates that Mn^{4+} in Mn-oxides (e.g. MnO_2) have been reduced to Mn^{2+} , which is the predominate form of dissolved Mn in natural waters (Hem, 1985). The standard reduction potential at which Mn^{4+} in MnO_2 is reduced to Mn^{2+} [1.224 V] is similar to the standard reduction potential of V^{5+} in $\text{V}(\text{OH})_4^+$ reduction to V^{4+} in VO^{2+} [1.00 V] (Weast, 1989–1990). Given that the standard reduction potential of Fe^{3+} to Fe^{2+} is 0.771 V, an assumption that reduction potentials were low enough for V^{4+} species to occur in the samples classified as suboxic is reasonable.

Vanadium $4+$ cations are not favored at $\text{pH} > 7.0$ (Fig. 1). pH values in suboxic samples range from 7.0 to 8.6 (Supplemental Table 2), suggesting that V^{4+} would not be the dominant species in solution. However, slow reaction kinetics and/or complexation with inorganic and organic ligands can extend the stability of V^{4+} to higher redox potentials and more alkaline pH values (Wehrli and Stumm, 1989; Wanty and Goldhaber, 1992). When V in suboxic samples is assumed to be in the 4+ oxidation state, SM does not predict the existence of V^{4+} as a complex with inorganic ligands, for example VOF^+ , but rather as a hydrolysis product in the form $\text{V}(\text{OH})_3^+$. If V^{4+} is indeed stable as a hydrolyzed cationic species under suboxic conditions, then adsorption reactions with mineral surfaces would explain the observed variations in V concentration with respect to pH.

Complexes of V^{4+} with organic ligands that may occur in nature include positively, negatively and/or uncharged species (Wanty and Goldhaber, 1992). A positively charged V^{4+} -organic ligand complex could extend the stability limits of V^{4+} in groundwater and help explain the distribution of V concentrations observed with respect to pH in suboxic conditions. Organic ligands were not analyzed as part of this study, but a comparison of V concentrations with DOC concentrations was made in an effort to determine if complexation with DOM may be an important factor in influencing V solubility. The comparison showed that V concentrations did tend to increase with increasing DOC in some cases, but overall the correlation was not statistically significant (spearman's rho = 0.43, p -value = 0.16, $n = 12$). A comparison between pH and DOC concentrations in suboxic samples also showed no correlation (spearman's rho = -0.04, p -value = 0.88, $n = 13$). These results indicate that V-DOM complexes may not be an important influence on the solubility of V in suboxic groundwater sampled in this study.

3.2.3. Anoxic groundwater

The distribution of V concentrations in anoxic groundwater (Fig. 3) indicates that V is sparingly soluble when redox potentials are low enough for Fe reduction to occur; the reduction potential at which V^{4+} in VO^{2+} is reduced to V^{3+} is 0.337 V (Weast, 1989–1990). Vanadium concentrations in anoxic samples did not exceed $5.4 \mu\text{g/L}$ and 70% of the samples had concentrations $<0.8 \mu\text{g/L}$. Under anoxic conditions, SM predicted V to be in its reduced state

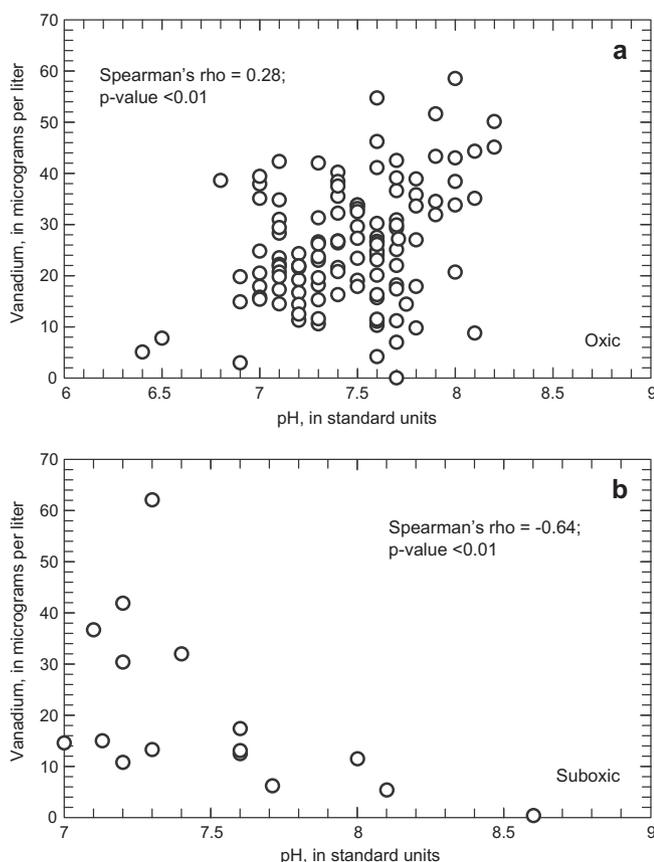


Fig. 4. Correlation of vanadium concentrations with pH. a. Oxic groundwater. b. Suboxic groundwater.

of V^{3+} and to occur predominately as the uncharged $V(OH)_3$ molecule. As an uncharged species V would have relatively little interaction with charged particle surfaces, suggesting that V concentrations in anoxic groundwater should be higher than those observed. A laboratory study conducted by [Wanty and Goldhaber \(1992\)](#) showed that V^{3+} can be removed from the aqueous phase under reducing conditions. In that study the researchers showed that H_2S is capable of reducing V^{4+} to V^{3+} and that V^{3+} subsequently precipitates as an oxide solid. In this study, a H_2S odor was detected in 50% of the anoxic samples collected and colorimetric measurements showed H_2S concentrations in these samples ranged from $<10 \mu\text{g/L}$ to $30 \mu\text{g/L}$. Even though the concentrations are less than those used in the laboratory experiments, the presence of H_2S indicates that the precipitation of a V^{3+} -solid phase may be a viable mechanism for the removal of aqueous V under anoxic groundwater conditions.

Another possible removal mechanism of V^{3+} from anoxic groundwater may be co-precipitation with Fe-oxides. Because V^{3+} has similar chemical and physical properties as Fe(III), it can substitute for Fe in oxides ([Kaur et al., 2009](#); [Schwertmann and Pfab, 1996](#)). Naturally occurring montroseite [e.g. $(Fe^{3+}, V^{3+}OOH)$] has a similar structure to goethite and has been shown to contain considerable amounts of V^{3+} ([Wanty et al., 1990](#)). Because reliable thermodynamic data is not available for the precipitation of montroseite, saturation indices were calculated for goethite and ferrihydrite, an amorphous precursor of goethite, to determine the feasibility of this mechanism for the removal of V^{3+} from the aqueous phase. The range of SI calculated for anoxic samples show that both goethite (3.8–5.6) and ferrihydrite (1.5–2.7) are oversaturated in solution. These results indicate that V^{3+} co-precipitation with Fe-oxides is also a possible removal mechanism of V under anoxic conditions.

3.3. Association of vanadium with the solid phase

Sequential extraction procedures (SEP) were applied to six core samples in order to study the association of V with particle surfaces comprising aquifer matrices. Core information, trace element concentrations in extracts and selected water quality constituents in “associated” groundwater samples are given in [Table 2](#). Detailed information about core mineralogy can be found in [Jurgens et al. \(2008\)](#). Core material was collected from several different depths from two monitoring wells located approximately three km apart in the Modesto GWB ([Fig. 2](#)). The dissolved O_2 values in associated groundwater range from 1.8 to 5.4 mg/L, pH values range from 7 to 8.1 and dissolved Fe concentrations range from non-detect to $10 \mu\text{g/L}$. The relatively high dissolved O_2 concentrations coupled with low dissolved Fe concentrations indicate that the core material was collected from an oxic portion of the GWB. The redox and pH conditions of associated groundwater indicate that V should exist predominately as $H_2VO_4^-$. As indicated by V distribution in

oxic groundwater, adsorption/desorption reactions with oxide surfaces may be the primary control on V solubility in the portion of the GWB at which the core material was collected.

Vanadium was not detected in any of the KCl extracts indicating that V was not associated with the solid phase as a non-specifically adsorbed constituent. Concentrations of V solubilized by the $(NH_4)_2H_2PO_4$ extract (0–3%) indicate that very small amounts ([Fig. 5](#)) of V were specifically adsorbed that could be reintroduced to the aqueous phase via ligand exchange reactions and/or increases in groundwater pH. The bulk of adsorbed V was removed by extracts that target amorphous and crystalline oxide minerals. Compared to the oxalate-ascorbic acid and HNO_3 extracts, concentrations were relatively low in the oxalate extract (3–14%), which targets V associated with amorphous oxide fractions. Concentrations were higher in the oxalate-ascorbic acid extract (19–60%), which targets V associated with poorly-crystalline and crystalline oxides. Concentrations were the highest in the HNO_3 extract (37–71%), which targets crystalline oxides that are too recalcitrant to be solubilized by the oxalate-ascorbic acid. These results indicate that V may be strongly adsorbed to oxide surfaces via inner-sphere complexation and/or co-precipitated with iron oxide minerals and amorphous phases that coat aquifer mineral grains. A laboratory study by [Peacock and Sherman \(2004\)](#) used surface spectroscopy techniques to show that V^{5+} was adsorbed to the Fe-oxide goethite as $H_2VO_4^-$ or HVO_4^{2-} . Their results showed that these species form robust inner-sphere complexes through bidentate adsorption, which is consistent with the results of the SEP in this study.

Vanadium concentrations in extracts were normalized to Al, Fe and Mn concentrations in extracts to indicate the density of V saturation on surface sorption sites of Al-, Fe- and Mn-oxides. The total amount of V associated with the solid phase was the highest for the HNO_3^- extract that targets crystalline Al-, Fe- and Mn-oxides, but V saturation appears to be the greatest on the poorly crystalline and amorphous oxides targeted by the oxalate-ascorbic acid and oxalate extracts ([Fig. 6](#)). Assuming similarity in redox and pH conditions and competing and/or complexing ions, aquifer systems with a greater percentage of amorphous or poorly crystalline oxides may have a greater affinity to adsorb aqueous V than an aquifer system with greater percentage of crystalline oxides; the degree of crystallization is dependent on such factors as time, pH and redox conditions.

Vanadium adsorbed to amorphous and crystalline Fe- and Mn-oxides may be solubilized via proton-promoted, ligand-promoted and reductive dissolution mechanisms ([Martin, 2005](#)). Of the three mechanisms for the dissolution of oxides, the most robust is reductive dissolution. Reductive dissolution may occur abiotically via H_2S reduction of Fe^{3+} and Mn^{4+} in oxides or biotically as microbes use Fe^{3+} and Mn^{4+} in oxides as electron acceptors during the oxidation of organic matter. The distribution of V concentrations in groundwater presented earlier in this paper, indicate that V is sparingly soluble under conditions favorable for reductive dissolution to

Table 2
Core information, concentrations of selected constituents in extracts and associated groundwater samples collected in the Modesto Groundwater Basin.

Core/well ID	Core depth (m, bls)	Total concentration of measured constituents recovered by all extract solutions used in the sequential extraction procedure				Well depth (m, bls)	Concentration in associated groundwater			
		Vanadium ($\mu\text{g/L}$)	Aluminum ($\mu\text{g/L}$)	Iron ($\mu\text{g/L}$)	Manganese ($\mu\text{g/L}$)		Dissolved Oxygen (mg/L)	pH (unitless)	Iron ($\mu\text{g/L}$)	Vanadium ($\mu\text{g/L}$)
FPA-29	8.8–10.4	6,120	256,000	519,000	45,400	11	2.5	7.0	10	39.4
FPA-139	42.4–43.9	1,280	296,000	452,000	60,000	37	3.9	7.4	–	35.5
FPA-249	75.9–77.4	2,390	466,000	603,000	38,400	67	4.5	7.7	–	30.9
FPA-359	109.4–110.9	2,050	318,000	295,000	61,300	106	1.8	7.8	7	38.9
FPA-207	63.1–64.6	4,820	265,000	463,000	96,300	53	5.4	7.8	–	27.0
FPA-354	107.9–109.4	4,410	472,000	309,000	84,800	109	2.7	8.1	–	35.1

m bls, meters below land surface; $\mu\text{g/L}$, micrograms per liter; mg/L, milligrams per liter; –, not detected.

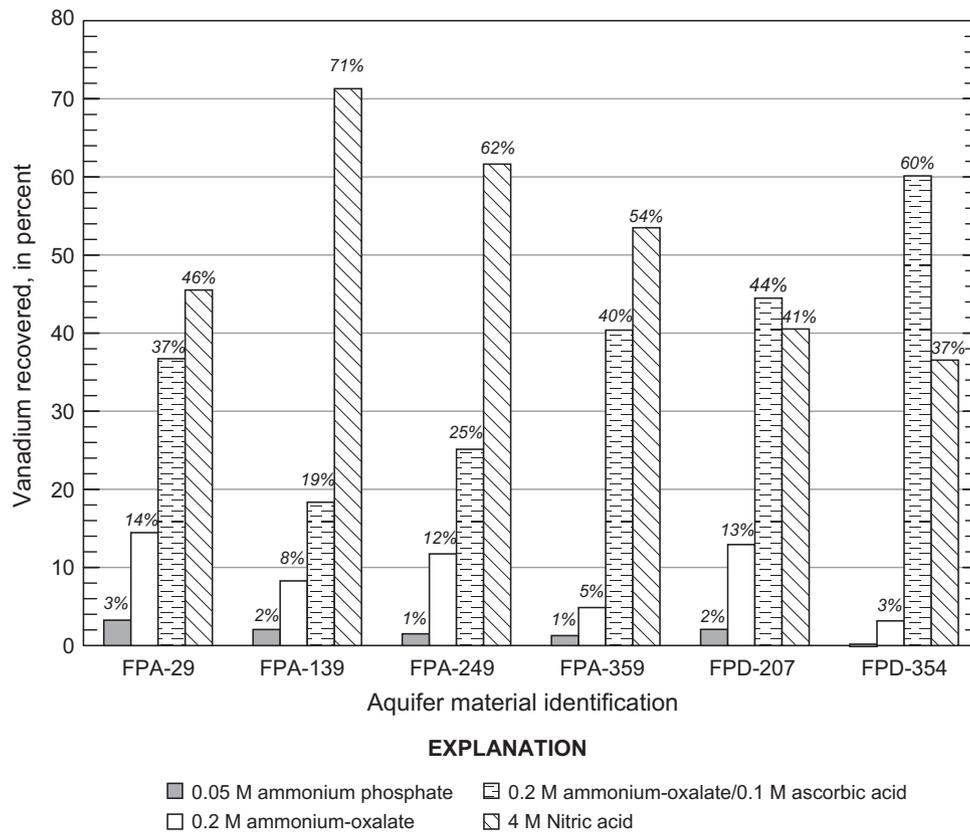


Fig. 5. Percent vanadium recovered by each of the extractants used in the sequential extraction procedure. Vanadium was not recovered in the potassium chloride extract. Recovery percentages are the median value of triplicate samples run for each extractant.

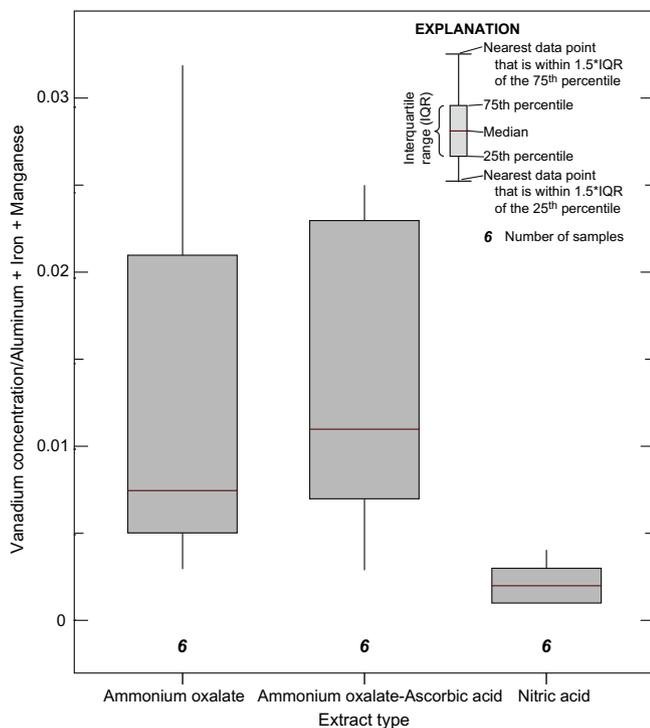


Fig. 6. Adsorbed vanadium (V) concentration normalized to aluminum (Al), iron (Fe) and manganese (Mn) in extracts as a way of estimating V saturation on amorphous and crystalline Al-, Fe- and Mn-oxides. Wilcoxon rank sum test results show median values of oxalate and oxalate-ascorbic acid are statistically different than median values for HNO₃ (p -value < 0.01) and median values for oxalate and oxalate-ascorbic acid are not statistically different (p -value = 0.12).

occur. Therefore, any V adsorbed to Fe- and Mn-oxides that are released from the solid via reductive dissolution may not remain in the aqueous phase, but rather precipitate as insoluble V^{3+} -oxides. This indicates that if groundwater conditions change from oxic to anoxic that adsorbed V would not be mobilized due to the dissolution of oxides which is a well-known mechanism that increases the mobility of As in aquifer systems (Stollenwerk, 2003). This hypothesis is further supported by the relation between V and As concentrations for samples collected in the study area. Fig. 7 shows that in oxic groundwater V and As concentrations had a significant positive correlation. In oxic samples, V occurred at greater concentrations than As (slope > 1). However, in anoxic groundwater, the opposite was observed; a slope near zero and 75% of V concentrations < 1.0 $\mu\text{g/L}$ while 75% of As concentrations were $\geq 9.8 \mu\text{g/L}$.

3.4. Vanadium adsorption

The distribution of V concentrations in groundwater samples collected in the study area and geochemical modeling of groundwater previously described in this paper indicate that adsorption/desorption reactions are the primary control on V concentrations in oxic groundwater. Vanadium⁵⁺ is strongly adsorbed by aquifer material collected from the study area (Fig. 8a and b). Maximum sorption was measured for sample FPD-207 where 80–90% of the V in solution was adsorbed. Minimum sorption was measured for OFPA 60–65' where 30–50% of the V in solution was adsorbed.

There was no correlation between the amount of V adsorbed and depth. However, aquifer material collected at depths greater than 60 m bls tended to have greater sorption capacity than aquifer material collected at shallower depths (Fig. 8a and b). Additionally, no correlation was evident between V sorption and any of the fractions identified by sequential extraction. The surface coatings for

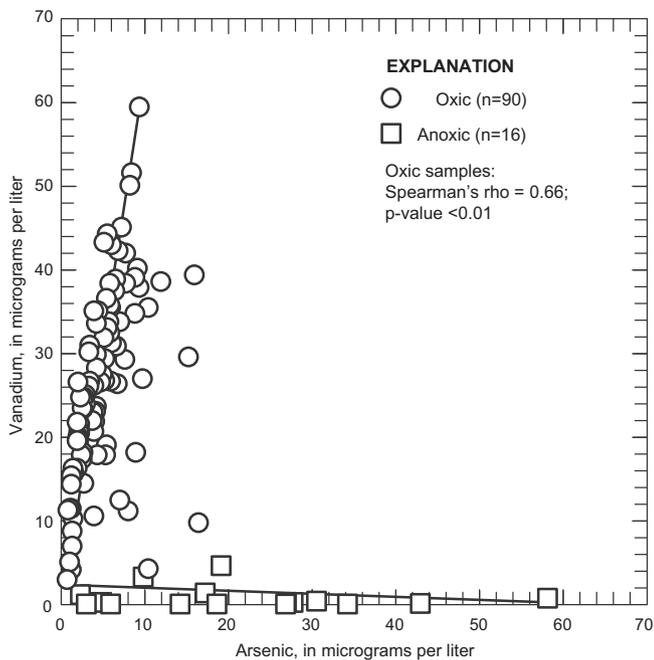
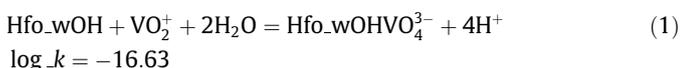


Fig. 7. Correlation between vanadium and arsenic concentrations in oxic and anoxic samples. Best fit lines are qualitative and are for highlighting the slopes of vanadium versus arsenic in oxic and anoxic samples.

each of the aquifer materials used in these experiments are a complex mixture of Fe, Mn, and Al oxides of varying degrees of crystallinity (Table 2 and associated discussion). There may be some additional sorption by the crystalline fraction of sediment, not included in the SEP; however, the surface coatings likely occlude most potential sorption sites. The lack of correlation between V sorption and surface coatings indicates that sequential extractions alone are not necessarily a good method for estimating V sorption in this aquifer system. However, it is possible that any correlation may have been obscured by sediment preparation for the sorption experiments, such as drying. The pH of the adsorption isotherm experiments ranged from 7.4 to 8.2. No obvious trend was observed between pH and V sorption (Fig. 8a and b) for these experiments, indicating that the inherent adsorption capacity of the aquifer materials had a more significant effect on V adsorption than did the minor variations in pH.

Geochemical modeling indicated that H_2VO_4^- was the predominant (>80%) species in solution with HVO_4^{2-} comprising the remainder. The MINTEQ.v4 database simulates V^{5+} sorption as surface complexation reactions:



where Hfo_wOH and Hfo_sOH represent weak and strong surface complexation sites as defined by Dzombak and Morel (1990). Weak and strong sites were defined by Dzombak and Morel (1990) to simulate sorption of cations. Anion sorption was represented as complexation on all surface sites (both weak and strong) which are considered to exhibit the same average affinity for the sorbing anion. In this study, only reaction (1) was simulated. Although defined in the MINTEQ.v4 database as a weak site reaction, we assumed reaction (1) to include all available sorption sites for V. In general, the fit between experimental data and model simulations were good, especially at lower concentrations (Fig. 8a

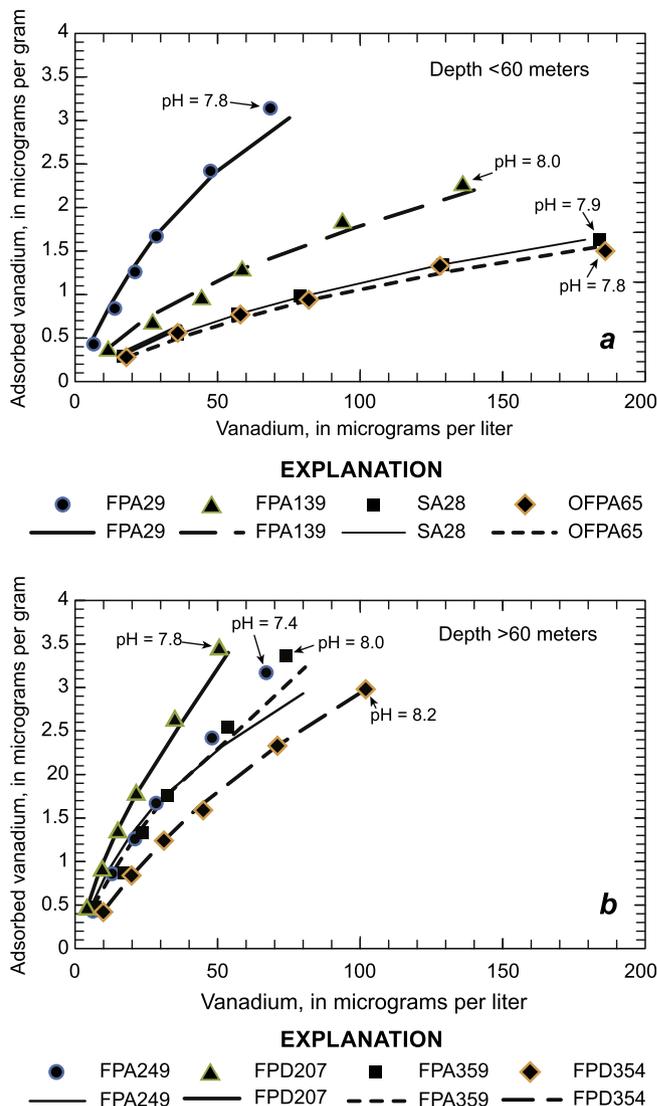


Fig. 8. Adsorption isotherms for aquifer material collected from the study area in the northeastern San Joaquin Valley. Symbols represent experimental data and lines represent simulated data. The x-axis shows the final adsorbate concentration. The y-axis shows the amount of adsorbate per unit of adsorbent. a. Aquifer material collected at depths less than 60 m. b. Aquifer material collected at depths greater than 60 m.

and b). The model slightly under predicted the sorption of V at higher concentrations in some cases. Use of a second sorption site did not improve the fit between experimental and simulated data; therefore, reaction (2) was not included.

There were three fitting parameters that could be adjusted to simulate V sorption; \log_k , surface area, and surface site concentration. To preserve database consistency, the \log_k defined in MINTEQ.v4 was fixed. Surface area was estimated at $2.89 \text{ m}^2/\text{g}$, which is reasonable for the size fraction of sediment used in these experiments. Therefore, surface site concentration was used as the fitting parameter. The aquifer material consists of a mixture of sorbing minerals, each with its own surface site concentration. An initial approximation of surface site concentration was measured for each aquifer material by potentiometric titration with H^+ . The surface site concentrations were then adjusted to give the best fit to the experimental data. To simulate these sorption experiments, surface site concentration ranged from a low of $62 \mu\text{mol/L}$ for OFPA65 to a high of $225 \mu\text{mol/L}$ for FPD354.

Reactive-solute transport modeling can be used to simulate V concentrations in groundwater. However, the data presented in Fig. 8a and b clearly show the need for site specific data. Better estimates of changes in V concentrations along a given flow path in any aquifer system will be obtained by conducting at least the basic adsorption isotherm experiments using aquifer materials and groundwater chemistry from the aquifer of concern.

4. Conclusions

Vanadium concentrations were highest in oxic and alkaline groundwater. In oxic groundwater, V^{5+} was predicted to exist as an oxyanion (e.g. $H_2VO_4^-$) and the solubility of V under these conditions appears to be primarily governed by adsorption/desorption reactions on mineral surfaces. The extent of the adsorption/desorption reactions are likely dependent on the type of oxides and amorphous phases coating aquifer minerals and groundwater pH. Adsorption isotherm experiments showed that the inherent adsorption site concentration of aquifer materials likely had a more significant effect on V adsorption under oxic conditions than did small variations of pH used in the experiment. In contrast, the environmental data showed that V concentrations in oxic groundwater increased with increasing pH, indicating the V adsorption was inhibited in alkaline groundwater. Vanadium concentrations were lower in suboxic groundwaters than in oxic groundwater and showed a negative correlation with pH. The negative correlation of V concentrations with pH indicates that under suboxic conditions the V exists as a V^{4+} cationic species. However, given the difficulty of SM under suboxic conditions, further studies are needed to get a clearer understanding of the controls on V solubility in suboxic groundwater. These studies would need to include an assessment of the interactions between dissolved V and organic ligands. In anoxic groundwater, V concentrations were mostly below analytical detection limits indicating that V is relatively insoluble in Fe-reducing groundwater. The insolubility of V in anoxic groundwater may be the result of precipitation of pure V^{3+} - or mixed V^{3+}/Fe^{3+} -oxides.

Sequential extraction of core material collected from an oxic portion of the Modesto GWB indicates that V was strongly adsorbed to oxide minerals and amorphous phases and was not associated with an easily exchangeable fraction. The SEP results also indicated that the greatest total amount of V was adsorbed by highly crystalline oxides, but that the greatest V saturation of sorption sites occurred on amorphous and poorly-crystalline oxides. Comparison of SEP results with the adsorption isotherm experiments indicated that SEPs alone are not necessarily a good indicator of V adsorption in aquifer systems and that site specific information and at least the most basic adsorption isotherm experiments would be needed to most accurately simulate V transport in groundwater.

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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.2014.06.025>.

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