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Land Use Modification and Changing Redox Conditions Releases Selenium and Sulfur from Historic Marsh Sediments

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Abstract: San Diego Creek Watershed forms the southern end of the Coastal Plain that covers much of Los Angeles County and Orange County, California. Prior to 1900, the central part of the watershed was marshland, and the edges of the watershed were used for grazing sheep and cattle. After 1900, cattle and sheep grazing were displaced by irrigated agriculture. Drainage ditches and channels were constructed to drain the marshes to "reclaim" the land for agriculture. Today, the drainage ditches and channels still exist in the watershed, which has undergone massive urban growth. Shallow groundwater discharges into these channels and ditches, which then flows as surface water, into Upper Newport Bay a thriving ecological habitat. Surface flows in these channels usually exceed the United States Environmental Protection Agency (EPA) aquatic water quality criterion for selenium (Se) of 3.1 µg/L (lotic) for protection of aquatic life. Selenium in surface flows is caused by groundwater inflows. The highest concentrations of Se in shallow groundwater in the watershed coincide with the marshland area that was displaced by agriculture. Concentrations of Se in shallow groundwater beneath the former marsh area often exceed 25 µg/L and are as high as 478 µg/L. In areas where marshes were absent, concentrations of Se in groundwater are usually less than 25 µg/L. In the marsh, Se accumulated due to chemically reducing conditions in the organic-rich marshland soils that caused it to precipitate as elemental Se(0) and metal selenides, Se(-II). We hypothesize that the elevated concentrations of Se in groundwater where the marshes once existed are a direct result of the destruction of the marsh. Today, oxidizing groundwater flows through the soils where the marshes once existed, remobilizing Se as selenate, a water soluble and oxidized form of Se(+VI) that is highly mobile in aquifer systems.

Keywords: *gaining stream, perennial stream, storm drain, seepage, watershed, bioaccumulation*

This paper documents the sources, fluxes, and spatial distribution of selenium in the surface water and shallow groundwater of the San Diego Creek Watershed, south-central Orange County, California. Boundaries of the study area include the Santa Ana Mountains to the north, the San Joaquin Hills to the southeast, and Upper Newport Bay to the south (Figure 1). Total land area in the study region is approximately 200 square miles.

The San Diego Creek Watershed forms the southern end of the Coastal Plain that covers much of Los Angeles County and Orange County, California. The aquifer beneath the watershed is composed of thick sequences of alluvial, fluvial, and marine sediments of Cretaceous to Quaternary age (Herndon and Reilly 1989).

Tectonic uplift and cycles of subsidence in the basin and corresponding changes in sea level have created many depositional environments over time. The deeper (older) sediments in the basin were deposited in a marine environment. As the coastal landmass was uplifted, the depositional environment changed to a nearshore, lagoonal environment. The lagoonal environment was later displaced by an alluvial fan and marshland

environment, which persisted until the historic period of agricultural development in the region (Camp Dresser & McKee, Inc. 1985). The central part of the basin was marshland as recently as 1900, and the edges of the basin were used for grazing sheep and cattle (Figure 1). The marsh was known to the locals of the time as the "Swamp of the Frogs Marsh". After 1900, cattle and sheep grazing were displaced by irrigated agriculture. Drainage ditches and channels were constructed to drain the marshes and reclaim the land for agriculture. Today, the ditches and channels still exist in the San Diego Creek Watershed, which has since undergone massive urban growth.

Problem Statement

Selenium is one of several elements and minerals that are needed in the diets of humans and many animals. Trace amounts of selenium contained in vegetables, other forms of vegetation, and water typically satisfy dietary requirements in humans and animals. However, selenium can become toxic at elevated concentrations in vegetation or water.

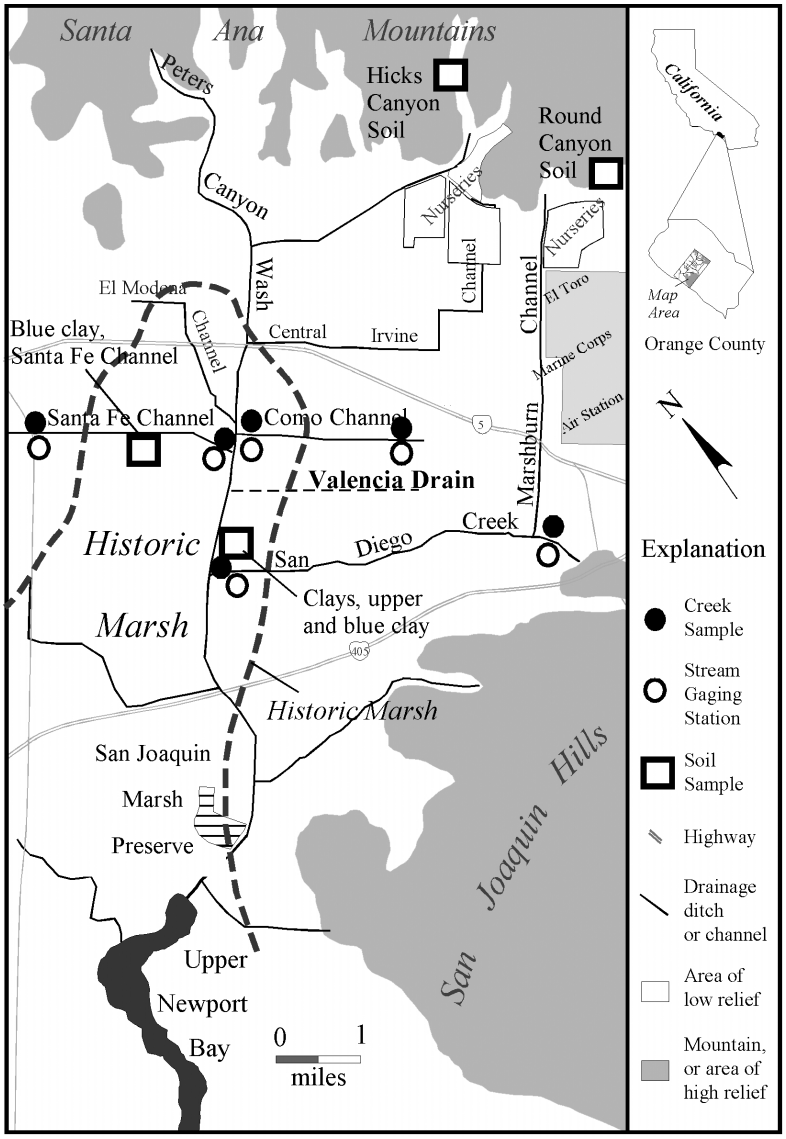


Figure 1. Study area location map covering a subregion of San Diego Creek Watershed, showing location of the historic marsh region in San Diego Creek Watershed, upstream and downstream sampling and gage stations on San Diego Creek, Como Channel, and Santa Fe Channel, and soil sampling locations. Dashed line is historic marsh boundary.

Selenium can also be a harmful element in aquatic habitats, even when concentrations are much lower than drinking water standards for humans and animals. In 1983, waterfowl deformities at Kesterson Reservoir, California were causally linked to selenium found in irrigation drainage systems. This discovery focused attention on selenium as a harmful toxin (Engberg et al. 1995). Plants absorb selenium through their roots. Insects and other organisms eat these plants, and predatory birds eat the insects and other organisms, causing bioaccumulation of selenium in the food chain (Lemly and Smith 1987; Lawrence Berkeley National Laboratory 1998). Fish and other aquatic organisms are also exposed to bioaccumulation of selenium.

In 1987 and again in 1999, the EPA recommended a 96-hour, 5 µg/L chronic water quality criterion for selenium concentration in surface water (EPA 2016). Drinking water for human consumption has a much higher Maximum Contaminant Limit in the United States of 50 µg/L. Although site specific criteria have been recommended for the San Diego Creek Watershed based on extensive studies (Nitrogen and Selenium Management Program Working Group 2009), in 2016 the national EPA revised its criterion to include new guidelines that recommend water quality limits of 1.5 µg/L (lentic) and 3.1 µg/L (lotic) over 30 days for surface water (EPA 2016). These criteria are combined with tissue concentration guidelines that together protect beneficial uses, including wildlife and aquatic life (EPA 2016). The existing water quality data indicate that shallow groundwater in the San Diego Creek Watershed often exceeds 20 µg/L selenium, reaching concentrations as high as 478 µg/L (Silverado 1997; Hibbs and Lee 2000). Thus, there was a need to determine if selenium-laden groundwater seeps into surface water in the watershed, placing aquatic organisms and waterfowl at risk.

Purpose of Investigation

The purpose of this study is two-fold: 1.) to characterize the interrelationships between surface water and shallow groundwater in the San Diego Creek Watershed; and 2.) to determine the sources and concentrations of selenium in surface water and groundwater in the watershed. With an understanding of the relationships between shallow groundwater and surface water in the study area, it is possible to determine the amount of groundwater that seeps into surface channels, becoming part of the surface flow. Similarly, by assessing water quality in the shallow aquifer, it is possible to determine if selenium in groundwater contributes to pollutant loading of surface water in the watershed.

A reconnaissance level investigation was conducted from 1999 to 2001, leading to a hypothesis of a source of selenium in the watershed (Hibbs and Lee 2000) known as the "Swamp of the Frogs Marsh Hypothesis." Additional investigations were conducted from 2004 to 2012 to test the hypothesis of the selenium source. The results developed from 2004 to 2012 have not been published except in contract reports (Hibbs et al. 2008). This manuscript is organized to review findings from the earlier reconnaissance study, and to present new information evaluating the earlier hypothesis based on extensive post-audit data sets. New information is developed using environmental isotopes and selenium speciation analysis of water and soils that were not available in the reconnaissance study completed by Hibbs and Lee (2000).

Methods

Field Methods

A variety of methods were used to collect the samples from the diverse number of sites investigated. These included surface water and groundwater samples and streambed and land surface sediment samples. Most field water samples were collected via grab sampling in polyethylene and glass bottles. Some samples were collected using a peristaltic pump with polyethylene tubing. Sample bottles and tubing were soaked and triple-rinsed in deionized water and inspected prior to field usage. Additionally, all bottles (and tubing at sites where the pump was used) were triple-rinsed with the water being sampled in the field prior to filling.

Samples collected for anion analysis and selenium speciation were filtered and kept refrigerated below a temperature of 4˚C. Samples

analyzed for dissolved selenium were filtered and acidified to less than pH 2 with nitric acid (HNO_3) then kept refrigerated (< 4˚C). For stable isotopes of sulfur in sulfate, unpreserved sample was collected in a 250-mL polyethylene bottle filled to the rim to ensure no headspace remained in the bottle. Samples were stored on ice until returned to the laboratory. All sites had conductivity, temperature, dissolved oxygen, and pH measured in the field using portable meters. Meters were calibrated according to manufacturer's guidelines.

Surface water sampling included grab sampling and width/depth integrated sampling, depending on judgements based on conditions observed in the field. Monitoring well sampling was done with battery operated purge pumps. Before sampling groundwater from monitoring wells, the wells were purged two or three well volumes until index parameters stabilized. Surface water discharge measurements were made using Marsh-McBirney Model 2000 portable flowmeters and top-setting wading rods. A straight stream reach with a relatively symmetrical channel cross section and shallow depth of flow was chosen. Stream gaging followed USGS procedures (Buchanan and Somers 1969; Turnipseed and Sauer 2010).

Sediment samples were collected using stainless steel hand augers or stainless steel shovels or spades. Auger samples were collected, properly identified (depth and location information), and sealed in glass jars. After the soil sample was collected and preserved in an ice chest and later in a refrigerator for shipment to the laboratory for chemical analysis, a portion of the soil sample that had been separated from the main sample was examined at the recovery site for color, field grain size characteristics (qualitative such as silty-sand, clayey-sand, silt), organic matter, odor (organic matter, hydrogen sulfide), and cohesiveness.

Laboratory Methods

Anion analysis was conducted by ion chromatography in the Hydrogeology Laboratory at California State University-Los Angeles. Selenium analysis was performed in reconnaissance data sets (collected between 1999 and 2001) using inductively coupled plasma – optical emission spectrometry (ICP-OES) by Associated Laboratories of Orange, California. The detection limit (DL) for selenium by this method was usually 4 µg/L. In subsequent studies, analysis of total dissolved selenium and selenium speciation was conducted by hydride generation atomic absorption (HG-AA) following the method described by Zhang et al. (1999) at the University of California-Riverside, with DL below 1 µg/L. For isotope ratios of sulfur in dissolved sulfate, sulfur was precipitated by adding BaCl at pH of 2 and then combusted at 1030°C with O_2 and V_2O_5 and analyzed using an elemental analyzer coupled with a continuous-flow ion ratio mass spectrometer (IRMS) by the Isotope Geochemistry Laboratory at the University of Arizona. Selenium speciation of soils was done by Applied Speciation of Washington State using extractions and high performance liquid chromatography linked to inductively coupled plasma mass spectrometry (HPLC-ICP-MS).

Findings of Initial Reconnaissance Investigation

Analysis of surface water samples indicates that selenium increases between upstream and downstream sampling stations and remains consistent in 1999 and 2009 data sets (Figure 1, Table 1). All creeks are perennial and samples were collected during a dry part of the season. No rain was recorded in the area for at least two weeks prior to the collection of all samples.

Selenium in San Diego Creek increased from 2.9 to 4.0 µg/L at the upstream station to 18.0 to 21.2 µg/L above the confluence of San Diego Creek and Peters Canyon Wash, a distance of 3.9 miles downstream (Figure 1, Table 1). Selenium in Como Channel was below 4.0 µg/L at the upstream sampling point, and tested at 33.4 to 38.0 µg/L at the confluence with Peters Canyon Wash, a distance of only 2.2 miles downstream. Selenium in Santa Fe channel was also below 4.0 µg/L at the upstream sampling location, increasing to 26.7 to 32.0 µg/L above the confluence with Peters Canyon Wash (Figure 1, Table 1).

Stream gaging indicates that discharge also increases between upstream and downstream locations in each of these channels (Figure 1, Table 1). The increase in streamflow is attributed to groundwater discharge to creeks. Measurements

Table 1. Results of stream gaging and total selenium analysis at upstream and downstream stream stations in 1999 and 2009 (see Figure 1 for locations).

Channel (Date)	Upstream Flow (ft^3/s)	Downstream Flow (ft^3/s)	Change of Flow (ft^3/s)	Upstream Se Concentration (µg/L)	Downstream Se Concentration (µg/L)	Change of Selenium (µg/L)
San Diego Creek (8/28/1999)	1.63	2.32	+0.69	4.0[a]	18.0[a]	+14.0
San Diego Creek (6/21/2009)	1.25	1.98	+0.73	2.9[b]	21.2[b]	+18.3
Como Channel (5/1/2000)	0.0004	0.44	+0.44	<4.0[a]	38.0[a]	~ +34.0
Como Channel (6/22/2009)	0.001	0.37	+0.37	2.9[b]	33.4[b]	+30.5
Santa Fe Channel (5/1/2000)	0.019	0.46	+0.44	<4.0[a]	32.0[a]	~ +28.0[a]
Santa Fe Channel (6/22/2009)	0.003	0.39	+0.39	1.4[b]	26.7[b]	25.3

[a] Analyzed using ICP-OES by Associated Laboratory of Orange, California (detection limit = 4 µg/L).
[b] Analyzed using HG-AA by University of California – Riverside (detection limit < 0.6 µg/L).

of water levels in nearby water wells indicate that water tables are typically higher than the stream stage in the creeks (Hibbs and Lee 2000). Water wells are very shallow and penetrate only the upper ten feet of the shallow water table aquifer. Water level measurements in the water wells indicate that water tables occur at depths as little as 5 ft below land surface, and rarely exceed 20 ft below land surface. Several springs and weepholes flow perennially into the creeks. Most groundwater discharge to creeks is by direct seepage along channels unlined with concrete grout. Along channels lined with concrete grout, groundwater flows from weepholes at rates as high as 2 gallons per minute.

The increase in selenium concentrations between upstream and downstream sampling locations in creeks is attributed to high concentrations of selenium in groundwater (Figure 2). In this hypothesis, selenium-laden groundwater seeps into the creeks, increasing selenium loads in surface flows. To verify the hypothesis, several water wells, weepholes, and springs were sampled for selenium (Figure 3). Springs, weepholes, and water wells provided samples of the same shallow aquifer zone.

Groundwater sampling confirms the source of elevated selenium is groundwater baseflow. Groundwater concentrations of selenium in areas where the marsh once existed usually exceed 25 µg/L, reaching concentrations as high as 478 µg/L. However, in areas where the marsh did not exist, selenium in groundwater is usually less than 25.0 µg/L (Figure 3). The highest selenium concentrations are clustered about an area that coincides with the interior part of the historic Swamp of the Frogs Marsh (Figure 3). Shallow groundwater sampled throughout the basin also contains 0.3 mg/L to 2.0 mg/L dissolved oxygen, reflecting contemporary oxidizing conditions (Hibbs and Lee 2000; Meixner et al. 2004).

Hypothesis Formulation for Selenium Remobilization from Marsh Deposits

From reconnaissance investigations done in 1999 and repeated in 2009, we found that the selenium concentrations increased between upstream and downstream sampling locations in creeks (Table 1). We attribute this phenomenon to seepage of

selenium-laden groundwater into the creeks that increase selenium loads by several factors.

Selenium concentrations are highest in the aquifer region around Peters Canyon Wash, extending from the area just above El Modena Channel and Peters Canyon Wash to the area just below Santa Fe Channel and Peters Canyon Wash (Figures 1 and 3). This area corresponds to the interior portion of the historic Swamp of the Frogs Marsh.

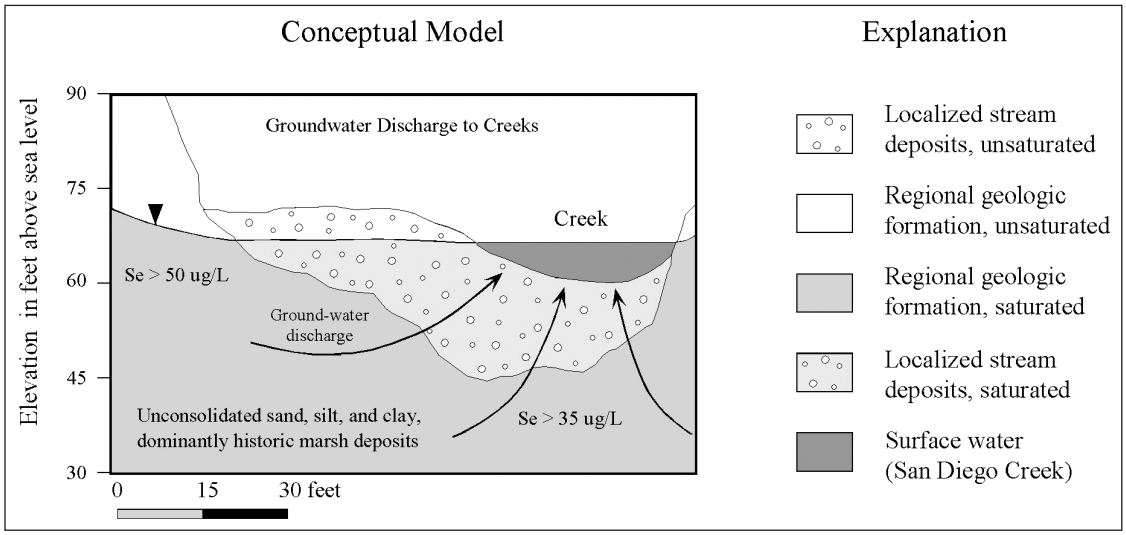


Figure 2. Conceptual model for selenium loading from groundwater baseflows. Extensive groundwater sampling and stream gauging confirmed groundwater baseflow as an important source of dry-weather pollutant loading in San Diego Creek Watershed. Increasing pollutant concentrations between upstream and downstream sampling stations is from the additive inputs of groundwater in specific channels shown in Figure 1 and Table 1.

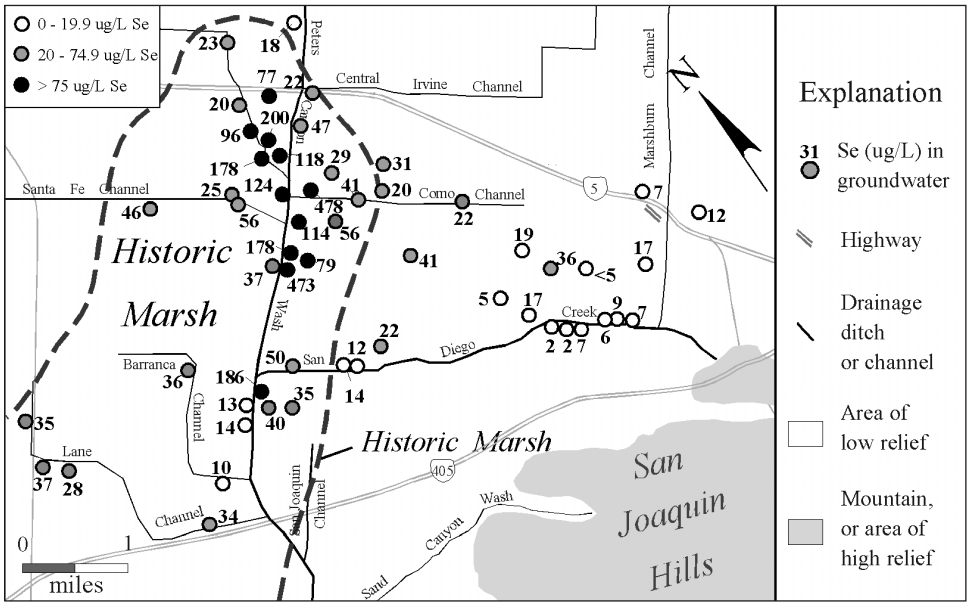


Figure 3. Selenium concentration in groundwater (µg/L). Sample points include shallow water wells, weepholes, and springs. Data indicate that selenium concentrations are highest in the historic marsh areas that were displaced by agriculture and urban development.

Within the interior portion of the former Swamp of the Frogs Marsh, where selenium in groundwater often exceeds 50 µg/L, we discovered a positive correlation between sulfate and selenium concentrations in groundwater. A possible explanation for this correlation is provided by an analysis of the chemistry of these elements. The chemistry of selenium is similar in many respects to the chemistry of sulfur. Both elements are located in Group VI of the periodic table of the elements. Both elements behave somewhat similarly in groundwater (Hem 1985; Johnson et al. 1999).

To assess further the correlation between selenium and sulfur in shallow groundwater, selenium and sulfate couplets in groundwater samples are plotted on a bivariate plot of ions (Figure 4). The relationship between selenium and sulfate becomes apparent when the data are divided into groundwater data sets extracted from areas within the historic Swamp of the Frogs and areas outside the former marsh. Selenium and sulfate are clearly elevated in groundwater within the marsh area. These observations suggest that the sediments of the historic marsh are a likely source of elevated sulfate and selenium in groundwater. The reason for two sub-linear trends in selenium and sulfate in the groundwater dataset inside the former marsh is not entirely understood, but may relate to soil facies changes within the marsh (Figure 4). Chloride data do not show a similar enrichment. Chloride data and water isotopes indicate the enrichment of selenium and sulfate in groundwater beneath Swamp of the Frogs Marsh area is not due to evaporation of groundwater (Hibbs and Lee 2000; Hibbs et al. 2016). Selenium and sulfate have an apparent geological source related to the historic marsh deposits.

Forms of Selenium and Sulfur in Oxidizing and Reducing Environments

The historic Swamp of the Frogs Marsh was described as a "giant peat bog" (Liebeck 1990)

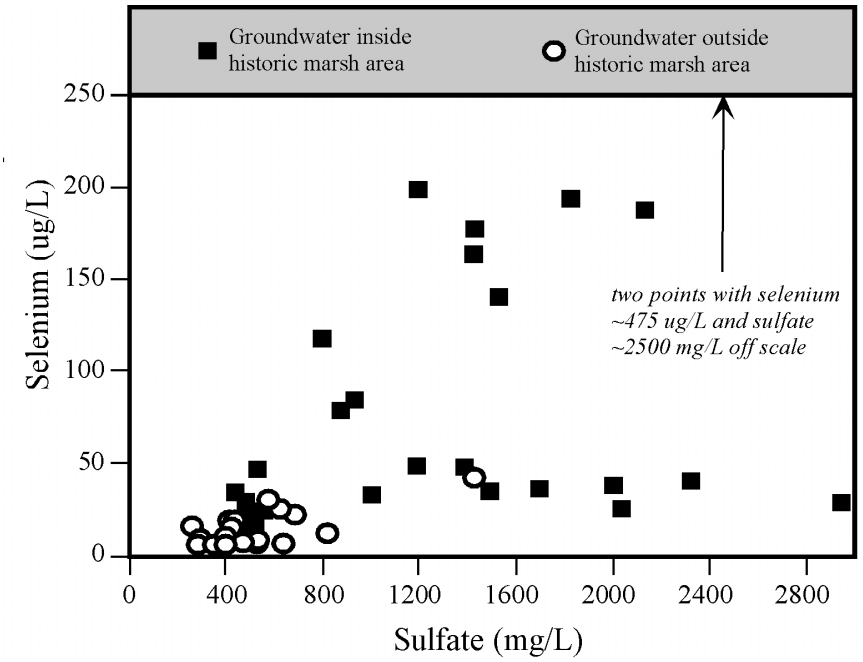


Figure 4. Bivariate scatter plot showing selenium/sulfate couplets for shallow groundwater samples in the study area for groundwater samples extracted outside of the historic marsh area (white circles) and for groundwater samples extracted within the historic marsh area (black squares), showing elevated selenium and elevated sulfate concentrations in groundwater collected in historic marsh area. The reason for two sub-linear trends in selenium and sulfate data in the groundwater data set beneath the marsh is not entirely understood, but probably relate to soil facies features within the marsh containing variable concentrations of selenium. Two anomalous samples with selenium concentration about 475 µg/L (sulfate ~2500 mg/L) are omitted from the graph due to scale. This figure includes most, but not all of the data in Figure 3, due to absence of sulfate data from a few sampling points in Figure 3.

that consisted of impassable marshy and wet areas that were overgrown with willows, tules, and water grasses. Similar wetland and marshy areas today are characterized as moderately to highly reducing (Drever 1997) because abundant organic material and dead and decaying plant tissue at the bottom of these marshy areas create anoxic, reducing environments.

To understand the fate of selenium and sulfur under the anoxic conditions that probably existed in the historic Swamp of the Frogs Marsh, it is necessary to review the different forms of selenium and sulfur in oxidizing versus reducing settings. Selenium can occur in four oxidation states under natural conditions. Selenium exists in its highest (+VI) oxidation state as selenate (SeO_4^{2}), in the (+IV) oxidation state as selenite (SeO_3^{2-}), in the zero oxidation state as elemental selenium (Se(0)), and in its lowest oxidation state (-II) as selenide (Se^{2-}) (Masscheleyn et al. 1990; White and Dubrovsky 1995).

In the highest oxidation state (+VI, selenate), selenium usually occurs as a dissolved ion in oxidizing aqueous environments. Selenate is a very mobile ion in oxic groundwater. In its next highest oxidation state (+IV, selenite), selenium can also exist as a dissolved ion, but frequently exists as a sorbed ion. Therefore, selenite is often somewhat mobile to highly immobile (White and Dubrovsky 1995; Lawrence Berkeley National Laboratory 1998). In the zero, or elemental Se(0) oxidation state, selenium exists as crystalline and amorphous polymorphs (Elrashidi et al. 1987; White and Dubrovsky 1995). In its most reduced form (-II, selenide), selenium is a solid bound with transition metals (Elrashidi et al. 1987). Thus, selenium is observed to cycle geochemically between species in different oxidation states, depending on oxidation/reduction conditions and external biogeochemical constraints (Losi and Frankenberger 1998).

Sulfur also exists as several possible species: SO_4^{2-}(VI), H_2S(-II), HS^-(-II), and S^{2-}(-II). In oxidizing environments, SO_4^{2-}, or sulfate, is the dominant species of sulfur. When SO_4^{2-} dominates, essentially none of the (-II) species (H_2S, HS^-, and S_2^-) are present. When conditions become reducing, the S(-II) species are the dominant forms of sulfur (Domenico and Schwartz 1990).

In the higher (VI) oxidation state, sulfate is dominantly a dissolved ion because there are no solubility constraints that remove the ion from solution. In reducing environments, nearly all of the sulfur is in the reduced (-II) form, and is removed from the system as insoluble metal sulfides and precipitates, although some sulfur may exist as H_2S gas in solution. Thus, sulfur in the oxidized (VI) form is the relatively mobile SO_4^{2-} ion in solution. Upon entering highly reducing settings, sulfate is typically reduced to H_2S and HS^- and is therefore transformed into insoluble metal sulfides and precipitates, or dissolved gas. Sulfur rarely exists in the S_2^- form because pH must be above 9 or 10 for it to precipitate (Hem 1985).

Fate of Selenium and Sulfur in the Swamp of the Frogs Marsh

During the historic period of the Swamp of the Frogs Marsh, any forms of selenium and sulfur that flowed into the marsh were likely dissolved in surface runoff from the highlands as the oxidized forms (SeO_4^{2-} and SO_4^{2-}). Once the oxidized forms of selenium and sulfur reached the anoxic waters of the marsh, these oxidized species were probably reduced to SeO_3^{2-}, elemental Se(0), Se^{2-}, H_2S, and HS^-. These forms would be expected to be removed from the waters in the marsh and sorbed onto solid particles, precipitated as crystalline and amorphous polymorphs, or transformed into volatile gases (Figure 5).

Once immobilized in solid forms, the selenium and sulfur solids would tend to remain stable in the soil substrate as new sediments and organic matter in the marsh continued to accumulate. Cores extracted from old marsh sediments reveal sedimentary facies consistent with anoxic environments, including thick sequences of olive-gray clay, dark gray to dark brown silt and silty clay, and sandy clay and clayey sand that is usually medium to dark brown (Silverado 1997). Some of the core logs show traces of carbonized fragments indicative of decaying plant material.

When the Swamp of the Frogs was drained in the late 1800's and early 1900's, the shallow subsurface was transformed into an oxidizing environment. In fact, the shallow groundwater flow system today is being recharged by oxygen- and nitrate-enriched water that retains some dissolved oxygen and

nitrate as it flows through the old marsh deposits. The groundwater data collected during this study indicate that groundwater contains moderate to relatively high concentrations of dissolved oxygen (usually 0.3 to 5 mg/L), very high ratios of dissolved nitrate to nitrite, and the general absence of iron and manganese. These hydrochemical signatures indicate an oxidizing groundwater flow system.

Oxidizing groundwater flowing through the old marsh sediments today remobilizes the bound forms of selenium and sulfur into their oxidized and mobile forms (SeO_4^{2-} and SO_4^{2-}). Thus, we can account for high sulfate and selenium in groundwater in large part from remobilization of reduced forms of selenium and sulfur as oxidizing soil water and groundwater flows through the historic marsh sediments (Figure 5).

Based on the thickness of sedimentary strata and estimated sedimentation rates (Herndon and Reilly 1989), the selenium and sulfur probably became concentrated during hundreds to thousands of years in the marsh sediments. In more recent times, these elements were remobilized in great amounts by oxidizing soil water and groundwater, reaching concentrations that exceed by many factors the concentrations of selenium that are considered safe in aquatic systems (EPA 2016). Insofar as it has been established that many drainage ditches and channels are replenished by seeping groundwater, it is apparent that the selenium-laden groundwater and surface water exceed EPA (2016) recommended criteria for protection of aquatic life.

Hypothesis Testing

The hypothesis of the remobilization of selenium and sulfur due to drainage of the Swamp of the Frogs Marsh and conversion to an oxidizing environment was formulated with reconnaissance

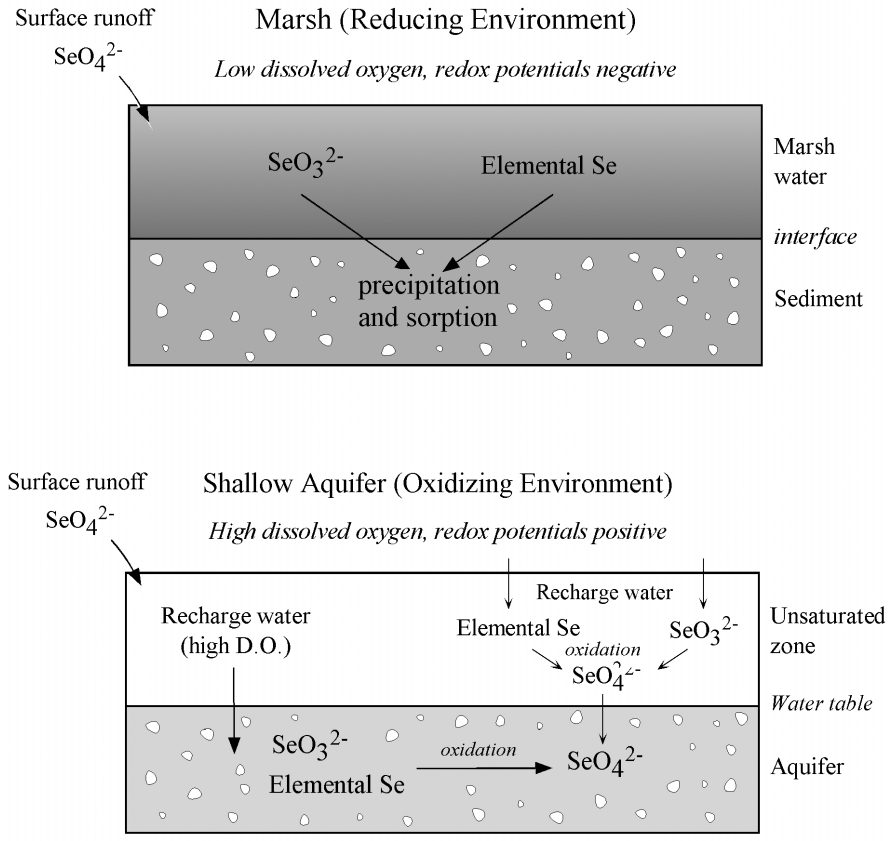


Figure 5. Conceptual model for accumulation of selenium in the anoxic Swamp of the Frogs Marsh due to reducing conditions that prevailed there (top image). When the marsh was drained, oxygen-rich waters were able to remobilize the reduced forms of selenium (SeO_3^{2-} and elemental selenium) into selenate (SeO_4^{2-}), a mobile and oxidized form of selenium (bottom image).

data sets based on total dissolved selenium and major ion concentrations. The spatial relationships are compelling but additional data were needed to evaluate and lend possible support to the hypothesis. The additional data collected in subsequent studies included groundwater flowpath analysis, selenium speciation of water and soils, and sulfate isotope analysis in groundwater. This new information is presented in these subsections:

- Evidence from Groundwater Flowpath Analysis
- Evidence from Selenium Speciation Analysis of Groundwater
- Evidence from Selenium Speciation Analysis of Soils
- Evidence from Sulfur Isotope Analysis of Groundwater

Evidence from Groundwater Flowpath Analysis

Previous investigations by Hibbs and Lee (2000) indicated that many of the subsurface storm drain laterals in the San Diego Creek Watershed receive a significant amount of dry weather flows from groundwater seepage. Baseflow was confirmed by analysis of concentrations of hydrochemical constituents (e.g., selenium, nitrate) emitted by the drains, and by inspection within the drains which indicated flowing weepholes and flowing seams where groundwater was identified by sampling and analysis of hydrochemistry.

Valencia Drain, a key storm drain in the watershed, was investigated for flow sources inside the drain. This was done to identify possible seeps, springs, weepholes, and dewatering operations. Inspection within Valencia Drain indicated a large number of groundwater flows from seams and weepholes that were sampled for selenium and other constituents (Figure 6). Sample points in Figure 6 are labeled by distance from Peters Canyon Wash to the point in the drain where the sample was collected, in feet. The data proved to be a fortuitous information set because Valencia Drain is oriented almost perfectly in-line with a shallow groundwater flowpath in the shallow aquifer. This provided an opportunity to assess how selenium changes along the groundwater flowpath that moves downgradient above and then through the historic Swamp of the Frogs Marsh region, into Peters Canyon Wash (Figure 6). A shallow monitoring well very close to Valencia Drain, IRWD Well 86N, was included in the flowpath analysis. This well is the upgradient point in flowpath analysis.

Selenium concentrations between IRWD Well 86N and the first sample point (3533 ft) in Valencia Drain are less than 30 µg/L. Concentrations then increase within the historic marsh region to more than 50 µg/L dissolved selenium (Figure 6). For an uncertain reason, selenium concentrations reach concentrations in excess of 175 µg/L close to Peters Canyon Wash (Figure 6). This could be due to: 1.) gradation of reducing conditions that may have existed historically within the interior of the Swamp of the Frogs Marsh, or 2.) a soil facies change at the lower end of the groundwater flowpath. The marsh boundary clearly delineates a region of increasing selenium along the well-defined groundwater flowpath, offering support for the Swamp of the Frogs Marsh selenium remobilization hypothesis as a principal source of selenium in groundwater.

Evidence from Selenium Speciation Analysis of Groundwater

The hypothesis of selenium remobilization from the Swamp of the Frogs Marsh predicted that oxidizing conditions in shallow groundwater accounted for selenium release from marsh sediments. Speciation analysis was not performed in the report by Hibbs and Lee (2000) where the hypothesis was first formulated. Only total dissolved selenium was tested in shallow groundwater in that early report. Several samples were later collected from shallow groundwater in 2005-2006 and tested for selenium species. A set of these are presented here, including three groundwater samples collected above the marsh, and ten samples collected within the marsh boundary (Table 2).

Selenium speciation data were used to compute oxidation-reduction potential (Eh) using the Nernst equation as follows:

$$Eh = E^o + (RT/nF)\,[\log a(SeO_4^{2-}) - \log a(SeO_3^{2-}) + 2pH] \qquad \textit{Equation 1}$$

where $E^o = -(\Delta Gr^o/nF)$; R = ideal gas constant; T = temperature in degrees Kelvin; F = Farraday's constant; a = activity of the species shown in

parenthesis (with the assumption that activity is equal to molar concentration); and ΔGr^o = the Gibb's free energy of formation given the following reaction:

$$SeO_4^{2-} + 2H^+ + 2e^- \rightarrow SeO_3^{2-} + H_2O \qquad \textit{Equation 2}$$

Selenium speciation data used in the Nernst equation computed redox potential (Eh) in millivolts. Selenium speciation revealed that Se^{6+} makes up 92% to 99% of total dissolved selenium in all except one sample, Val-Jeff Spring (Table 2). Figure 7 shows where these waters plot on an Eh-pH diagram, showing the stability range for samples based on speciation results as dominating in the oxidizing range.

Selenium speciation and other groundwater data allowed the characterization of these waters as oxidizing. The concentrations of other redox-sensitive trace species included generally low (<0.1 mg/L) to non-detectable concentrations of iron and manganese (Andrus 2008; Hibbs et al. 2008). Selenium-nitrate correlations were also noted in shallow groundwater, where nitrate was frequently measured between 2.0 and 20 mg/L

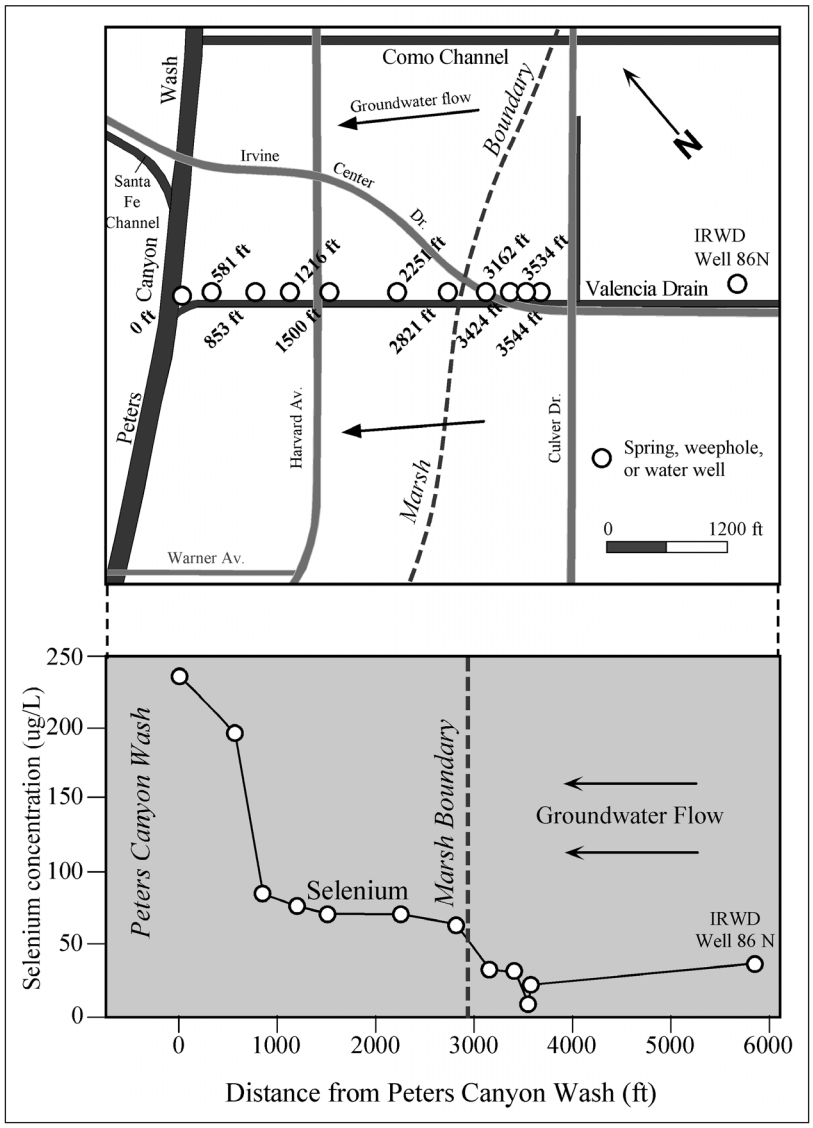


Figure 6. (Top) Groundwater at discrete points within Valencia Drain oriented along a groundwater flowpath. Samples are identified by distance from Peters Canyon Wash. (Bottom) Concentrations of selenium in groundwater flowing into Valencia Drain. Marsh boundary indicated by dashed line. Selenium elevates in concentration when the marsh boundary is crossed.

Table 2. Results of selenium speciation analysis of shallow groundwater samples located within and outside the limits of the historic Swamp of the Frogs Marsh.

Groundwater Sample	Type (µg/L)	Se(VI) (µg/L)*	Se(IV) (µg/L) *	Organic Se (µg/L) *	Total Se (µg/L) *
Above Swamp Boundary					
B2 El Modena	Weephole	11.25	0.76	<DL	12.01
Val-Jeff Spring	Spring	5.94	0.95	<DL	6.89
Well 103-N	Well	14.99	0.74	<DL	15.74
Within Swamp Boundary					
B4 El Modena	Weephole	51.34	1.31	<DL	52.65
B3 El Modena	Weephole	79.26	0.83	<DL	80.09
Valencia 1	Weephole	122.32	0.82	<DL	123.14
Valencia 2	Weephole	106.57	0.85	<DL	107.42
Valencia 3	Weephole	90.67	0.84	<DL	91.51
Well 85-W	Well	19.78	1.62	<DL	21.41
Well 63-S	Well	55.08	1.14	<DL	56.22
Bar-Alt-Spring	Spring	218.56	3.41	<DL	221.97
Como-Harv-Cul	Weephole	29.39	0.79	<DL	30.18
PCW-SW Rail	Weephole	47.24	1.49	<DL	48.74

* Analyzed using HG-AA by University of California-Riverside

NO_3-N when selenium was at least 20 µg/L (Andrus 2008; Hibbs et al. 2008). The fact that oxidized species such as nitrate and selenate (Se^{+6}) dominate in these groundwater samples, while dissolved iron and manganese are virtually absent, points to moderately to strongly oxidizing conditions in the shallow aquifer, as predicted by Hibbs and Lee (2000). Such conditions favor oxidation and remobilization of selenium that was once bound in sediments under reducing conditions typical of marsh settings (Masscheleyn et al.1990; Dowdle and Oremland 1998).

Evidence from Selenium Speciation Analysis of Soils

Soil samples were collected for testing selenium content of soils: three soil samples collected within and two outside of the historic marsh boundary (Figure 1). Two clays were collected from a fresh trench along Peters Canyon Wash within the boundary of the historic swamp. The "upper clay" was collected approximately 8 feet below land surface from the unsaturated zone. From a lower layer within the same trench, local channel construction at a temporary dewatering operation permitted the collection of a "blue clay", which normally resides below stream head in the saturated zone, from approximately 20 feet below land surface. A blue clay about 1 foot beneath land surface was also collected near Santa Fe Channel (Figures 1 and 8). Soils were also collected for control from the dry streambeds of Hicks Canyon and Round Canyon washes (Figure 1). Brief physical descriptions of these soils are shown in Table 3. Soils were analyzed in most samples for total selenium and selenium speciation. Blue clays and upper clay were collected within the Swamp of the Frogs Marsh boundary while Hicks Canyon and Round Canyon streambed soils were collected in the uplands, well above the marsh boundary (Figure 1).

Background concentrations of total selenium in typical soils (i.e., those that are not impacted by selenium) are on the order of 0.4 mg/kg, while

soils derived from some fine textured marine rocks have higher total selenium content on the order of 5 mg/kg (Thomas et al. 1998). Data for total selenium and selenium species in soils are shown in Table 3. Selenium data reveal that total selenium levels in the upland soils as well as in the "upper clay" are comparable to those found in normal soils without selenium enrichment. Selenium data reveal the blue clay has order of magnitude higher concentrations (Table 3). Speciation data show that selenium oxyanions comprise about 40% of total selenium in the soils collected from within the boundary of the historic swamp. The dominant form of selenium in the "upper clay" is selenate (Se^{6+}), whereas there is more than twice as much selenite (Se^{4+}) as selenate (Se^{6+}) in the "blue clay." This indicates that selenium in these soils exists in leachable forms.

Results of this limited soil investigation reveal that much higher quantities of selenium are present in soils within the marsh area. Also apparent at one site is the large difference in selenium content between vertical clay horizons in the same location. Blue clay is found commonly in shallow vadose zone and shallow saturated zone horizons within the historic Swamp of the Frogs Marsh boundary (Figure 8).

Evidence from Sulfur Isotope Analysis of Groundwater

Several groundwater samples sampled for sulfur isotope were collected from shallow water wells, springs, and weepholes within and outside of the region formerly occupied by the historic Swamp of the Frogs Marsh (Figure 9). The sulfur isotope work is done to further delineate regions of sulfur/selenium reduction and to further refine conceptual

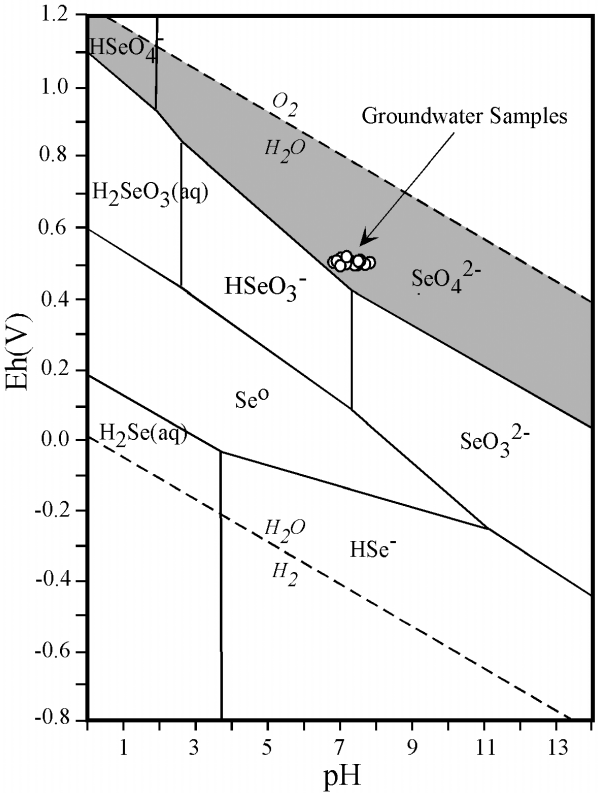


Figure 7. Eh-pH diagram for groundwater from Table 2 indicates stability in the domain occupied by the oxidized form of selenium, Se(+VI), in the shaded area of the figure.



Figure 8. Blue clay near land surface on the side of Santa Fe Channel within the historic marsh boundary is indicative of sediment formed in an anoxic marsh environment.

Table 3. Soil selenium content and selenium speciation data (see Figure 1 for location).

Soil ID	Soil Type	Selenium IV (mg/kg)	Selenium VI (mg/kg)	Total Selenium (mg/kg)
Santa Fe Channel Blue Clay	blue clay	--	--	13.3
PCW Blue Clay	blue-grey clay	2.98	1.27	10.4
PCW Upper Clay	brown clay	< 0.02	0.155	0.383
Round Canyon Streambed	grey-brown silty sand	ND (< 0.02)	ND (< 0.046)	0.360
Hicks Canyon Streambed	grey-brown silty sand	ND (< 0.02)	ND (< 0.046)	0.198

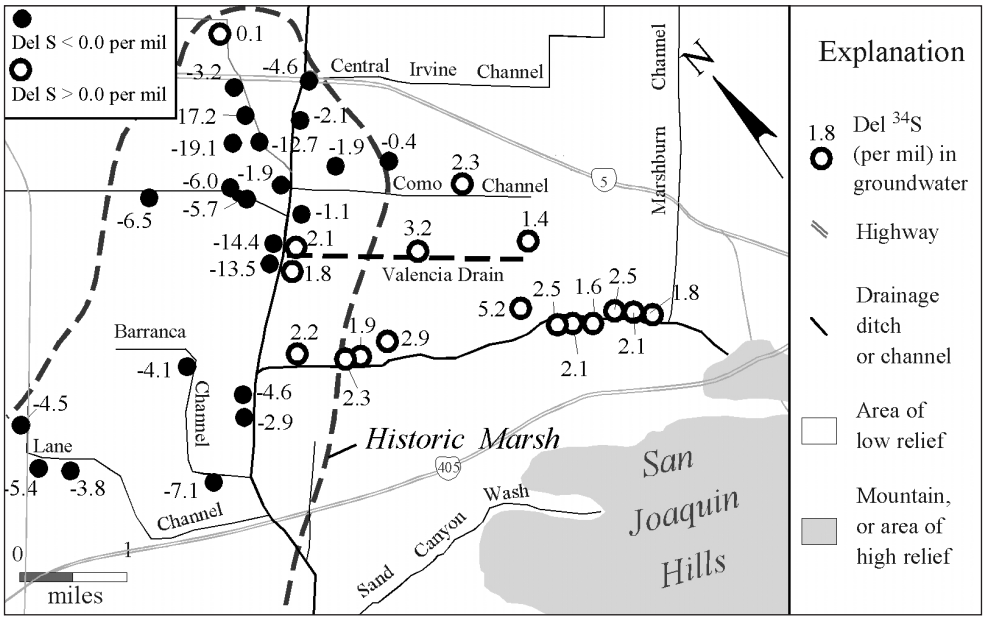


Figure 9. Per mil values of sulfur isotopes in groundwater collected from springs, weepholes, and shallow water wells in the study area. Mostly negative sulfate sulfur isotope values within the historic marsh boundary imply oxidation of metal-sulfides that were originally sequestered in the marsh sediments.

understanding of the flow system for groundwater model development. East of the Swamp of the Frogs Marsh area, measured $\delta^{34}S[SO_4^{2-}]$ values are positive in all except one groundwater sample collected from an IRWD well near Como Channel (-0.4 $\delta^{34}S[SO_4^{2-}]$). Inside the Swamp of the Frogs Marsh area, other sulfur isotope values in groundwater wells are negative in most samples (Figure 9). The -0.4 $\delta^{34}S[SO_4^{2-}]$ sample near Como Channel is located on the approximate boundary of the historic marsh, reflecting an intermediate sulfur isotope composition.

Positive sulfur isotope values varied moderately in groundwater, from 1.4 to 5.2 per mil $\delta^{34}S[SO_4^{2-}]$. Negative values varied more widely, from –0.4 to –14.4 per mil $\delta^{34}S[SO_4^{2-}]$. Positive $\delta^{34}S[SO_4^{2-}]$ values may indicate multiple sulfate sources and mixtures, including fertilizers, organic matter, marine salts, geologic strata, and atmospheric deposition (Krouse and Grinenko 1991). Negative sulfur isotope values are consistent with oxidation of Fe-sulfides, or dissolution of second-cycle terrestrial evaporitic salts that were derived originally from oxidation of metal sulfides (e.g., Thernardite or Mirabolite

salts). The negative $\delta^{34}S[SO_4^{2-}]$ signature often develops as a result of the lower energy required by bacteria to break ^{32}S – Fe bonds, resulting in a negative sulfur isotope signature (Toran and Harris 1989; Clark and Fritz 1997). The negative sulfur isotope signature across most of the Swamp of the Frogs Marsh region is generally consistent with the hypothesis of origin of sulfate from oxidation of reduced forms of sulfur. By proxy it is assumed the same set of redox processes operates on selenium redox systematics.

Summary Conceptual Model for Selenium and Sulfur Sequestration and Release in Marsh Sediments

The initial basic reconnaissance data provide a solid hypothesis for the origin of selenium from the Swamp of the Frogs Marsh (Hibbs and Lee 2000). The subsequent data provide strong supporting evidence for release of selenium from the historic marsh sediments. We suspect that selenium in groundwater in the San Diego Creek Watershed was originally derived from oxidation and weathering of Miocene marine sedimentary strata such as the Monterey and Puente formations exposed in the highlands flanking the watershed (Morton and Miller 1981; Tracy et al. 1990; Hibbs et al. 2008). Selenium, originally incorporated in marine soils and sediments deposited in Miocene time and subsequently lithified into shales and mudstones, likely existed as metallic selenide (FeSe) and metallic sulfide (FeS_2) in these parent rocks, which subsequently weathered to selenate and sulfate under alkaline oxidizing conditions in the Santa Ana Mountains (Figure 1).

Prior to the historic period of agricultural development in the watershed, selenium and sulfur weathered from upland marine sediments and rocks were transported in surface runoff and groundwater seepage to the Swamp of the Frogs marshlands (Figure 5). Runoff waters probably had very dilute concentrations of sulfate and selenate. The interior parts of the marshlands into which the runoff waters flowed were probably oxygen deficient due to decaying organic material in the marsh. When selenium and sulfur first entered the marsh by surface drainage and groundwater seepage, they were in the form of selenate and sulfate, a pair of water-soluble and oxidized anions. The deficiency of oxygen in the marsh created conditions in which selenium and sulfate acted as electron acceptors for microorganisms that decompose organic material (Quinn et al. 1994; White and Dubrovsky 1995; Zawislanski and Zavarin 1996; Losi and Frankenberger 1998). Most of the selenium became elemental selenium (a water-insoluble crystal) or selenite (often a sorbed anion) (McNeal and Balistrieri 1989). Likewise, most of the sulfur became insoluble metal sulfides. These immobile forms of selenium and sulfur accumulated in the organic-rich sediments in the marsh where they remained stable under the anoxic conditions that prevailed there (Figure 5). The chemical species were thus reconverted to reduced forms of selenium in the anoxic waters of the marsh where dissolved oxygen and oxidizing components were not available.

When the marshes were drained, oxygenated groundwater began to replace the oxygen-deficient waters within and below the marsh (Figure 5). Our hypothesis established that contemporary oxidizing groundwater flows through sediments beneath the historic marsh areas, remobilizing residual selenium and sulfur as dissolved selenate and sulfate, a highly mobile pair of ions in the oxidizing groundwater flow system. Increased loads of selenium in the watershed are likely a direct result of destruction of the marshland.

The conversion from a marshy environment to agricultural and later suburban land use changed the hydrology of the system to a shallow baseflow-dominated system. Drainage controls and depression of the water table allowed organic material in soils to rapidly oxidize. The groundwater flow system changed to an oxidizing environment in just over 100 years. Elements are released from bound forms in the soil matrix into groundwater, which flows directly into channels along lined and unlined segments of channel (Hibbs et al. 2016).

Selenium enrichment in the groundwater in the San Joaquin Valley of Central California is concentrated by a different set of hydrological processes. Common selenium enrichment processes in San Joaquin Valley include: 1.) leaching of soil salts and soluble selenium from infiltrating irrigation waters; 2.) evaporative concentration

of soluble selenium and other salts in areas where water tables are shallow; and 3.) release from weathering of selenium-laden bedrock material and sedimentary rock detritus (Deverel and Fujii 1988; Deverel and Gallanthine 1989; Dubrosky and Deverel 1989). The highest concentrations of soluble selenium in soils and groundwater in San Joaquin Valley are found where evaporation processes enrich soluble forms of selenium, leading to strong correlations between selenium and salt concentrations in groundwater (Deverel and Fujii 1988; Dubrosky and Deverel 1989). In San Diego Creek Watershed, sulfate and selenium enrichment are correlated, but chloride enrichment is not correlated with sulfate and selenium enrichment in groundwater (Hibbs and Lee, 2000; Hibbs et al. 2016). The information presented in this paper indicates that selenium and sulfur are released from marsh sediments following redox transformations during land use change in San Diego Creek Watershed. However, the weathering of selenium bearing rocks and sediments of marine origin, and subsequent runoff of both dissolved selenium and selenium particulates onto valley floor areas, is the initial source of selenium in both the San Joaquin Valley and Swamp of the Frogs Marsh.

Conclusions

The toxic trace element selenium occurs naturally in geologic units in the San Diego Creek Watershed. Release of selenium is related to land use modification and associated change of redox conditions. Land use change from natural marshlands to agricultural and urbanized landscapes resulted in drainage of the anoxic Swamp of the Frogs Marsh and conversion to a shallow, oxidizing groundwater environment. Many drainage channels initially installed to drain the marshlands still exist, preventing groundwater in the shallow water table aquifer from rising into residential and commercial areas. Selenium concentrations and stream flow increase along a downstream trend in these drainage channels in the San Diego Creek Watershed due to groundwater seepage. The highest concentrations of selenium in groundwater correspond to the marsh areas that were drained in the early 1900's. Contemporary oxidizing groundwater flows through the sediments beneath the historic marsh, dissolving selenite and elemental Se from shallow soils. Increased loads of selenium in the watershed are a direct result of destruction of the marshland. Concentrations of selenium in surface flows exceed the EPA aquatic standards by several factors, potentially placing waterfowl and other wildlife at risk. A lesson learned is that existing and proposed land use developments in other areas must consider how the modification of the hydrology of natural systems could impact ecosystems and beneficial uses of watersheds.

This first journal paper lays out a regionally-based model for release of selenium from the historic Swamp of the Frogs Marsh sediments. The model is operative at the macroscopic scale (Figure 5). Future papers based on our work will highlight site-specific analysis where redox phenomena are associated with small scale gradations in soil facies within the historic Swamp of the Frogs Marsh area. These papers will include discussions of arsenic and sulfur anomalies within the Swamp of the Frogs Marsh area, origin of salinity, and analysis of seasonal controls on trace element and nutrient loading to San Diego Creek Watershed.

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