

MARCH 26, 2008

**CALLEGUAS CREEK WATERSHED  
MANAGEMENT PLAN**

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**Calleguas Creek Watershed Metals  
and Selenium TMDL**

**Special Study #2  
Selenium in Groundwater  
Work Plan**

*submitted to:*

LOS ANGELES REGIONAL WATER QUALITY CONTROL  
BOARD

*on behalf of:*

CALLEGUAS CREEK WATERSHED MANAGEMENT PLAN

*prepared by:*

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## Introduction

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The *Total Maximum Daily Load for Metals and Selenium in Calleguas Creek, Its Tributaries, and Mugu Lagoon* (TMDL) for the Calleguas Creek Watershed (CCW) was adopted by the Los Angeles Region Water Quality Control Board on June 8, 2006 and became effective on March 26, 2007. The TMDL was developed to address impairments in Calleguas Creek and its tributaries caused by metals (copper, zinc, mercury, and nickel) and selenium. Metals and selenium sources come from urban and agricultural runoff, groundwater, and POTW effluent. Additionally, the source analysis indicates that selenium in groundwater may be a significant source. As part of the TMDL implementation, this work plan is being submitted to address Special Study #2 required in the Basin Plan Amendment (BPA).

The purpose of Special Study #2 is to identify groundwater with high concentrations of selenium that is either being discharged directly to the stream or used as irrigation water in areas where runoff could reach receiving waters in the Revolon Slough subwatershed of the CCW. The study will identify:

1. Groundwater with elevated selenium concentrations and a high probability of reaching the stream.
2. Practical actions to reduce the discharge of groundwater to the stream.
3. Available alternative supplies for high selenium irrigation water.
4. Costs of actions and alternatives.

The approach for conducting Special Study #2 is outlined in this work plan. The analysis will contain the following tasks:

1. Gather existing data on groundwater and well construction.
2. Develop a geological and hydrogeological map based on existing data.
3. Identify data gaps and develop monitoring program to address gaps, prioritized by the locations that may contribute selenium to surface waters.
4. Use information from first three steps to identify areas where high groundwater concentrations of selenium are potentially reaching surface waters, and evaluate potential solutions for identified areas.

## Background

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Selenium is both an essential nutrient and a chemio-toxic trace element for humans, animals and plants, the safety margin between beneficial and toxic doses being narrow. Therefore, understanding selenium behavior in soils is of major concern for both eco-toxicologists and radio-toxicologists. Biogeochemical transformations of selenium include sorptions/desorptions on solids, and abiotic and biotic reductions/oxidations that can favor its volatilization. Among the factors controlling selenium mobility, the redox status of the soil, mainly governed by the soil geochemical features and microbial activities, appears as a major one.

In general, selenium in the environment can occur as a result of both natural and anthropogenic sources. In the CCW, selenium derived from ancient marine sediments in local foothills

accumulated over the last several thousands years. Soils containing selenium well above the normal levels are found in the arid and semi-arid areas of the world, including the Western United States. Soils high in selenium can contribute to groundwater with high values of selenium.

Anthropogenic sources of selenium include fuel (coal and oil) combustion, primary and secondary non-ferrous metal industries, waste (domestic, municipal and industrial) disposal and incineration, manufacturing processes, mining, smelting, refining, and steam electric (electric utilities that employ steam produced by burning fossil fuels for power generation). These anthropogenic sources are not significant in the CCW and are unlikely to contribute to elevated selenium concentrations in groundwater. However, anthropogenic activities that mobilize groundwater to the surface (i.e. agricultural irrigation) may contribute to elevated groundwater concentrations and/or the discharge of groundwater with elevated selenium concentrations to the surface waters. Groundwater pumping for irrigation may mobilize groundwater to the surface that contains high concentrations of selenium. Additionally, in some areas, irrigation can increase the water table elevation and saturate part of the unsaturated zone. If the unsaturated zone is rich in selenium (and also salts and metals), the increase in elevation can increase the distribution of selenium in the aquifer.

Because natural and anthropogenic influences can potentially impact the selenium concentrations in groundwater, the work plan is designed to evaluate the contribution of both types of sources.

## Task 1: Data Collection

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Data collection will provide general information about available data that can be used to identify potential areas of higher groundwater selenium concentrations and develop a targeted monitoring program for areas in the Revolon Slough subwatershed that may contribute groundwater to the surface water.

### **TASK 1.1 COLLECTION OF INFORMATION ABOUT WELL CONSTRUCTION (WELL DEPTH, PERFORATION DEPTH, ETC)**

Selenium can be measured at very different concentrations depending on the depth of the wells where the sample is taken and can vary significantly even in wells which are close to each other. In general, seleniferous layers of soil can be found at some specific depths depending on the characteristics of the area, historical irrigation, drainage practices and vertical hydraulic gradients. For example, data collected by Ventura County Watershed Protection District (VCWPD) Groundwater Section in the Santa Clara River watershed showed that selenium concentrations were very high in few wells in an area west of Piru, and that these high selenium values were measured only in wells that are perforated in a narrow band (Barbara Council, VCWPD Groundwater Section, written comm.).

An extensive study carried out in the Western San Joaquin Valley (Deverel et al., 1994) showed in detail the different selenium concentrations measured at different depths. For example, Figure 1 (Deverel et al., 1994, p. 169) presents the depth distribution of selenium concentrations in groundwater samples collected in the Western San Joaquin Valley in 1986 and 1987. Selenium concentrations were significantly correlated with dissolved solids concentrations and with

isotopic enrichment (isotopic enrichment is the process by which the relative frequency of an isotope in an element is increased).

Figure 2 (Deverel et al., 1994, p.177) shows other examples of selenium concentration measured at different depths and in wells perforated in soils with different textures at different depths.

Because the soil characteristics at different depths can significantly impact the selenium concentrations being discharged from the wells, collecting information about the well construction will be important for understanding the data collected in this study. This information will be also important in Task 2 for the geological and hydrogeological map preparation.

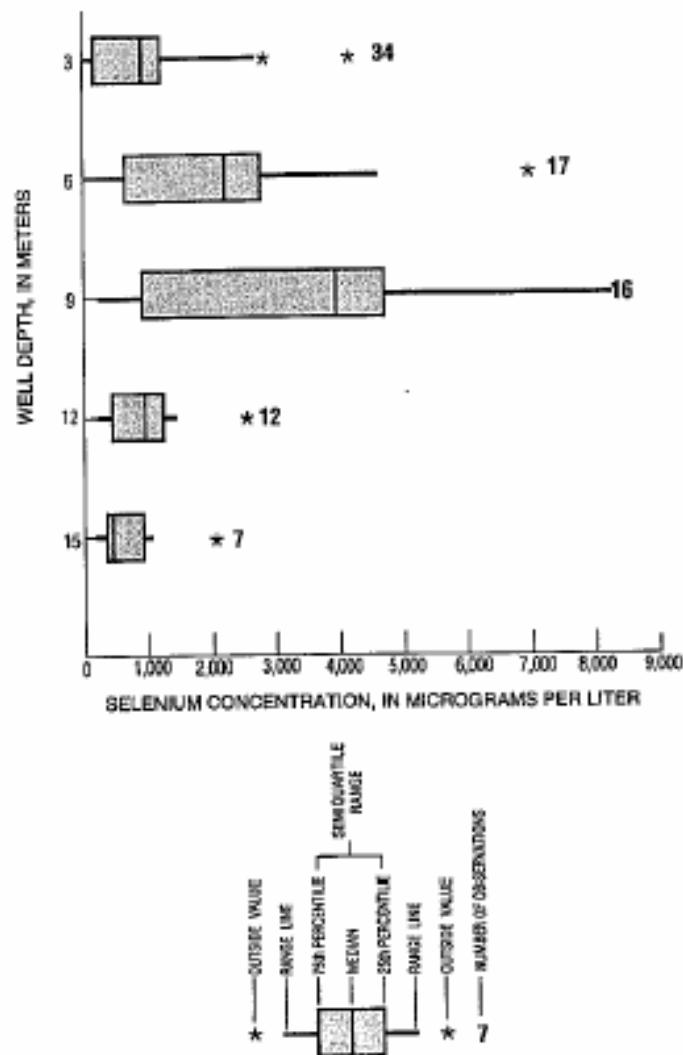


Figure 1. Depth distribution of selenium in samples collected in observation wells in San Joaquin Valley in 1986 and 1987 in the field study by Leighton et al (1992). Outside values are between 1.5 and 3.0 times the semiquartile range from the end of the rectangle. Range lines extend a distance equal to 1.5 times the semiquartile range away from the end of the rectangle or to the limit of the data, whichever is the lesser. Numbers to the far right equal number of observations.

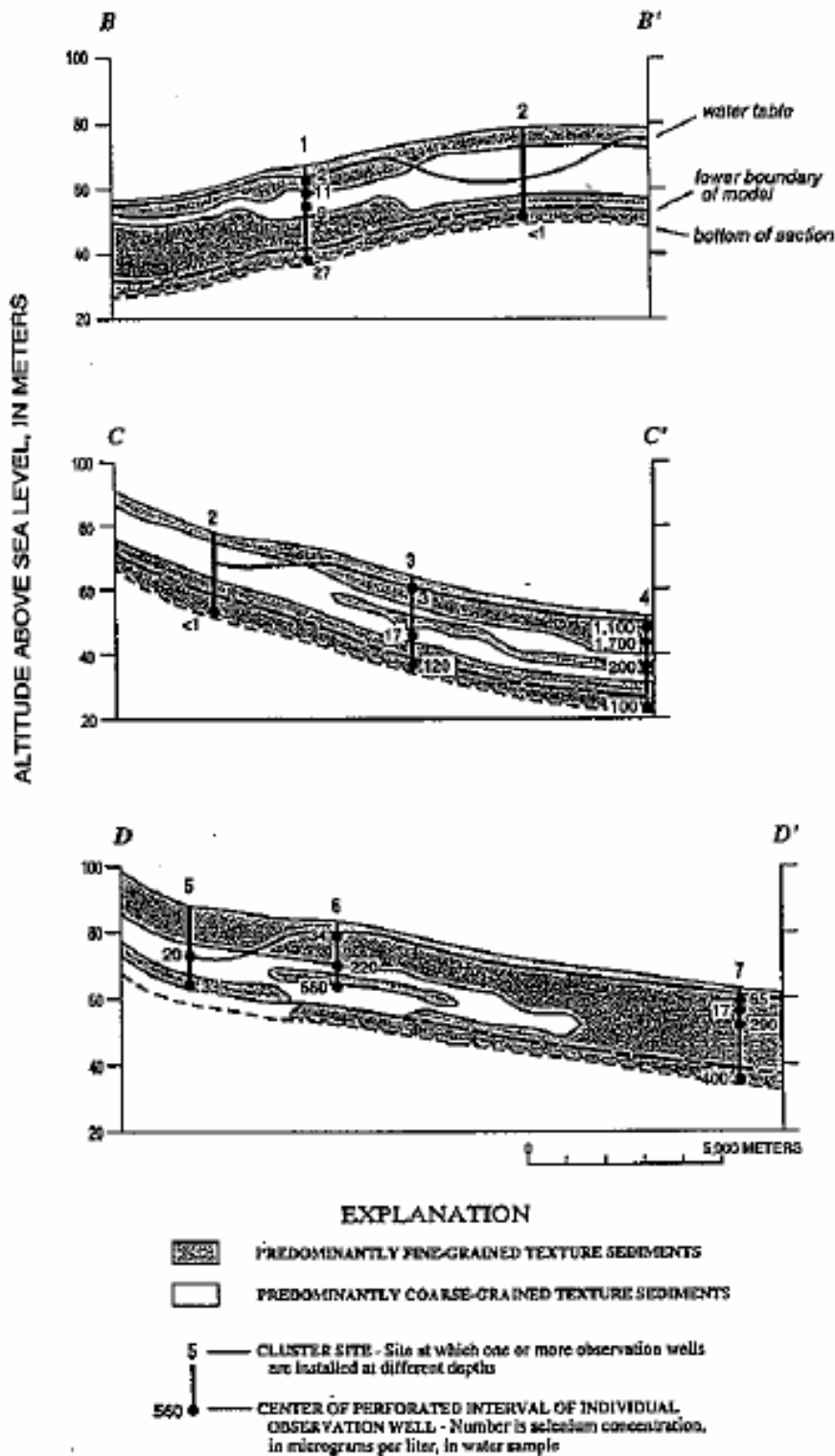


Figure 2. Cross-sectional diagram showing selenium concentrations in observation well samples and texture of deposits (Deverel et al., 1994, p. 177).

## TASK 1.2 COLLECTION OF THE AVAILABLE WATER QUALITY DATA

The collection of selenium data should be accompanied by the collection of all the available data for iron, manganese, nitrate, dissolved oxygen, sulfate, and isotopes of water to provide information about the aquifer, the geology, and the flow system. Wells are sampled by the VCWPD Groundwater Section (Figure 3 was generated from VCWPD water quality data). Other potential sources of data are: Department of Water Resources, United Water Conservation District (UWCD), Calleguas Municipal Water District (CMWD), and agricultural users. UWCD maintains a comprehensive database that includes selenium data from many of the other potential sources. This database will be obtained and utilized for this study.

The VCWPD Groundwater Section samples wells throughout the county annually in August and September, but only measures selenium in few wells. Selenium data available in the CCW are presented in Figure 3 and Table 1. The highest concentration is measured in a well located in the Revolon Slough subwatershed (Well 10 in Figure 3).

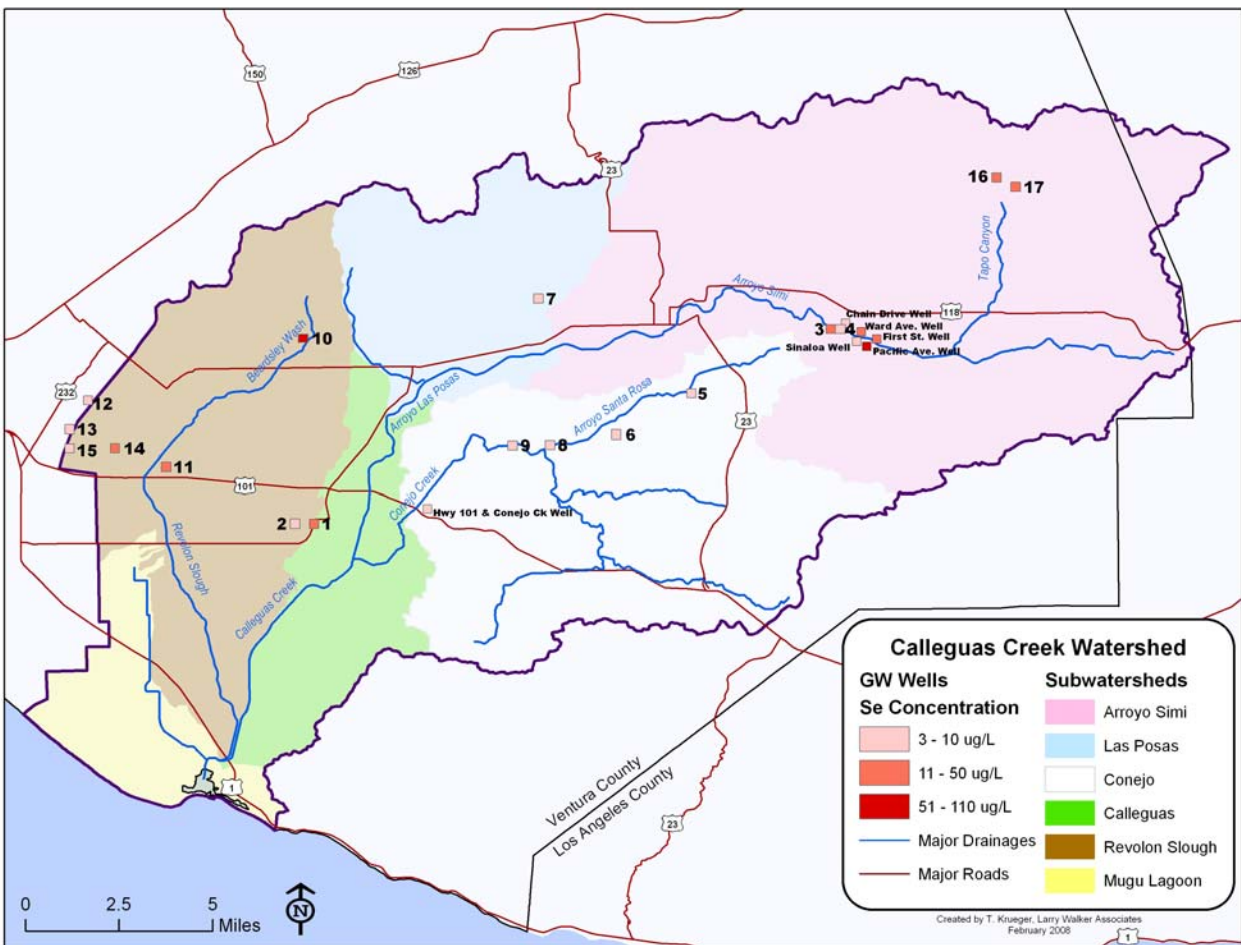


Figure 3. Map of the available selenium data in the CCW. Some of the wells located in the Simi Valley area are dewatering wells presented in the Metals TMDL report (LWA, 2006, p. 79).

**Table 1. Available Selenium Data Measured in the CCW (dewatering wells in Simi Valley are not included).**

Well	Date	Se ug/L
1	4/22/1997	15.0
2	4/22/1997	7.0
3	10/31/1996	12.0
4	2/24/2006	7.0
5	12/21/2005	3.0
6	12/15/2005	4.0
7	11/8/1996	6.0
8	12/21/2005	3.0
9	12/15/2005	8.0
10	10/10/1996	110.0
11	5/26/1998	49.0
12	4/24/1997	5.0
13	10/13/2004	6.0
14	10/10/1996	15.0
15	10/13/2004	5.0
16	1/10/2006	44.0
17	1/10/2006	17.0

Based on Figure 3 and Table 1, most of the wells with high selenium values are located in the Revolon Slough subwatershed.

The California Toxics Rule (CTR) criteria for selenium are shown in Table 2. Only 19% of the available groundwater data from the VCWPD Groundwater Section shown in Table 1 are below the CTR.

**Table 2. California Toxics Rule Water Quality Criteria for Selenium**

Compound	CAS #	Freshwater (ug/L)		Saltwater (ug/L)		Human Health for Consumption of:	
		Criterion Maximum Conc.	Criterion Continuous Conc.	Criterion Maximum Conc.	Criterion Continuous Conc.	Water & Organisms (ug/L)	Organisms Only (ug/L)
Selenium	7782492	---	5.0 c	290 a,b	71 a,b	---	---

a. Criteria for these metals are expressed as a function of the water-effect ratio, WER.

b. These freshwater and saltwater criteria for metals are expressed in terms of the dissolved fraction of the metal in the water column.

c. This criterion is expressed in the total recoverable form.

### TASK 1.3 GATHER INFORMATION ON IRRIGATION

Irrigation has been already introduced as a potential anthropogenic source of selenium. For this reason, in addition to the information gathered above, information on wells used for irrigation,

and how the water is used (i.e. applied in a specific area or distributed to a wide area), will be gathered. Potential sources include the agencies identified in Task 1.2 and the Pleasant Valley Water District. Additionally, a map with the location of irrigation runoff and the relative interaction between runoff and groundwater will be developed if feasible.

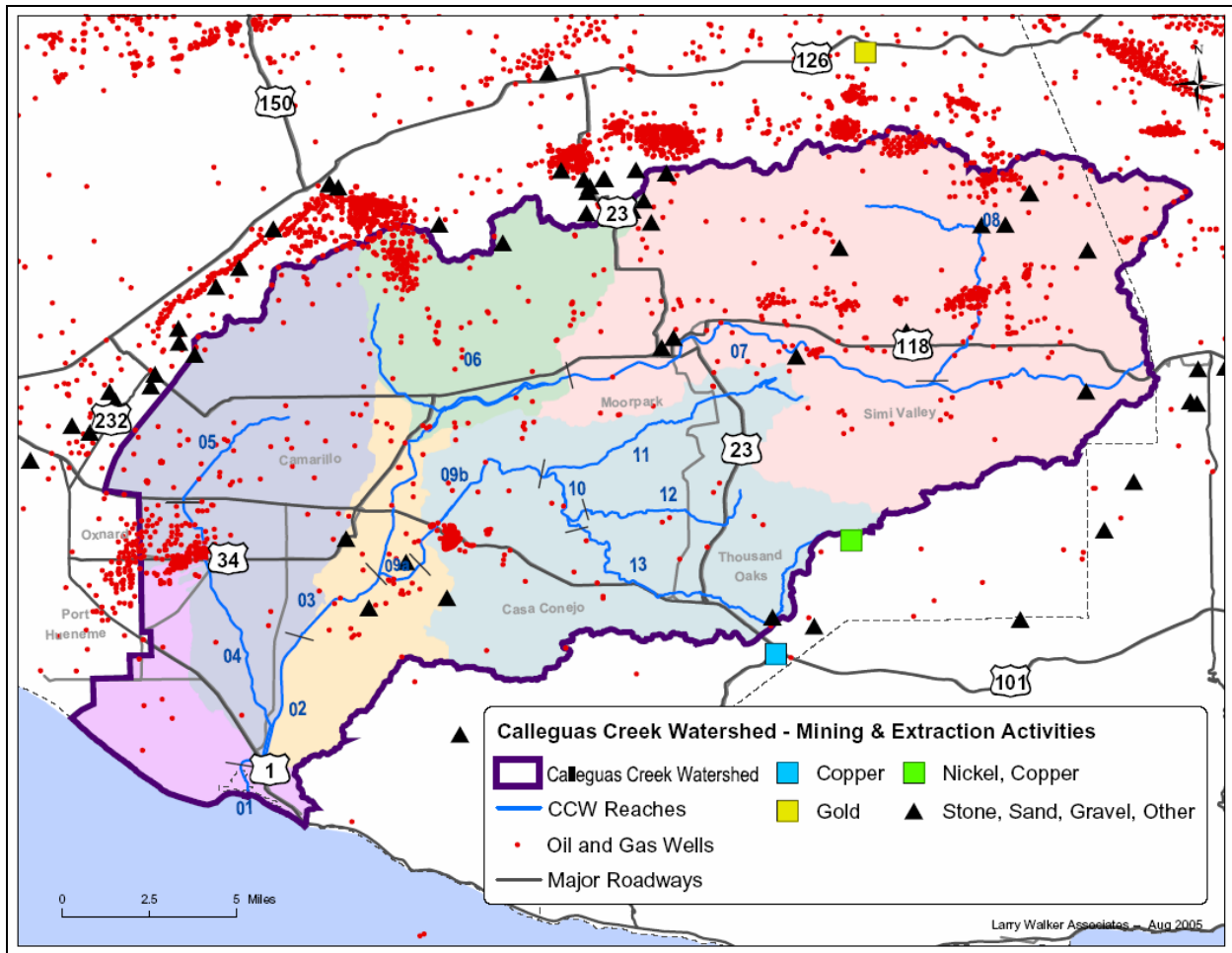
## Task 2: Data Analysis

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### **TASK 2.1 GEOLOGICAL AND HYDROLOGEOLOGICAL ANALYSIS**

The development of a geological and hydrogeological map will be achieved using the information collected in Task 1.1 and from existing documents. The most complete analysis of the groundwater of the CCW is provided by the 2003 USGS Report (Hanson et al., 2003) where the simulation of the groundwater/surface water flow is described for both the Santa Clara and Calleguas basins.

Additionally, the possible influence of mining, oil extraction, and refining will be evaluated in the analysis. The information presented in the Metals and Selenium TMDL (LWA, 2006, p. 107) will be utilized to the extent possible. Figure 4 shows the location of active and inactive mining/extraction sites in the Calleguas Creek Watershed.



**Figure 4. Active and Inactive Mining/Extraction Sites in the CCW (USGS Mineral Resources Data System (MRDS) and California Department of Conservation Division of Oil, Gas, and Geothermal Resources).**

For wells with higher selenium concentrations, an analysis of the land type and use, and the geology of the aquifer (using the information collected in Task 1.1) will be performed. This will allow understanding of whether the high selenium values are confined in layers at certain depths. The different areas will also be characterized by land use (i.e. agricultural, urban, or industrial/commercial areas).

Using the geological and hydrogeological map, and the results obtained in previous studies, areas and types of soils potentially containing high concentrations of selenium will be selected. Additionally, the analysis will identify which groundwater areas have the potential to impact surface waters. These areas will include places where runoff from irrigation wells could reach the surface water and areas where groundwater could seep into the surface waters.

## **TASK 2.2 - EVALUATE SELENIUM AND OTHER WATER QUALITY DATA**

Water quality data collected during Task 1.2 will be evaluated and mapped with the data from Task 2.1 to identify areas of potentially higher groundwater selenium concentrations. The water quality data will also be evaluated, to the extent possible, in comparison to the hydrogeologic data to identify the source of the selenium (i.e. anthropogenic or natural).

## **TASK 2.3 - IDENTIFY DATA GAPS AND PRIORITIZE GROUNDWATER AREAS**

Based on the results of Task 2.1 and 2.2, groundwater wells that have the potential to influence surface water and that have potentially higher selenium concentrations will be identified. Any data gaps for these areas of groundwater will be highlighted.

## **Task 3: Monitoring**

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To address the data gaps identified in Task 2.3, a targeted monitoring program in the Revolon Slough area will be conducted. A monitoring plan will be identified that includes measurements of selenium, iron, manganese, nitrate, dissolved oxygen, sulfate, and/or isotopes of water. Selenium is relatively immobile in anoxic water and very mobile in oxic water. Dissolved oxygen, nitrate, manganese, iron, and sulfate will be measured to help determine whether the water is oxic. Dissolved oxygen can be measured with a probe and does not require laboratory analysis. Furthermore, there may also be a relationship between selenium and dissolved solids or salts in water. This can be determined by measuring the specific conductance of the water with a probe (Clifton and Gilliom, 1989; Gilliom, 1989). A relationship between selenium and dissolved solids may indicate that shallow groundwater is evaporating during infiltration leading to high dissolved solids and selenium. The isotopes of water will be measured because they can show an evaporation trend in waters with high dissolved solids and selenium.

It may be possible to coordinate some of the monitoring with existing groundwater monitoring conducted by the agencies that monitor the wells. To the extent possible, initial monitoring will be coordinated with the existing sampling program to gather selenium data on existing wells throughout the Revolon Slough subwatershed. Additional monitoring will be conducted where possible and as necessary to address the data gaps identified in Task 2.3.

## **Task 4: Identify Priority Areas and Potential Solutions**

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### **TASK 4.1 IDENTIFY PRIORITY AREAS**

After monitoring has been completed, the results of all of the above tasks will be used to identify areas where high concentrations of selenium that can potentially impact surface waters are located. The analysis will identify specific irrigation wells with high selenium concentrations and areas where groundwater may reach surface waters through seepage.

## TASK 4.2 EVALUATE POTENTIAL SOLUTIONS

In previous similar studies conducted in Orange County (Nitrogen and Selenium Management Program, 2005), feasible and cost effective treatment technologies to remove selenium from groundwater were not identified. As a result, the steps to address selenium will most likely involve evaluating the feasibility of using alternative water supplies for irrigation wells with high selenium concentrations. The evaluation of potential solutions will include:

- Availability of alternative water supplies
- Costs of alternative water supplies
- Costs of reducing groundwater discharges.

If the sources of selenium are determined through this study to be primarily natural, alternative regulatory strategies, such as SSOs, may need to be considered to address the selenium concentrations.

## Schedule

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The results of this study will be submitted to the Regional Board within one year of EO approval of the work plan. The following schedule provides an approximate timeframe for completion of each of the work plan tasks.

**Table 3. Estimated Schedule to Complete Tasks**

Task		Timeframe for Completion
Task 1	Data Collection	2 months after EO approval of work plan
Task 2	Data Analysis	4 months after EO approval of work plan
Task 3	Monitoring	TBD based on Task 1 and Task 2 results, but could be up to 6 months after completion of Task 2 (10 months from EO approval of work plan)
Task 4	Identify Priority Areas and Potential Solutions	1 year after EO approval of work plan

## References

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