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CALLEGUAS CREEK WATERSHED MANAGEMENT PLAN

Calleguas Creek Watershed Metals and Selenium TMDL

Special Study #2
Selenium in Groundwater
Work Plan

submitted to:

CALLEGUAS CREEK WATERSHED MANAGEMENT PLAN

prepared by:

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Introduction

The *Total Maximum Daily Load for Metals and Selenium (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. Sources of metals and selenium originate from urban and agricultural runoff, groundwater, and POTW effluent. Additionally, the source analysis indicates that selenium in groundwater may be a significant source. 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 control strategies for selenium discharges with the potential to cause or contribute to exceedances of selenium water quality objectives in receiving waters.
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 for areas that could contribute to discharges of selenium to surface waters in the Revolon Slough subwatershed of the CCW, with a focus on areas where elevated surface water selenium concentrations have been historically observed.
2. Develop a geological and hydrogeological map for these areas based on existing data.
3. Identify data gaps and develop a monitoring program to address gaps for the locations that may contribute selenium to surface waters in concentrations that would cause or contribute to an exceedance of water quality objectives.
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

Selenium is both an essential nutriment and a chemio-toxic trace element for humans, animals and plants, with 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 numerous variables controlling selenium mobility, the redox status of the soil, mainly governed by the soil geochemical features and microbial activities, appears as a major factor.

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 elevated concentrations 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. 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

The 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 the Revolon Slough subwatershed focusing on areas that may contribute groundwater to the surface water.

The data collection effort will be concentrated in areas of the Revolon Slough subwatershed with the following characteristics:

1. May contribute selenium to surface waters through irrigation runoff or groundwater seepage to the receiving water.
2. Where elevated surface water concentrations of selenium have been observed that would indicate contribution from groundwater sources.

Groundwater data from areas of the subwatershed which do not have the potential to discharge selenium to surface waters will not be evaluated as part of this study. Additionally, groundwater data from shallow wells will be obtained where possible to provide information on groundwater seepage to receiving waters.

Data collection for the specified areas will include:

- Map and detailed list of existing wells, including available information on depth, location, groundwater depth, perforation depth, groundwater elevation and gradient

- All the available groundwater quality data, but with special interest for the constituents listed in Task 1.2
- Analysis of soil samples previously collected and information about the subsurface geological formation.

The data collection efforts are described in more details in Task 1.1, 1.2, and 1.3. To obtain the data necessary to complete the following tasks, the following agencies, at a minimum, will be contacted:

- Ventura County
- Department of Water Resources (DWR)
- USGS
- United Water Conservation District (UWCD)
- Calleguas Municipal Water District (CMWD)
- Pleasant Valley Water District

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 in the Santa Clara watershed showed that selenium concentrations were very high in a 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, Ventura County, 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.

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. However, well construction data may not be available for all wells considered in the study. While a reasonable effort will be made to obtain the information, it may not be possible to gather the data for all wells considered in the study.

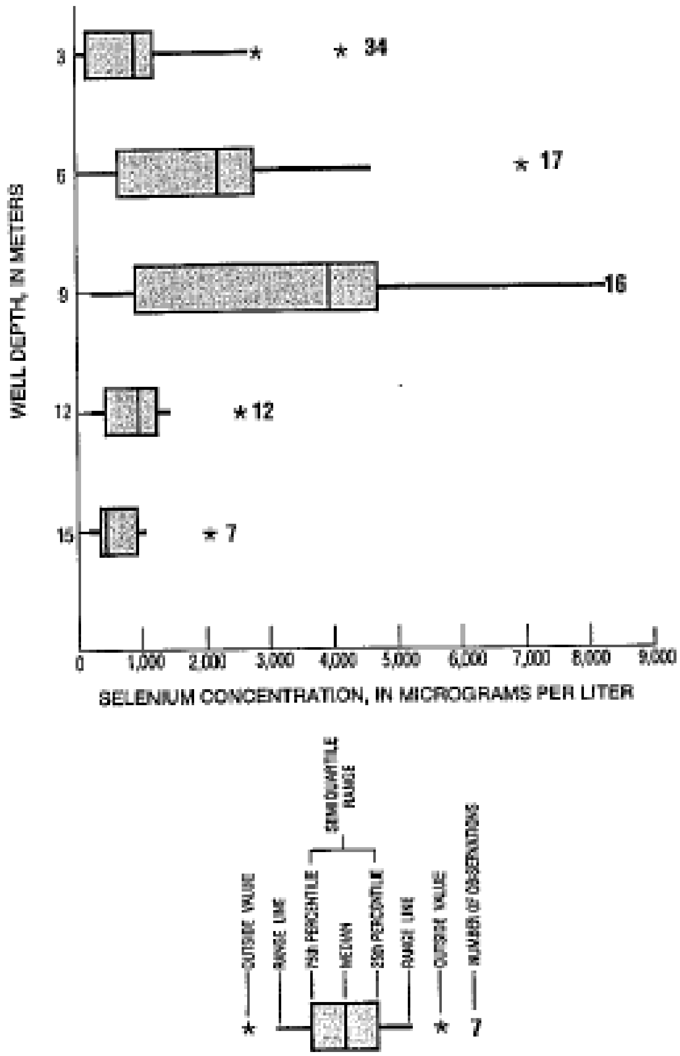

Figure 1 Depth distribution of selenium in samples collected in observations wells in San Joaquin Valley in 1986 and 1987 in the field study by Leighton et al (1992). Outside values are between 1.5 and 3.0 times the semiquartile range from the end of the rectangle. Range lines extend a distance equal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

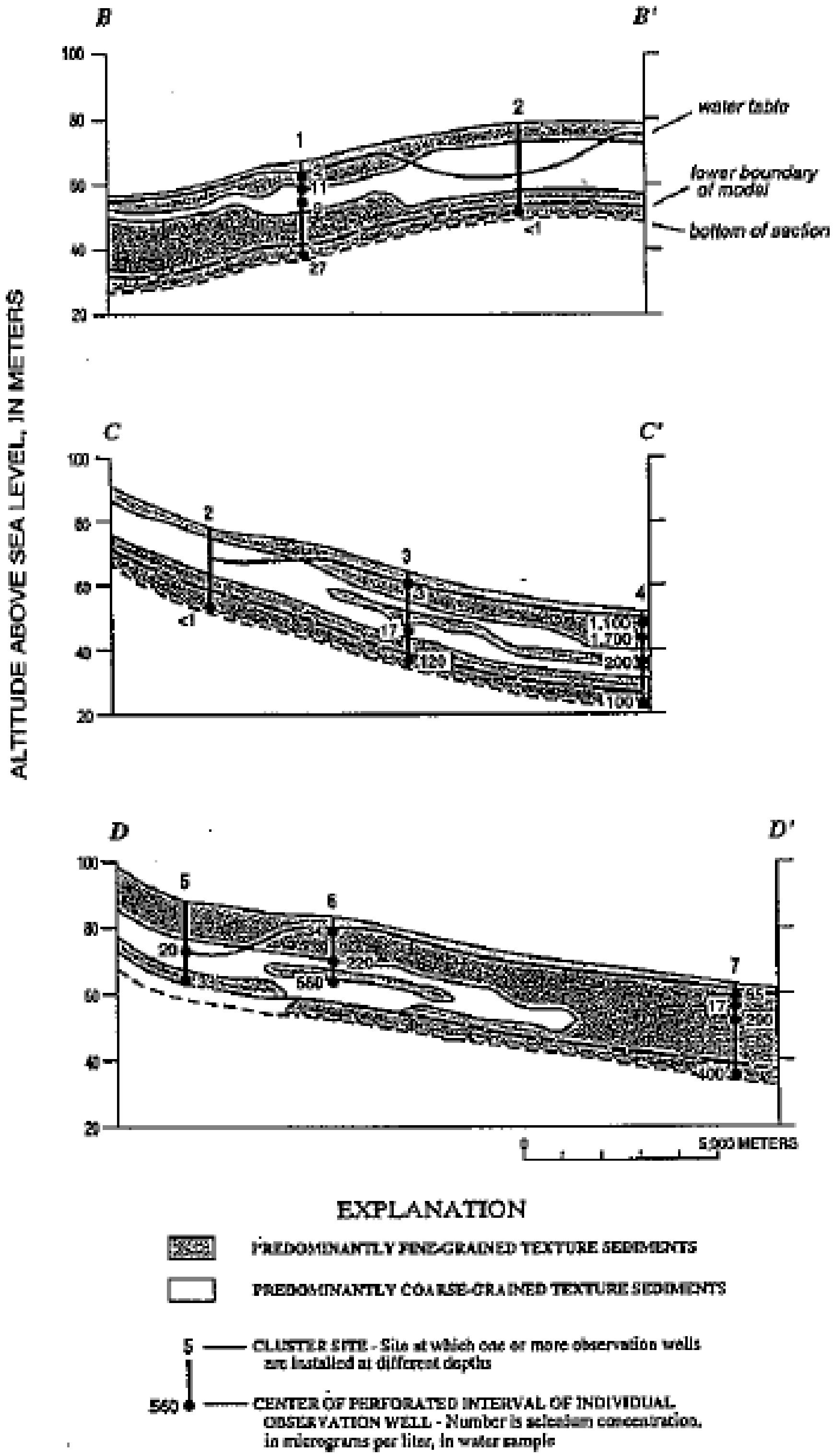

Figure 2 Cross-sectional diagram showing selenium concentrations in observation well samples and texture of deposits (Deverel et al., 1994, p. 177).

TASK 1.2 COLLECTION OF THE AVAILABLE WATER QUALITY DATA

The collection of selenium data will 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.

Currently, Ventura County samples wells in the whole county annually in August and September, but only a small amount of sampled wells include selenium as a measured constituent. 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 other agencies above potentially monitor or collect selenium data within the CCW that may be useful to the study. Data from construction dewatering wells may also be collected where available.

An initial analysis of the CCW selenium data collected by Ventura County is presented in Figure 3 and Table 1. The highest concentration was measured in a well located in the Revolon Slough area.

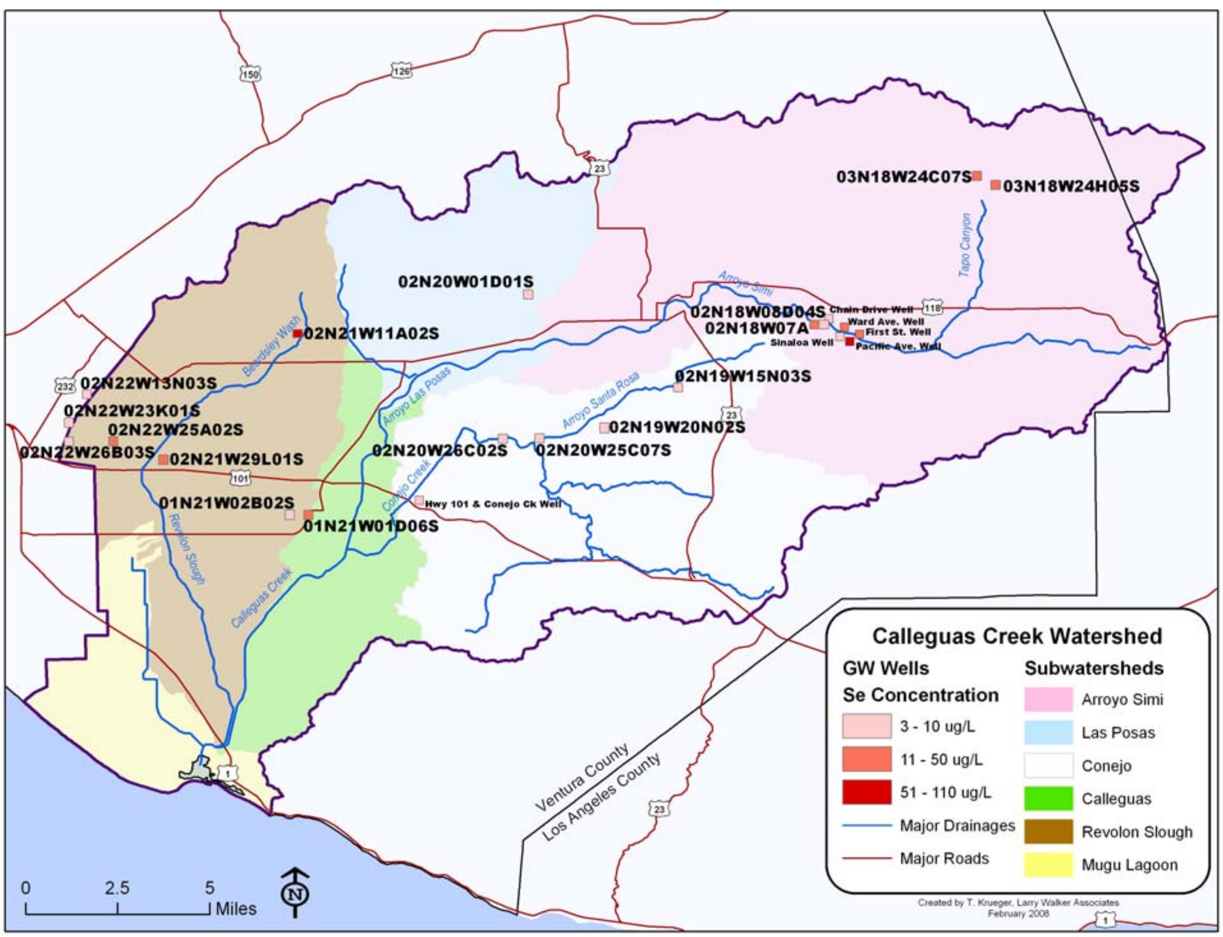

Figure 3 Map of the available selenium data in the Calleguas watershed. The wells located in the Simi Valley area are dewatering wells and they were presented in the Metals TMDL report (LWA, 2006, p. 79).

Table 1. Available selenium data measured in the Calleguas watershed (dewatering wells in Simi Valley are not included).

Well location	Date	Se ug/L
03N18W24H05S	1/10/2006	17.0
03N18W24C07S	1/10/2006	44.0
02N18W08D04S	2/24/2006	7.0
02N18W07A	10/31/1996	12.0
02N19W15N03S	12/21/2005	3.0
02N20W01D01S	11/8/1996	6.0
02N19W20N02S	12/15/2005	4.0
02N20W25C07S	12/21/2005	3.0
02N20W26C02S	12/15/2005	8.0
02N21W11A02S	10/10/1996	110.0
01N21W01D06S	4/22/1997	15.0
01N21W02B02S	4/22/1997	7.0
02N21W29L01S	5/26/1998	49.0
02N22W26B03S	10/13/2004	5.0
02N22W25A02S	10/10/1996	15.0
02N22W23K01S	10/13/2004	6.0
02N22W13N03S	4/24/1997	5.0

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

The California Toxics Rule (CTR) criteria for selenium are shown in Table 2. Only 26% of the available groundwater data from Ventura County are below the CTR (including the wells in Table 1 and the Simi Valley dewatering wells presented in the Metals and Selenium TMDL).

Table 2. California Toxics Rule Water Quality Criteria for Listed Metals and 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 is a potential anthropogenic source of selenium. For this reason, in addition to the information gathered above, information on which wells are 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. Furthermore, a map with the location of drainage and the relative interaction between drainage and groundwater will be developed if feasible.

Task 2: Data Analysis

TASK 2.1 GEOLOGICAL AND HYDROLOGEOLOGICAL ANALYSIS

A geological and hydrogeological map for the Revolon Slough subwatershed will be developed using the information collected in Task 1.1 and from existing documents. The most complete analysis of the groundwater of the Calleguas watershed 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.

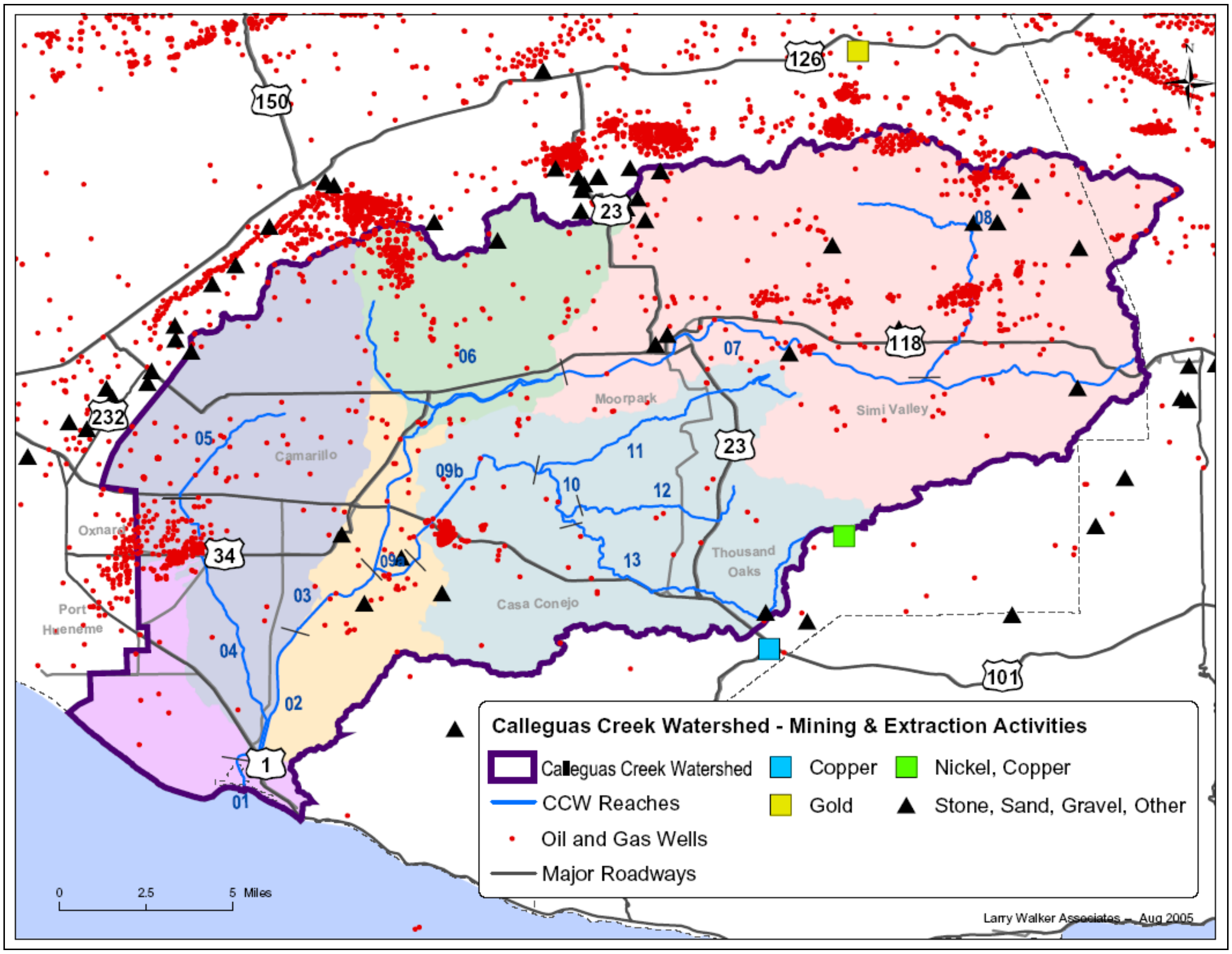

Figure 4. Active and Inactive Mining/Extraction Sites in the Calleguas Creek Watershed (USGS Mineral Resources Data System (MRDS) and California Department of Conservation Division of Oil, Gas, and Geothermal Resources).

For wells with higher selenium concentrations, an analysis of the land type and use and of 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 which have the potential to impact surface waters will be identified. These areas will include locations 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 (HCAs) that could impact surface waters and to evaluate background 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).

HCAs will be characterized as wells/areas with selenium concentrations exceeding the 95th percentile of selenium concentrations measured in the collected groundwater data that have the potential to contribute to surface water exceedances (either through groundwater seepage or irrigation discharges). Sites with concentrations below appropriate TMDL targets and allocations or those sites with no connection to surface water (either through pumping discharges or groundwater seepage) will not be considered as HCAs. Sites with selenium concentrations between the numeric TMDL targets and the 95th percentile that have the potential to discharge to surface waters will not be considered HCAs, however as they may have the potential to contribute to exceedances of the TMDL numeric target they will be addressed, as necessary, to meet the TMDL allocations. Identified HCAs, and sites with concentrations between the numeric target and the 95th percentile of the data will be carried through the remaining steps of the analysis in this workplan, but sites below the numeric targets will receive no additional analysis in the study.

TASK 2.3 - IDENTIFY DATA GAPS AND PREPARE MONITORING PLAN

Based on the results of Task 2.1 and 2.2, gaps in the existing data will be identified and types and locations of additional monitoring requirements will be determined. Based on the results of this analysis, a monitoring plan will be developed to address the identified data gaps. The proposed monitoring plan, along with a status report summarizing the data collected during the first two tasks, the evaluation of the data, and the conclusions, will be submitted to the RWQCB for review and discussion. Additional monitoring will utilize existing well locations and be coordinated with existing monitoring programs to the extent possible.

Task 3: Monitoring

Once the results of Task 2 have been discussed with RWQCB staff, a targeted monitoring program in the Revolon Slough area may be conducted to address the data gaps identified in Task 2.3 per the proposed monitoring plan.

The proposed monitoring plan will include a number of constituents other than selenium to help in the prioritization of HCAs and identification of control strategies. Selenium is relatively immobile in anoxic water and very mobile in oxic water. Thus dissolved oxygen, nitrate, manganese, iron, and sulfate can be used to tell whether the water is oxic or not. Furthermore, dissolved oxygen can be measured with a field probe and does not require offsite laboratory analysis. Based on the high values of selenium, the water will likely be oxic, hence there may also be a relationship between selenium and dissolved solids or salts in water. This can be easily figured out by measuring the specific conductance (SC) of the water with an SC probe. If there is a relationship between selenium and dissolved solids, then it could be that shallow ground water is evaporating during infiltration leading to high dissolved solids and selenium. The isotopes of water will show an evaporation trend in waters with high dissolved solids and selenium.

Based on information gathered from previous studies conducted in the area and on the analysis of the geology typical of the Monterey formation which underlies part of the interested area (B. Hibbs, 2009[1], Nitrogen and Selenium Management Program, NSMP, developed for Orange County[2]), monitoring of phosphorous and phosphate will also be included.

The proposed list of the water quality parameters and analytical methods are presented in Table 3. Additional constituents may be identified during Task 2 and will be included in the proposed monitoring plan.

Table 3. Water Quality Parameters and Analytical Methods

Parameters	Analytic Method	Reporting Limit
Iron (total)	SM 3111B	0.1 mg/L
Manganese	SM 3111B	0.05 mg/L
Dissolved oxygen	SM 4500-0	-
Sulfate	EPA 300.0	1 mg/L
Chloride	EPA 300.0	3 mg/L
Electrical conductivity	SM 2510	-
Total dissolved solids	SM 2540 D	3 mg/L
Nitrate	EPA 300.0	0.6 mg/L
Nitrite	EPA 300.0	0.4 mg/L
Nitrate+Nitrite	EPA 353.2	0.1 mg/L
Total nitrogen	SM 4500-N	
Total inorganic nitrogen	SM 4500	
Total Phosphorous	SM 4500-P	0.01 mg/L
Phosphate	SM 4500-P	0.01 mg/L
Isotopes of water		
Total recoverable Selenium	EPA 6010 [a]	
Dissolved Selenium	200.8	

[a] Selenium speciation analysis may be included in the proposed monitoring plan if it will assist in the prioritization of areas or identification of control strategies. However, no standard method exists for the speciation of selenium at this time and appropriate methods will be evaluated at the time of monitoring plan development.

In addition to the constituent and method identification, the proposed monitoring plan will include:

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[1] Hibbs, B., Merino, M., Andrus, R., Hu, W., Doro-on, A., Groundwater baseflow sourced from Miocene Rocks and Residuals carries elevated selenium into Southern California Streams, World Environmental and Water Resources Congress, 2009: Great Rivers.

[2] NSMP, A Comparison of Methods for Measuring Total Selenium and Selenium Species in Water, April 2006.

1. Sampling frequency
2. Criteria used for sampling site/well selection
3. Descriptions and maps of sampling locations

It may be possible to coordinate some of the monitoring with existing groundwater monitoring conducted by the agencies that monitor the wells. Monitoring will be coordinated with existing sampling programs to gather selenium data from existing wells throughout the Revolon Slough area that also address the data gaps identified in Task 2.3.

Task 4: Identify Priority Areas and Potential Solutions

TASK 4.1 IDENTIFY PRIORITY AREAS

After the monitoring has been completed, the results of all of the above tasks will be used to identify areas where high concentrations of selenium can potentially impact surface waters using the criteria identified in Task 2.2. The analysis will prioritize these areas for evaluation of potential solutions based on the potential of the area to cause or contribute to an exceedance of the TMDL or load allocation in the Revolon Slough subwatershed.

TASK 4.2 EVALUATE POTENTIAL SOLUTIONS

Task 4.2 will consist of investigating actions to be taken for the identified priority areas. These actions may include options to reduce discharges of selenium through source control or treatment BMPs, minimize use of groundwater with high selenium concentration for irrigation, or evaluation of regulatory options to address background loads. Each of these options is discussed in more detail below.

As a first step, potential source control or other best management practices that can be employed to reduce discharges of high selenium groundwater to impaired surface waters will be evaluated. Strategies to be considered include methods of reducing runoff from irrigated agriculture as outlined in the Ventura County Irrigated Lands Group (VCAILG) Water Quality Management Plan (WQMP). Methods identified in the WQMP will be evaluated first for addressing HCAs prior to consideration of the other options outlined below.

Should source control strategies not address the identified sources, the feasibility of minimizing the use of groundwater with high selenium concentrations for irrigation in areas where the discharge could reach receiving waters in the Revolon Slough subwatershed will be considered. To evaluate the feasibility of using alternative water supplies for irrigation wells with high selenium concentrations for identified HCAs, the following factors will be utilized:

- Availability of alternative water supplies and feasibility of obtaining alternative water supplies at the site and over the long term (given potentially reduced water availability over time).
- Costs of alternative water supplies and impacts of the cost difference on agricultural operations.

- Costs of reducing discharges of irrigation water through other means.

The costs and long-term viability of alternative water sources for irrigation may preclude the ability of dischargers to utilize this option to address selenium discharges to receiving waters.

Potential treatment control Best Management Practices will also be evaluated if necessary. 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. However the Nitrogen Selenium Management Program (NSMP) Best Management Practice (BMP) Strategic Plan is currently in the process of evaluating potential structural control technologies for selenium. The results of the NSMP BMP pilot-testing program will be utilized to determine if feasible and cost effective treatment technologies can be employed in the CCW to address prioritized HCAs.

The following six BMPs were selected as part of the pilot testing for the NSMP Plan:

- Reverse Osmosis (RO)
- Anaerobic Bacterial Removal (ABMet®/GE)
- Katchall Systems Heavy Metals Removal (HMR) Media
- Ferrous Hydroxide Iron Treatment (Kemira/ORCA)
- Constructed Wetlands (Portable Wetlands System)
- Adsorption Media (MES)

These six technologies were tested for their potential to remove nitrate and selenium to 5 milligrams per liter (ppm) and 5 micrograms per liter (µg/L), respectively, using water from Warner Channel. Five treatment technologies were recommended for testing from the *BMP Selection and Pilot-Scale Testing Considerations Interim Report, November 2006.* The Adsorption Media (MES) was added to the pilot test as a promising technology for removal of nitrogen and selenium in a portable format. Currently, treatment BMPs appear to be more feasible on a regional scale and treatment of individual wells or small areas would be economically and technically challenging.

If the sources of selenium are determined through this study to be primarily ambient background loads (as highlighted in the Metals and Selenium TMDL, 2006), alternative regulatory strategies, such as SSOs, may need to be considered to address the selenium concentrations. As defined in the Metals and Selenium TMDL, ambient sources are environmental sources of metals and selenium in the watershed, such as natural soil concentrations, specific geological formations known to exhibit high selenium concentrations, atmospheric deposition, and natural groundwater seepage, and background load is defined as discharges from undeveloped open space due to ambient sources and/or natural groundwater seepage (agricultural and urban ambient sources not included). Best management practices to address ambient background loads will not be identified through this study.

Schedule

The results of this study will be submitted to the Regional Board within 1 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 4. 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	3 months after EO approval of work plan
Task 3	Monitoring	Within six months of EO approval of work plan (pending discussions with RWQCB staff on proposed monitoring plan)
Task 4	Identify Priority Areas and Potential Solutions	1 year after EO approval of work plan

References

Deverel, S.J., Fio, J.L., Dubrovsky, N.M., 1994, Distribution and Mobility of Selenium in Groundwater in the Western San Joaquin Valley of California, pp. 157-183, in Selenium in Groundwater, ed. by Frankenberger, J.R., and S. Benson.

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Orange County, 2005, Nitrogen and Selenium Management Plan, Work Plan and Compliance Strategy.