

May 17, 2013

**VIA ELECTRONIC MAIL AND FEDERAL EXPRESS**

Ms. Dyan Whyte  
Assistant Executive Officer  
California Regional Water Quality Control Board  
San Francisco Bay Region  
1515 Clay Street, Suite 1400  
Oakland, California 94612

Re: *Submittal of Selenium Impact Assessment Study Work Plan – January 22, 2013 Water Code section 13267 Order, Order No. R2-2013-1005, Directive 9*

Dear Ms. Whyte:

Enclosed, pursuant to the Regional Water Quality Control Board, San Francisco Bay Region's, ("Regional Water Board") January 22, 2013 Water Code section 13267 Order, Order No. R2-2013-1005, ("Order"), as modified per the parties' discussions, Lehigh Southwest Cement Company ("Lehigh") timely encloses the requested Selenium Impact Assessment Study Work Plan, prepared for Lehigh by Robertson-Bryan, Inc., in accordance with Directive 9 of the Order. If you or your staff have any questions regarding the enclosed Work Plan, or would like to discuss further, please do not hesitate to contact me or Mike Bryan and Ben Giudice of RBI.

Very truly yours,

*Nicole E. Granquist*

Nicole E. Granquist

Enclosure

Cc: Brian Thompson, Regional Water Quality Control Board, San Francisco Bay Region  
Ellen Howard, Counsel, State Water Resources Control Board  
Greg Knapp, Director Environmental Region West, Lehigh  
Dr. Michael Bryan, Robertson-Bryan, Inc.  
Dr. Ben D. Giudice, Robertson-Bryan, Inc.

# PERMANENTE QUARRY AND CEMENT PLANT SELENIUM IMPACT ASSESSMENT STUDY WORK PLAN

*Prepared for:*

REGIONAL WATER QUALITY CONTROL BOARD, SAN FRANCISCO  
BAY REGION

*On Behalf of:*

LEHIGH SOUTHWEST CEMENT COMPANY

*Prepared by:*



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# 1 Introduction

The Lehigh Southwest Cement Company (Lehigh) operates the Permanente Quarry and Cement Plant (Permanente Facility) within the drainage of Permanente Creek in southwestern Santa Clara County, California. Discharges to Permanente Creek are currently regulated by a general National Pollutant Discharge Elimination System (NPDES) permit for sand and gravel operations (San Francisco Bay Regional Water Quality Control Board (“SFBRWQCB”) Order R2-2008-0011; NPDES general permit number CAG982001) and a general NPDES permit for stormwater discharges associated with an industrial activity (State Water Resources Control Board (“SWRCB”) Order No. 97-03-DWQ). The plant has several discharges of water into the creek, including quarry dewatering, industrial stormwater, and process water. Discharges from the quarry pit dewatering have a long term average flow rate of 1000 gallons per minute (gpm), or 2.2 cubic feet per second (cfs), and can be as high as 2000 gpm during the wet season (SFBRWQCB 2013). In the dry season (May-November), Permanente Creek just upstream of the quarry discharge can be dry, and thus, the discharge can make up all or a significant portion of the streamflow at the downstream end of Lehigh property. The quarry receives groundwater and stormwater inflows which are currently filtered for sediment, allowed to further settle out in a detention pond, and discharged to the creek.

In 2006, Permanente Creek was added to the State’s 303(d) list as impaired by selenium. Permanente Creek is listed as impaired for selenium because observed water column concentrations in the creek were above the applicable California Toxics Rule (CTR) water quality objective (WQO) for total selenium for the chronic protection of freshwater aquatic life (5 micrograms/liter ( $\mu\text{g/L}$ )). The 303(d) listing was based on data collected by the Water Board’s Surface Water Ambient Monitoring Program (SWAMP) in 2002/2003 at an upper reach location of the Creek (PER070, which is the East Fork of Permanente Creek at Rancho San Antonio). Reported total selenium concentrations at this location were all above the chronic WQO of 5  $\mu\text{g/L}$  (5.8  $\mu\text{g/L}$ , 10.3  $\mu\text{g/L}$ , and 18.7  $\mu\text{g/L}$ ) (SFBRWQCB 2007, 2013).

Lehigh has applied for an individual NPDES permit and is anticipating effluent limits for selenium based on the WQO of 5  $\mu\text{g/L}$ . Although Lehigh cannot currently comply with these limits, treatment for selenium, among other constituents, in the discharge is currently being designed, and it is anticipated that the majority of water discharged from the quarry will comply with anticipated limits beginning in 2014, and all water discharged from the site will comply within several additional years.

Available water quality data suggest a selenium concentration gradient along the Creek that is higher near the Permanente Facility and decreases downstream. Selenium is present in the limestone used for cement manufacture. Quarrying of the limestone exposes the selenium to oxygen, leading to oxidation into soluble forms. Selenium is contained in quarry discharge water at levels greater than water quality criteria applicable to Permanente Creek.

## 2 Study Objectives

Findings Section C and Directive 9 of the Water Code section 13267 Order require that Lehigh conduct a Selenium Impact Assessment (“Study”). The findings section reads:

*“More information about selenium concentrations in Permanente Creek is needed in order for the Water Board to fulfill its regulatory requirements. Selenium that is discharged by the Permanente Facility into Permanente Creek is likely transported downstream where, through interaction with sediment and plants, transformation, deposition, uptake, and bio-accumulation of different elemental species of selenium may all occur. This process could result in significant impacts to the beneficial uses of Permanente Creek. Therefore it is important for the Discharger to submit a Selenium Impairment Assessment Study so the potential impacts to beneficial uses are better understood. Any proposed study should include water bodies that are influenced by the discharge, including reaches of Permanente Creek adjacent to the Permanente Facility and reaches of Permanente Creek and Stevens Creek downstream of the Permanente Facility and the Discharger’s quarry discharge zone.” (SFBRWQCB 2013)*

The objectives of this Study are to: (1) evaluate potential impacts to beneficial uses of elevated selenium levels, and (2) develop the information needed for the Regional Water Board to fulfill its regulatory requirements.

It should be noted that for a study of this magnitude and complication, the timeframe allotted for work plan development, refinement per coordination with the SFBRWQCB, and sampling mobilization prior to the first sampling event is remarkably short. Thus, issues are expected to be encountered that could not be foreseen or resolved prior to the submittal of this work plan. As described later, issues encountered in the sampling or analysis, deviations from the work plan, and actions taken or proposed to be taken to resolve these issues will be included in reporting required as part of the Study.

## 3 Study Area

Downstream of the Lehigh property, Permanente Creek enters an urban area and travels through significant physical alterations. Permanente Creek is diverted via the Permanente Creek Diversion Channel to Stevens Creek approximately 4 miles upstream of the creek mouth at San Francisco Bay. During the wet season (October-April) all of the flow is diverted (except in rare cases of extremely high flooding) into Stevens Creek, where it continues north and enters South San Francisco Bay via Whisman Slough. During the dry season, water can flow in Permanente Creek downstream of the diversion channel, but the channel still generally dries out prior to the confluence of Hale Creek downstream. Permanente Creek eventually enters the southern end of San Francisco Bay via Mountain View Slough. The Regional Water Board has designated beneficial uses to these water bodies listed in Table 1.

The study area includes Permanente Creek upstream of the Permanente Facility, on the facility site, and downstream of the facility to Mountain View Slough; the Permanente Diversion

Channel; and Stevens Creek downstream of the Permanente Diversion Channel to Whisman Slough. A map of the study area is shown in Figure 1.

Table 1. Beneficial Uses of Permanente Creek, Stevens Creek, Mountain View Slough, and South San Francisco Bay. <sup>a</sup>

Water Body	Beneficial Uses
Permanente Creek	GWR, REC-1, REC-2, WILD, COLD, SPWN, WARM, RARE
Stevens Creek <sup>b</sup>	FRSH, GWR, REC-1, REC-2, WILD, COLD, MIGR, SPWN, WARM, RARE
Mountain View Slough	REC-1, REC-2, WILD, EST, RARE
South San Francisco Bay	IND, REC-1, REC-2, WILD, NAV, SHELL, COMM, MIGR, SPWN, EST, RARE

SOURCE = SFBRWQCB 2011

<sup>a</sup> GWR=Groundwater Recharge, REC-1=Water Contact Recreation, REC-2=Non-contact Water Recreation, WILD=Wildlife Habitat, COLD=Cold Freshwater Habitat, SPWN=Fish Spawning, WARM=Warm Freshwater Habitat, RARE=Preservation of Rare and Endangered Species, EST=Estuarine Habitat, IND=Industrial Service Supply, NAV=Navigation, SHELL=Shellfish Harvesting, COMM=Commercial, and Sport Fishing, MIGR=Fish Migration

<sup>b</sup> Whisman Slough, located where Stevens Creek empties into South San Francisco Bay, is not a named water body in the Region 2 Basin Plan.

#### 4 Assessment of Potential Impacts to Aquatic Life and Wildlife Beneficial Uses

Selenium is a trace element that is essential for organism nutrition that occurs naturally in the environment. In the San Francisco Bay watershed, selenium is enriched in marine sedimentary rocks of the Coast Ranges on the western side of the San Joaquin Valley (Presser and Piper 1998). Sources of selenium also include agricultural drainage, refinery discharge, and naturally occurring groundwater. Selenium occurs in three primary forms in surface waters: selenite [ $\text{SeO}_3^{2-}$  or Se(IV)], selenate [ $\text{SeO}_4^{2-}$  or Se(VI)], and organoselenide (*e.g.*, selenomethionine, Se(II)). Selenium is bioaccumulative, and is of greatest concern because it can cause chronic toxicity in fish and birds (Ohlendorf 2003; San Francisco Bay Regional Water Quality Control Board 2009). Effects can include reproductive and development effects leading to reduced species viability.

The concentration of selenium in a water body at which toxicity occurs in fish and birds is dependent on site-specific factors related to bioaccumulation and toxicity. In essence, toxicity is dependent on the selenium concentration in the water, factors affecting bioaccumulation in the food chain, and the tissue levels of selenium at which toxicity occurs. Critical factors affecting bioaccumulation in the food chain are: (1) the speciation of selenium, and therefore the distribution coefficient,  $K_d$ , which is defined as the ratio of the particulate-bound selenium concentration to the dissolved concentration, and (2) the local food-web, since certain species bioaccumulate selenium to a greater or lesser degree. Factors affecting the tissue levels at which selenium toxicity occurs include: (1) other water quality constituents, for example, sulfate, which reduces selenium toxicity at high levels, and (2) the specific species present, since some species are more sensitive to selenium toxicity than others.

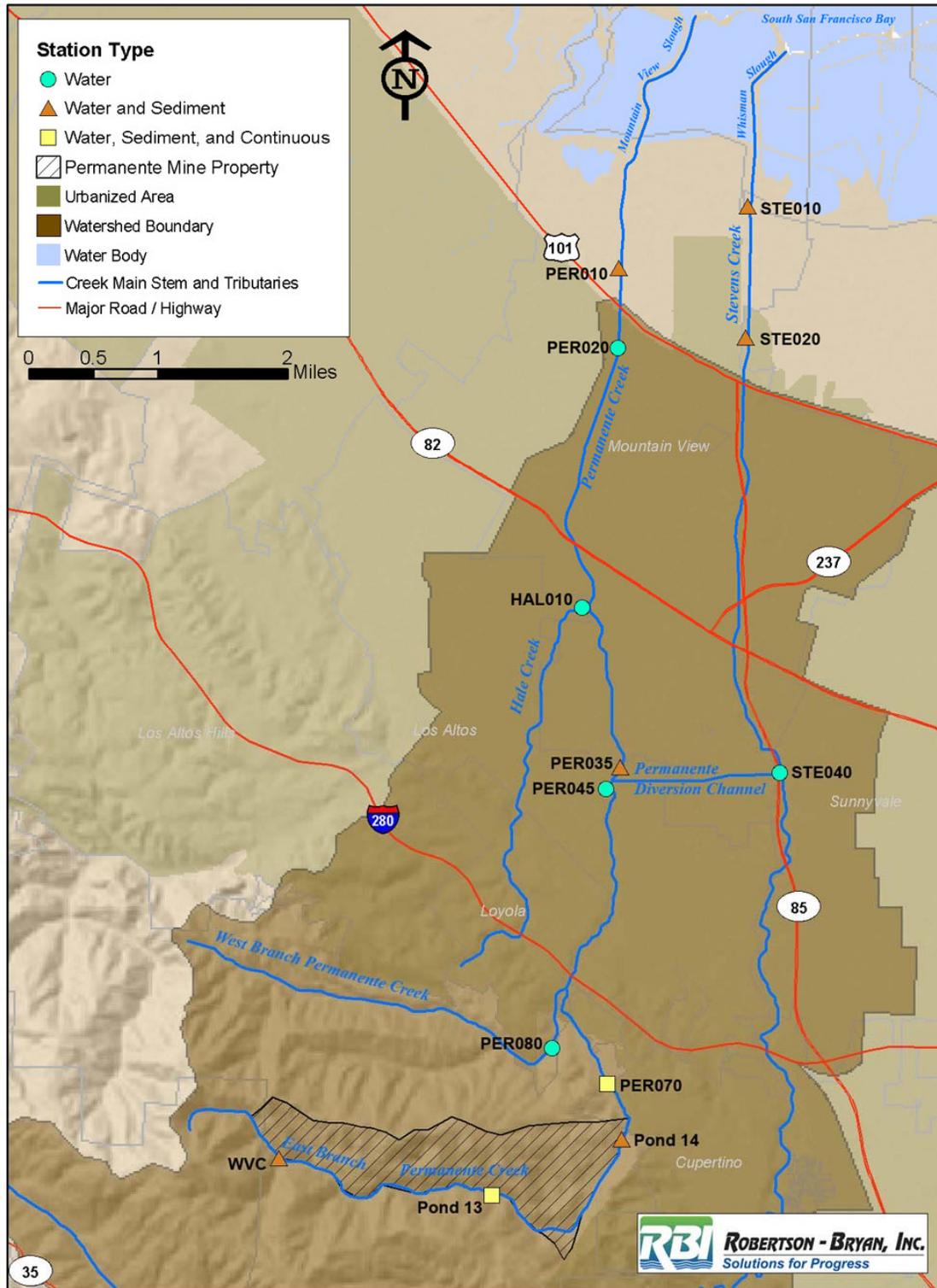


Figure 1. Study area showing locations of the Permanente Facility and sampling locations on Permanente, Hale, and Stevens Creek. Constituent categories (water, sediment, continuous) are defined in Table 5.

The most appropriate approach to assessing potential impacts on aquatic life beneficial uses is to use the Presser and Luoma model, which is the basis of USGS modeling in San Francisco Bay (Presser and Luoma 2006; 2010a) and San Diego Creek/Newport Bay site-specific objectives (“SSO”) (Presser and Luoma 2009), and which will likely be integral to upcoming efforts to set a state wildlife criterion. Based on data collected as part of the Study, the model will be applied to assess risk to aquatic life and wildlife at different sites and for different seasons under current selenium concentrations. The model will also be used to estimate tissue levels under the proposed, treated selenium discharge concentrations, which are substantially lower than current levels. Conceptual components of the model, areas of the creek assessed, and environmental endpoints are described in the sections below.

#### 4.1 Conceptual Model

The conceptual model is based on speciation and partitioning of selenium to particles (*e.g.*, bed sediment, suspended sediment, plankton, algae), uptake by invertebrates, and uptake by fish and birds. To model partitioning of selenium from the water phase to the particulate phase, a distribution coefficient  $K_d$  is used. To model uptake of selenium from the particulate phase into invertebrates and fish, a trophic transfer factor (TTF) is used. Therefore, the model requires information on selenium concentrations in water, the site-specific distribution coefficient  $K_d$ , and the local food web (and TTFs, either literature-based or site-specific, if available). Outputs from the model are tissue concentrations in invertebrates, fish, and bird eggs that can then be compared against scientific literature values for these that are considered protective. Elements of the model and how they will be applied in this study are described in further detail in the sections below.

#### 4.2 Assessment Areas

Selenium exposure and risk in Permanente Creek and Stevens Creek downstream of the diversion channel fall into four logical categories based on differences in habitat, food chain, and selenium concentrations. These assessment areas are shown in Table 2. By breaking the assessment into different areas, a distinction is made between Mountain View Slough/Whisman Slough/South San Francisco Bay and areas of Permanente Creek and Stevens Creek. Mountain View Slough/Whisman Slough/South San Francisco Bay have higher food chain risk because of high habitat value and an abundance of fish and birds, but low selenium concentration due to dilution and attenuation. Areas of Permanente Creek and Stevens Creek have higher selenium concentrations, but more limited food chain availability due to limited habitat value.

Table 2. Assessment areas, associated habitat types, wildlife receptors, and selenium concentrations.

Assessment Area	Habitat Type	Receptors	Selenium Concentrations <sup>a</sup>
Permanente Creek, upstream of Permanente facility	Riparian	Fish, waterfowl	Medium (4-7 µg/L)
Permanente Creek, on the Permanente facility	Riparian, channelized, portions lined, open ponds	Fish, waterfowl	High (10-75 µg/L)
Permanente Creek and Stevens Creek, downstream of Permanente facility	Channelized, some riparian, concrete channels, intermittent water	Limited birds and fish	High (10-40 µg/L)
Mountain View Slough, Whisman Slough, and South San Francisco Bay	Open water, tidal, estuarine	Shorebirds, waterfowl, fish	Low (< 4 µg/L)

<sup>a</sup> – Based on data from SFBRWQCB 2007; Golder 2011; Lehigh 2011, 2012.

### 4.3 Distribution Coefficient

The distribution coefficient,  $K_d$ , is defined as the instantaneous ratio of the particulate-bound selenium concentration to the dissolved concentration, as

$$K_d = \frac{[Se]_{part} \left( \frac{\mu g}{kg} \right)}{[Se]_{diss} \left( \frac{\mu g}{L} \right)}$$

where  $[Se]_{part}$  is the particulate selenium concentration, and  $[Se]_{diss}$  is the dissolved selenium concentration.  $K_d$  values in the literature vary from 100 to over 40,000. Bays and estuaries tend to have  $K_d$  values of greater than 1000, and commonly greater than 10,000 (Presser and Luoma 2010b). Most rivers and creeks show  $K_d$  values between 100 and 300.

Speciation of selenium in the water affects phase distribution and, therefore,  $K_d$ . In some cases, speciation in the water can be used to model or predict phase transformation and distribution (*e.g.*, Meseck and Cutter 2006), but even these models at least partially rely on empirical observations of partitioning between dissolved and particulate selenium (Presser and Luoma 2010). Therefore, although speciation in the water is helpful in understanding and interpreting particulate concentrations and associated  $K_d$ s, there is no direct use for speciation data in the model.

Particle type can also affect  $K_d$ . For example, studies have shown variability in the concentrations in fine grained (<100 µm) surficial sediment, biofilm, benthic or suspended algae, detritus. In this study,  $[Se]_{part}$  will be measured in two ways: direct measurement of total selenium in the surficial bed sediment, and calculation of total selenium associated with suspended particulates (see section 7.1 for more information). These two concentrations will be averaged to define  $K_d$  at each site, in order to better take into account partitioning in different

media and best represent dynamic conditions, per the recommendation in Presser and Luoma 2010<sup>1</sup>. Interpretation of sediment concentrations will take into consideration the grain size distribution (*i.e.*, what fraction of the sediment samples are <100  $\mu\text{m}$ ), since sandy sediments can dilute concentrations with a high mass of inorganic material and may yield  $K_{ds}$  that are anomalously low.

#### 4.4 Trophic Transfer Factors and Model Food Webs

Trophic transfer factors (TTFs) define the relationship between concentrations in an animal and its food. An experimentally derived TTF accounts for assimilation efficiency from ingested particles, ingestion rate of particles, efflux rates, and growth rates. TTFs can be experimentally derived for site-specific conditions, but have been derived for many species in the literature. Literature values found in Presser and Luoma 2010b will be used in this study.

Defining the local food webs is vitally important in predicting tissue concentrations in fish and birds, owing to the large variability in TTFs among invertebrates. Although extensive biological surveys have not been conducted in Permanente Creek for this purpose, some data are available. The best information that could be found regarding species present in the assessment areas is provided in Table 3. Based on the information in Table 3, the most likely food web pathways for selenium exposure in fish and birds in the assessment areas will be derived and used in combination with literature values of TTF to estimate tissue concentrations in invertebrates, fish, and/or birds.

#### 4.5 Protective Dietary or Tissue Concentrations

There is currently no consensus among toxicologists on a value for dietary or bioaccumulated selenium concentrations that is protective of all species. Values determined by different toxicologists can vary based on:

- Degree of acceptable toxicity ( $EC_{10}$  vs.  $EC_{50}$ ),
- What species to protect (most sensitive or average species),
- Choice of life stage and endpoint,
- Whether to consider risk to individuals or risk to populations, and
- Whether to accept field studies or base risk levels purely upon well constrained toxicity tests.

In documentation supporting the San Diego Creek SSO, a good summary of the available literature and risk thresholds is provided, and four risk categories are defined based on diet and tissue guidelines. These categories are summarized in Table 4.

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<sup>1</sup> If the large majority of the total selenium concentration in the water column is made up of the dissolved selenium concentration, calculation of suspended particulate selenium may be biased by imprecision in the analytical method. That is, the method may not be able to reliably differentiate between two water samples with very similar selenium concentrations. If this is determined to be the case, values of  $[\text{Se}]_{\text{part}}$  from the surficial sediment alone will be used to calculate site-specific  $K_{ds}$ .

Table 3. Invertebrates, fish, and raptors/shorebirds/waterfowl found in Permanente Creek that make up assumed food webs for purposes of modeling.

	Permanente Creek, upstream	Permanente Creek, on-site	Permanente Creek, downstream	Whisman and Mountain View Slough and South San Francisco Bay
Invertebrates	Aquatic Insects (mayflies, stoneflies, caddisflies, other) <sup>a</sup>	Aquatic Insects (mayflies, stoneflies, caddisflies, other) <sup>a</sup>	Aquatic Insects (chironimids, black flies, mayflies) <sup>b,c</sup>	Chironimids, shrimp, worms, snails, bivalves <sup>c,d</sup>
Fish	Rainbow trout <sup>a</sup>	Rainbow Trout, Sacramento Sucker, Western Mosquitofish <sup>a</sup>	Sacramento Sucker, California Roach <sup>b</sup>	Numerous (anchovy, topsmelt, shad, striped bass, sculpin, surfperch, herring, jacksmelt, halibut, etc.) <sup>d</sup>
Birds	Great Blue Heron, ducks (mallard, wigeon, shoveler, merganser, goldeneye, bufflehead), Turkey Vulture, raptors (osprey, kite, hawks, falcons, kestrel), other non-fish eating birds <sup>a</sup>		Ducks, geese, occasional birds-of-prey <sup>d</sup>	Numerous special status and common raptors/shorebirds/waterfowl (rail, snipe, curlew, sandpiper, owl, kite, egret, heron, duck, etc.) <sup>d</sup>

<sup>a</sup> – WRA Environmental Consultants 2011

<sup>b</sup> – Santa Clara Valley Urban Runoff Pollution Prevention Program 2007

<sup>c</sup> – San Francisco Bay Regional Water Quality Control Board 2007 (Mountain View Slough)

<sup>d</sup> – LSA Associates 2011 (Mountain View Slough)

Table 4. Risk categories and typical ranges of diet, fish tissue, and bird egg selenium concentrations cited in the literature.

Risk Category	Diet (µg/g dw)	Fish Tissues (µg/g dw)	Bird Eggs (µg/g dw)
R1: No adverse effects likely	≤3	<3	<4
R2: Some effects on individuals detectable. Effects on sensitive populations possible but uncertain	2-10	4-10	6-15
R3: Deformities in some species and reproductive failure in sensitive species.	10-20	10-40	20-40
R4: Expect evidence of gross deformities and examples of reproductive failure.	>20	>40	>40

SOURCE: Larry Walker Associates et al. 2007

Specific examples of selenium thresholds which fall into the R2 category above include:

- 2-5 µg/g dw diet of fish (based on 50% mortality at 5.1 µg/g dw diet in lab study of winter stress in juvenile bluegill, Lemly 1993);

- 4-6 µg/g dw whole-body fish tissue (based on 10% mortality at 4.5 µg/g dw fish tissue in winter stressed bluegill, interpretation of Lemly 1993 by USFWS 2004);
- 4.87 µg/g dw diet in birds, (10% effect level in mallards, hatchability; Ohlendorf 2003); and
- 6.4-16.5 µg/g dw in bird eggs (based on 12.5 parts per million dw in eggs, 10% effect level in mallards, hatchability; confidence intervals 6.4 to 16.5 µg/g dw, Ohlendorf 2003)

These values provide a context on thresholds derived based on studies already conducted. However, it is possible that fish and wildlife in Permanente Creek have higher tolerances for selenium due to site-specific factors. For example, the high level of sulfate in Permanente Creek may provide some degree of protection from the effects of selenium to resident fish species. For the purposes of this assessment, the range of thresholds in the literature (*e.g.*, those referenced above) will be used to assess potential impacts on beneficial uses.

## 5 Assessment of Impacts to the Domestic and Municipal Supply Beneficial Use in Groundwater

Maximum selenium concentrations measured in the discharge and Permanente Creek downstream of the discharge are above the drinking water maximum contaminant level (MCL) for selenium of 50 µg/L. Although Permanente Creek is not designated for MUN, the Creek is designated with the GWR beneficial use, correlating to the Santa Clara Valley groundwater basin, which is designated for MUN. The Region 2 Basin Plan states that groundwater designated for use as MUN shall not contain concentrations of constituents in excess of MCLs. However, the Santa Clara Valley Water District 2012 Groundwater Management Plan summarizes groundwater quality data collected from 2002-2011, and indicates that selenium was never measured above 5 µg/L in the shallow aquifer zone (*i.e.*, wells primarily drawing water from depths less than 150 feet) in samples from 139 wells. The shallow aquifer zone is the most likely zone to be impacted by any groundwater recharge from Permanente Creek. In the principal aquifer zone (*i.e.*, wells primarily drawing water from depths greater than 150 feet), the median value of 272 wells was 1.3 µg/L, and the 75<sup>th</sup> percentile was 2.3 µg/L (SCVWD 2012). Based on this information, there is no evidence to indicate that selenium levels in Permanente Creek are impacting the MUN beneficial use in groundwater.

## 6 Project Team

The following summarizes the personnel that will be involved in the study.

- Lehigh – project management, Permanente Facility on-site sampling assistance.
- Robertson-Bryan, Inc. (RBI) – project management, preparation of the work plan, coordination with contract laboratories, sampling and data collection, review and management of analytical data, and preparation of reports.
- Golder Associates Inc. – assistance with sampling and data collection, as needed.

- Applied Speciation and Consulting, Inc. – analysis of selenium in water and sediment, and selenium speciation in water. At the start of the study, Applied Speciation and Consulting, Inc. will be the primary analytical laboratory for these parameters, and this work plan is written according to analyses, specifications, and QA/QC protocols at Applied Speciation and Consulting, Inc. Pending the results of initial round(s) of split sampling, the primary analytical laboratory for these parameters may change to Brooks Rand Labs, LLC, and the laboratory for split sample analyses changed to Applied Speciation and Consulting, Inc., if it is determined that Brooks Rand Labs, LLC analyses resulted in higher technical quality data (considering accuracy, precision, and laboratory QA/QC results).
- Brooks Rand Labs, LLC – analysis of selenium in water and sediment, and selenium speciation in water. At the start of the study, Brooks Rand Labs, LLC will be the analytical laboratory for split sample analysis. Pending the results of initial round(s) of split sampling, the primary analytical laboratory for these parameters may change to Brooks Rand Labs, LLC, and the laboratory for split sample analyses changed to Applied Speciation and Consulting, Inc., if it is determined that Brooks Rand Labs, LLC analyses resulted in higher technical quality data (considering accuracy, precision, and laboratory QA/QC results).
- Alpha Analytical Laboratories, Inc. – analyses and reporting of laboratory measured basic water quality/chemistry parameters.

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## 7 Monitoring Approach and Methodology

### 7.1 Parameters

Parameters, units for reporting, and analytical techniques and associated reporting limits (RLs) and method detection limits (MDLs) are shown in Table 5.

Table 5. Analytes to be measured, the associated analytical method, reporting units, reporting limits (RL) and method detection limits (MDL).

Matrix	Analyte	Analytical Method	Units	RL	MDL
Water Column, Flow	Total organic carbon	SM5310C	mg/L	0.3	0.04
	Temperature	Meter	°C	--	--
	pH	Meter	Standard Unit	--	--
	DO	Meter	mg/L, % saturation	--	--
	Electrical Conductivity	Meter	µS/cm	--	--
	Total hardness	SM2340B	mg/L as CaCO <sub>3</sub>	5	1
	TSS	SM2540D	mg/L	1	0.3
	Chlorophyll <i>a</i>	SM1020-OH	µg/L	10	0.05
	Sulfate	EPA 300.0	mg/L as SO <sub>4</sub> <sup>2-</sup>	0.5	0.09
	Oxidation reduction potential	Meter	mV	--	--
	Total alkalinity	SM2320B	mg/L as CaCO <sub>3</sub>	5	0.05
	Stream flow	USGS Rantz 1982	cfs	--	--
	Total Se	EPA 200.8	µg/L	0.10 <sup>a</sup>	0.020 <sup>a</sup>
	Dissolved Se	EPA 200.8	µg/L	0.05 <sup>a</sup>	0.003 <sup>a</sup>
	Dissolved Se speciation (Se(VI), Se(IV), SeCN <sup>-</sup> )	IC-ICP-DRC-MS	µg/L	0.10 <sup>a</sup>	0.020 <sup>a</sup>
Particulate Se	Calculation	µg/L	0.10 <sup>a</sup>	0.020 <sup>a</sup>	
Sediment	Total Se	EPA 3050B/200.8	mg/kg	0.005	0.020
	Sulfate	EPA 300.0	mg/kg as SO <sub>4</sub> <sup>2-</sup>	5	0.5
	Grain size	ASTM D422	--	--	--
	Total organic carbon	EPA 9060A	mg/L	120	500
Cont. Water Column	Temperature	Continuous Logger	°C	--	--
	pH	Continuous Logger	Standard Unit	--	--
	DO	Continuous Logger	mg/L	--	--

<sup>a</sup> RLs and MDLs are for typical reagent water, and are not representative of those that will be obtained from field samples, since any samples will need to be diluted depending on their complexity (e.g., TDS).

The following are deviations in the list of monitoring parameters from the 13267 Order.

- Dissolved Selenium II (organo-selenium):** Selenium (II) exists in water only as organic species. There is no readily available method for quantifying the total amount of selenium that is Se(II). Individual organo-selenium species can be measured, but even by adding together a number of common Se(II) species, the total amount of Se(II) may still be underestimated. However, in water, selenium exists in the dissolved phase as Se(IV) and Se(VI) (SeO<sub>3</sub><sup>2-</sup> and SeO<sub>4</sub><sup>2-</sup>), Se(II), and to a lesser extent, Se(0) (as SeCN<sup>-</sup>). Since Se(IV), Se(VI), and SeCN<sup>-</sup> will be measured, and total dissolved selenium will be measured, Se(II) will be calculated in this study as:

$$[\text{Se(II)}] = [\text{Se}]_{(\text{diss})} - ([\text{SeO}_4^{2-}] + [\text{SeO}_3^{2-}] + [\text{SeCN}^-])$$

- Selenium speciation (Se(IV), Se(VI), Se(II), elemental Se, total organic Se, total inorganic Se) on sediment/particles:** Speciation of selenium dissolved in the water

column affects phase partitioning, and will be measured as part of this study. Speciation of selenium in the solid phase is not typically considered in assessing the partitioning and uptake of selenium (and is, therefore, not relevant to the modeling procedure defined in section 4), and measurement of selenium speciation on solid phases is not commonly done outside of the university research setting. Handling of sediment, including sampling, homogenization, and drying affects selenium speciation. Furthermore, there are no standardized methods available, and all methods have limitations that affect their accuracy. There are two primary techniques used: single/sequential extraction techniques, and synchrotron-based X-ray absorption spectroscopy (XAS), which includes both X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS). Drawbacks of extraction techniques include failure to address analyte redistribution during extraction, lack of selectivity, and alteration of sample characteristics and/or speciation during fractionation steps (Martens and Suarez 1997). XAS techniques require access to a synchrotron light source, and require extended exposure of the sample that can cause radiation-induced changes in oxidation states (Ryser et al 2006).

- Particulate selenium:** direct measurement of total particulate selenium is not included in the study. There are several reasons for this. Direct measurement of total particulate selenium requires that samples be filtered in the field to collect the particulates. At a preliminary site visit in March 2013, water in the creek downstream of the Lehigh property was very clear, and contained very few solids in suspension. Thus, in order to collect enough suspended particulates such that selenium could be reliably measured, a large volume of water (likely at least 10 liters, but possibly much more depending on suspended solids concentration and selenium concentrations) would need to be filtered at each site. Not only can this be very time consuming, but also at some sites, water was very shallow (< 1" deep), which would make field filtration of such a volume nearly impossible without affecting sample integrity. Instead, total suspended particulate selenium will be calculated based on the difference of total and dissolved selenium in the water and TSS measurements, as:

$$[Se]_{Part} \left( \frac{\mu g}{mg} \right) = \frac{[Se]_{TOT} \left( \frac{\mu g}{L} \right) - [Se]_{diss} \left( \frac{\mu g}{L} \right)}{TSS \left( \frac{mg}{L} \right)}$$

where  $[Se]_{part}$  is the particulate selenium concentration,  $[Se]_{TOT}$  is the total recoverable selenium concentration, and  $[Se]_{diss}$  is the dissolved selenium concentration. Total particulate selenium will be used, along with total selenium in bed sediment, to derive the distribution coefficient, as described in section 4.3.

- Total organic/total inorganic selenium in water:** there are no standardized methods that measure these parameters. However, in the dissolved phase, total inorganic selenium is equivalent to the sum of Se(IV), Se(VI), and  $SeCN^-$ , and total organic selenium is equivalent to Se(II), as defined above. In the particulate phase, although the relative fraction of inorganic/organic selenium will not be known, the total particulate selenium

concentration will be calculated as defined above, and can be compared to the total dissolved selenium concentration to determine how important particulate selenium species are to the total organic/inorganic selenium concentration in the water. Finally, the values of these parameters are not used in the modeling approach described in section 4 and, therefore, do not add information useful to the assessment of beneficial use impacts.

## 7.2 Monitoring Locations

A map of the study area is shown in Figure 1. Monitoring locations, including which parameter groups are to be sampled at which locations, are summarized in Table 6. Photos of monitoring locations are shown in Appendix A.

Sampling will begin at the most upstream site (WVC) and will proceed downstream on Permanente Creek. If at any site, Permanente Creek or Stevens Creek are dry, the condition will be documented, and water sampling and flow measurement will be discontinued for that event for all sites downstream of that point, with one exception. Site PER010 will be sampled regardless of whether there is flow connectivity between the Permanente facility and the site on Permanente Creek, with the intention that data collected at this site may be used to support delisting Permanente Creek downstream of the Permanente Diversion Channel from the State's 303(d) list of impaired water bodies for selenium. Sediment samples will still be collected at every site, even if the creek has no water in it at the time of sampling. Selenium concentrations from sediment collected when the creek is dry may be used directly in modeling environmental risk, but will not be used to calculate  $K_d$ , since no associated water sample will be available for the calculation.

Table 6. Monitoring locations and parameter types to be measured at each location. <sup>a</sup>

Station	Description	Latitude	Longitude	Water	Sediment	Flow	Continuous Water Column
STE010 <sup>b</sup>	Near-shore Station on Stevens Cr	37.42822	-122.06881	Yes	Yes	--	--
PER010 *	Permanente Cr at Charleston Rd	37.42118	-122.08673	Yes	Yes	Yes	--
PER020 *	Permanente Cr at Crittenden Middle School	37.41206	-122.08663	Yes	--	Yes	--
HAL010	Hale Cr at Mountain View Ave.	37.38292	-122.09074	Yes	--	Yes	--
PER035	Permanente Cr at Covington Rd, 1000' downstream of diversion channel/PER040	37.36488	-122.08491	Yes	Yes	Yes	--
STE020 *	Stevens Cr at La Avenida	37.41357	-122.06865	Yes	Yes	Yes	--
STE040 *	Stevens Cr Below Diversion Channel Outfall	37.36475	-122.06224	Yes	--	Yes	--
PER045	Permanente Cr at Diversion Channel	37.36195	-122.08681	Yes	--	Yes	--
PER070 *	Permanente Cr at Rancho San Antonio	37.32941	-122.08586	Yes	Yes	Yes	Yes
PER080 <sup>c,*</sup>	West Branch Permanente Cr	37.33335	-122.09381	Yes	--	Yes	--
Pond 14	Pond 14 (Permanente Cr on Quarry Property)	37.32323	-122.08358	Yes	Yes, Sept 1-Oct 31 only <sup>d</sup>	Yes	--
Pond 13	Pond 13 (Permanente Cr on Quarry Property)	37.31661	-122.10168	Yes	Yes	Yes	Yes
WVC <sup>e</sup>	Wild Violet Creek, Background Station	37.32026	-122.13183	Yes	Yes	Yes	--

<sup>a</sup> Several sites require access to be granted by Santa Clara Valley Water District or the Midpeninsula Regional Open Space District. Due to the tight timeframe for work plan preparation, as of the submission of this work plan, access has not been able to be guaranteed for every site. Therefore, locations are subject to change following coordination with these entities and the SFBRWQCB.

<sup>b</sup> This station satisfies the requirement in the 13267 Order under the section titled "Near-Shore Location".

<sup>c</sup> This station satisfies the requirement in the 13267 Order under the section titled "Potential North Side WMSA Runoff pathway leading to Permanente Creek", since runoff pathways on the north side of WMSA drain to the West Branch of Permanente Creek.

<sup>d</sup> The United States Fish and Wildlife Service has indicated that sediment sampling in Pond 14 will only be allowed between September 1 and October 31, to protect the endangered population of red-legged frogs in the pond.

<sup>e</sup> This station is the proposed background station, based on the requirement in the 13267 Order under the section titled "Background Station".

\* Denotes SWAMP monitoring location (SFBRWQCB 2007).

The following are deviations in the list of sampling stations from the 13267 Order.

- **SWAMP Stations:** The Order states the following.

*“The sampling locations shall include all sampling stations on the Creek that were used in SWAMP monitoring on Permanente Creek in 2002-200 (see Attachment B), upstream of the Permanente Creek Diversion Channel, and on Stevens Creek downstream of the Permanente Creek Diversion Channel, unless it can be documented that individual sites are not necessary to completely characterize Permanente Creek downstream of the discharger. Individual sites may be recommended for exclusion in the Work Plan if it can be shown that they do not add useful information to the study.”*

The following stations from the SWAMP monitoring on Permanente Creek and Stevens Creek were recommended for exclusion, along with the justification for exclusion:

- **PER040:** During a site visit in March 2013, PER040 appeared to be in a culvert that may no longer be accessible. PER035 is proposed instead of PER040. PER035 is 1000 feet downstream of the diversion channel/PER040. It is not expected that water quality would substantially different between these two sites. PER035 has easy access, while PER040 appears to be inaccessible.
- **PER050:** PER050 is recommended for exclusion because it is not necessary to completely characterize Permanente Creek downstream of the Permanente Facility. Between PER050 and the next site upstream, PER070, the creek flows through predominantly urban area (along with a small stretch in the Rancho San Antonio Open Space Preserve) with no apparent additional sources of selenium or depositional areas. Between PER050 and the next site downstream, PER045, the creek travels through 0.65 miles of urban area with no apparent additional sources of selenium or depositional areas. Although the habitat changes substantially when the concrete channel begins upstream of PER045, water quality (including selenium and selenium speciation) is not expected to be substantially different between PER050 and PER045. Therefore, environmental risk in the reach associated with PER050 can be assessed via results obtained at PER045.
- **STE030:** STE030 is recommended for exclusion because it is not necessary to completely characterize Stevens Creek downstream of Permanente Creek, downstream of the Permanente Facility. Between STE030 and the next site upstream, STE040, Stevens Creek runs through 1.7 miles of urban area with no apparent additional sources of selenium, depositional areas, change in channel configuration, or habitat alterations. Water quality (including selenium and selenium speciation) is not expected to be substantially different between STE030 and STE040. Therefore, environmental risk in the reach associated with STE030 can be assessed via results obtained at STE040.
- **Background Station:** The 13267 Order specifies that this work plan “shall identify four candidates for a representative background station to establish a reference site of ambient conditions for Permanente Creek.” This is the same requirement as is defined elsewhere

in the Order, under the section titled “Background Monitoring Location Identification Plan.” For a discussion of background stations, as specified in this section of the order, refer to the Background Monitoring Location Identification Plan, submitted March 6, 2013 (Golder 2013) and the corresponding Background Monitoring Report submitted March 22, 2013 (Golder 2013). The proposed background station is shown in Table 6.

### 7.3 Sampling Frequency, Duration, and Schedule

The monitoring frequency is summarized in Table 7. Monitoring shall be performed for two years. However, the SFBRCQB will evaluate the first year’s data and may adjust the sampling parameters, frequency, location, and study duration after the first year. A proposed schedule is shown in Table 8. The proposed start of sampling is in June 2013, which is within the 45 day period subsequent to submittal of this work plan specified in the Order. The 13267 Order requires that one of the sampling events occur during the wettest month of the year, after a major rain event, and one of the dry season sampling events occur during the driest month of the year. February is the wettest month of the year, and thus sampling in February will target a period after a major rain event. July and August are, depending on the data source used, approximately equivalently dry. In most years, September is equally dry as July and August. In order to collect sediment samples in Pond 14, the United States Fish and Wildlife Service has indicated that samples must be collected between September 1 and October 31. Thus, in order to collect a sediment sample in Pond 14 during the same event as water and sediment at other stations, sampling for the dry season quarter 3 is specified for September. The sampling will be scheduled as early in September as possible, so as to minimize the chance of a rain event prior to sampling.

Table 7. Monitoring frequency for different types of constituents.

Matrix/Type <sup>a</sup>	Frequency
Water Column, Flow	Monthly wet season (November – April), Quarterly dry season (June, September)
Sediment	Quarterly (June, September, December, March)
Continuous Water Column	30-day continuous monitoring once every quarter (June, September, December, March)

<sup>a</sup> Constituents in each category are defined in Table 5.

Table 8. Proposed monitoring schedule and reporting deadlines. <sup>a,b</sup>

Year	Quarter	Month	Water Column, Flow	Sediment	Continuous Water Column	Quarterly Reporting Deadline	1 <sup>st</sup> year, Final Report Deadline
Year 1	Q2	Jun-13	x	x	x	30-Jul-13	30-Jun-14
	Q3	Jul-13				30-Oct-13	
		Aug-13					
		Sep-13	x	x	x		
	Q4	Oct-13				30-Jan-14	
		Nov-13	x				
		Dec-13	x	x	x		
	Q1	Jan-14	x			30-Apr-14	
		Feb-14	x				
		Mar-14	x	x	x		
Q2	Apr-14	x			30-Jul-14		
	May-14						
Year 2		Jun-14	x	x	x		30-Jun-15
	Q3	Jul-14				30-Oct-14	
		Aug-14					
		Sep-14	x	x	x		
	Q4	Oct-14				30-Jan-15	
		Nov-14	x				
		Dec-14	x	x	x		
	Q1	Jan-15	x			30-Apr-15	
		Feb-15	x				
		Mar-15	x	x	x		
Q2	Apr-15	x			30-Jun-15		
	May-15						

<sup>a</sup> Year 2 activities are proposed and shown here for reference, but may change based on requests made to the Regional Water Board in the 1<sup>st</sup> year study report.

<sup>b</sup> Continuous water column monitoring is specified as a 30-day period, and so may not begin and end at the start and end of a month, respectively.

#### 7.4 Sampling Methodology and Equipment

Sampling will be targeted for days for which the weather forecast predicts little to no chance of rainfall. A two-person sampling crew shall begin sampling at the most upstream site and proceed downstream. Due to the number and geographic extent of sampling sites, and the number of samples and flow measurements, which can be time consuming to perform, it is very likely that all sampling will not be able to be completed in a single day. In this case, sampling will resume as soon as possible on the following day at the next location downstream. Efforts will be made to avoid instances in which conditions would change from one day to the next (e.g., rainfall or different weather conditions from one day to the next). This is a deviation from the

13267 Order, which specifies in Table C that: “Sampling for all parameters shall occur on the same dates at all locations.”

Upon arrival at a site, a grab sample shall be collected into a temporary container, and field parameters (temperature, pH, DO/DO saturation, oxidation-reduction potential, electrical conductivity) shall be measured with a handheld meter, and results recorded on a field data sheet. Any noteworthy site conditions also will be recorded.

Pre-cleaned sample containers will be provided by the analytical lab. Sample containers will be labeled with waterproof labels with a unique sample identification number reflective of the sampling location and sample date.

Water samples to be analyzed at the analytical laboratories will be collected as discrete grab samples. Table 9 summarizes sample locations, parameters, container,s and preservation.

Table 9. Sample bottles and preservation for required analyses.

Sample Stations	Container (Volume) <sup>a</sup>	Container Quantity	Matrix	Field Filter	Field Preservation	Hold Time	Analytes	Lab <sup>b</sup>
STE010	G,A (40 mL)	2	Water		H <sub>3</sub> PO <sub>4</sub> , ≤6°C	28 d	TOC	AA
PER010	P (500 mL)	1	Water		HNO <sub>3</sub> , ≤6°C	180 d	Hardness	AA
PER020								
HAL010	P (1 L)	1	Water		≤6°C	7 d	TSS	AA
PER035	P,A (1 L)	1	Water		≤6°C	2 d	Chlorophyll <i>a</i>	AA
STE020								
STE040	P (500 mL)	1	Water		≤6°C	14 d	Sulfate, alkalinity	AA
PER045	P (125 mL)	4 <sup>c</sup>	Water		4±2°C	180 d	Total Se	AS
PER070								
PER080	P (125 mL)	4 <sup>c</sup>	Water	X	4±2°C	180 d	Dissolved Se	AS
Pond 14	P,PA (125 mL)	4 <sup>c</sup>	Water	X	4±2°C	≤180 d	Se speciation	AS
Pond 13 WVC								
STE010	P (4-8 oz)	3 <sup>d</sup>	Sediment		4±2°C	180 d	Total Se	AS
PER010								
PER035	G (4 oz)	3 <sup>d</sup>	Sediment		≤6°C	180 d	Sulfate, grain size, TOC	AA
STE020								
PER070								
Pond 14 Pond 13 WVC								

<sup>a</sup> P = polyethylene; G = glass; A = amber; PA = is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic).

<sup>b</sup> AA = Alpha Analytical; AS = Applied Speciation.

<sup>c</sup> Four sample containers are required for selenium analysis – one each for the sample, the matrix spike, the matrix spike duplicate, and one as backup in case of breakage.

<sup>d</sup> Three sample containers are required for sediment analyses – one for each subsample location at a site. Homogenization will be performed in the lab.

Grab samples of water shall be collected by submerging the sample container by hand or pole extension to a depth so as to prevent “skimming” and collection of surface water. In some cases, water may be so shallow so as to make skimming unavoidable (for example, under very low flow conditions in concrete channels). Alternatively, a composite sampler or peristaltic pump can be used to pump directly into the sampling container. At least three sample volumes will be pumped through the tubing prior to taking the sample to minimize the possibility of contamination. Under no circumstances will pump tubing or sample tubing be shared across sites. At each sampling location, water samples shall be collected in rapid succession so as to represent the same sample to the maximum extent practical.

Grab samples of sediment shall be collected using either a disposable, contaminant-free plastic scoop (when sediment is accessible via wading) or a petit Ponar dredge (when sediment is not accessible via wading). Depositional areas at each of the sites will be targeted for sampling. Three sediment samples will be taken at each site, and homogenization will be conducted by the laboratory prior to analysis.

Upon collection, samples will be appropriately preserved according to the requirements in Table 9. Water samples for total and dissolved selenium will be acidified to a pH < 2 in the lab upon receipt, and then held for 24 hours before digestion and/or analysis. Applied Speciation noted the following deviations from the SWAMP sample handling guidelines for selenium speciation.

- A plastic container other than polyethylene (e.g., polypropylene) may be used for sample collection,
- Samples for selenium speciation are never acidified. Despite what some older hydride generation methods call for, ample literature shows that acid can induce changes in the selenium speciation.
- The hold time is matrix-dependent, but may be as long as 6 months if the sample is stored properly.

Flow measurements will be made following sample collection. Measurements will be made according to USGS flow measurement standards (Rantz 1982) where possible. Methods will include:

- If channel is natural/irregular cross section and wadable, manual discharge measurements will be made using a portable flow meter and top-set wading rod. If channel is concrete rectangular or trapezoidal, flow may be estimated from several velocity measurements and channel width and depth measurements. Uncertainty in these flow measurements will be calculated according to USGS standard methods (Sauer and Meyer 1992) where applicable.
- If channel is not wadable due to high water, flows will be estimated based on measured flows at other sites (if available), visual observations, and measured data obtained from Santa Clara Valley Water District.
- If flows are very low and no traditional methods are applicable, flow may be estimated based on engineering judgment.

Continuous monitoring will be conducted via loggers placed at the locations specified in Table 6. The logging interval will be a maximum of 15 minutes. The specific manufacturer and model of

the loggers will be determined prior to deployment. Specifications of the loggers will be sufficient to account for the expected variability in continuous monitoring parameters. Because Permanente Creek downstream of the Lehigh property runs through a public open space preserve and urban area, it is possible that monitoring equipment deployed in these locations will be vandalized or stolen. If this occurs, Lehigh or RBI will coordinate with the SFBRWQCB to determine alternative sites for deployment.

All sampling activities will be documented on field data sheets, including the method of sampling and any deviations from the direction in this work plan. Blank field data sheets are provided in Appendix B.

## 7.5 Analytical Procedures

Samples will be delivered to the respective laboratories under proper chain-of-custody. Pertinent discussion of the various analyses listed in Table 5 are provided in the following sections.

### *Total selenium (water)*

Total selenium will be measured using EPA method 200.8 on unfiltered water samples following reflux with nitric acid and hydrochloric acids, as specified by the method. Measurement of selenium composition of the refluxed sample is made by an inductively-couple plasma mass-spectrometer with correction for isobaric interferences.

### *Total dissolved selenium (water)*

Selenium will be measured on a field-filtered sample following the addition of nitric acid. Measurement of selenium composition of the refluxed sample is made by an inductively-couple plasma mass-spectrometer, with correction for isobaric interferences.

### *Dissolved selenium speciation (water)*

Se(VI), Se(IV), and  $\text{SeCN}^-$  will be quantified by ion chromatography, inductively couple plasma, dynamic reaction cell, mass spectroscopy (IC-ICP-DRC-MS). This method effectively separates the inorganic selenium species based upon their charge prior to selenium quantification via ICP-MS. Using the concentration of the three selenium species above and the total dissolved selenium concentration, a sum of unknown selenium species will be reported. Per section 7.1, total Se(II) is defined as the sum of unknown selenium species.

### *Total particulate selenium (water)*

Total particulate selenium concentrations will be calculated as the difference between total selenium and total dissolved Se, normalized by the TSS concentration in the sample, as described in section 7.1.

### *Total selenium (sediment)*

Sediments are digested with repeated additions of nitric acid and hydrogen peroxide via EPA method 3050B. This method is not a total digestion, but rather a method to dissolve almost all elements that could become “environmentally available.” The extraction matrix is then analyzed for total selenium via ICP-MS (EPA 200.8).

### *Sulfate (sediment)*

In accordance with EPA method 300.0, sulfate is measured in sediment by extraction. The sediment is first extracted with reagent water and filtered, and sulfate is then measured in the extract by ion chromatography.

#### *Grain size (sediment)*

Sediment grain size will be measured according to ASTM method D422 using particle size sieves to resolve the % mass of sediment in size fractions. The following standard sieve sizes will be used in particle size determination: 2 mm, 1 mm, 0.5 mm, 0.25 mm, 0.125 mm, and 0.0625 mm. Sediment passing through the smallest pore-size sieve is quantified as total silt and clay

### 7.6 Data Handling and Analysis

Original lab reports will be stored as PDF files at RBI and transmitted to Lehigh. Following data review and QA/QC, the final data set, including laboratory QA/QC results, will be imported into a Microsoft (MS) Excel and/or Access database for storage, querying, and analyses. This database will additionally contain RBI QA/QC notes and will identify questionable data points. Upon completion of the project, a copy of this database will be transferred to Lehigh and the Regional Water Board for future use.

In addition to analysis of spatial and temporal trends, data will be used to model and assess impacts to aquatic life beneficial uses as described in section 4.

### 7.7 Quality Assurance/Quality Control

A field sampling quality control (QC) program was designed consistent with the California Surface Water Ambient Monitoring Program (SWAMP) quality control and sample handling guidelines (SWAMP 2013a, 2013b, 2013c), and includes the use of field blanks, field duplicates, and sample splits. The frequency and location of field sample QC collection is outlined in Table 10. Selenium analyses are the primary subject of the field sampling QC program; however, additional constituents such as TSS, grain size, TOC, and sulfate will be measured on the QC samples to facilitate interpretation of the selenium results.

Table 10. Quality control/quality assurance samples.

Matrix	Sample Type	Frequency	Analytes <sup>a,b</sup>
Water	Field Duplicate	≥ 5% of total project sample count, events distributed throughout the year	TSe, DSe, SSe, PSe (TSS)
	Field Blank	During first sampling event, future events if and only if field blanks demonstrate contamination in first event or if sample contamination is suspected in future events	TSe, DSe, SSe, PSe (TSS)
	Split	During one of the initial sampling events, future events only if interlaboratory variability is unacceptable or if questionable results from a single lab warrant additional splits	TSe, DSe, SSe, PSe (TSS)
Sediment	Field Duplicate	≥ 5% of total project sample count	TSe (GS, TOC, SO <sub>4</sub> <sup>2-</sup> )
	Split	During one of the initial sampling events, future events only if interlaboratory variability is unacceptable or if questionable results from a single lab warrant additional splits	TSe (GS, TOC, SO <sub>4</sub> <sup>2-</sup> )

<sup>a</sup> TSe = total selenium; DSe = dissolved selenium; SSe = dissolved selenium speciation; PSe = particulate selenium; TSS= total suspended solids; GS = grain size; TOC = total organic carbon .

<sup>b</sup> Analytes in parentheses will be measured to interpret the selenium results.

**Field blank sample collection:** Field blank water samples will be collected upon initiation of sampling. If field blank performance is acceptable, thereby demonstrating that the bottle and sampling protocol does not contaminate samples collected, no further collection and analysis of field blanks will occur for the duration of the project unless and until contamination is suspected. Field blanks demonstrate that sample contamination has not occurred during field sampling and sample processing, and will consist of laboratory prepared blank water. This water will be subjected to all field sampling procedures, including filtering, if applicable, and will be decanted into the appropriate sample containers in the field. Field blank samples will be collected prior to collecting all required samples.

If selenium is detected in the field blank at levels greater than the analytical reporting limit, the sampling personnel will be interviewed and the field logs reviewed so that the source of contamination can be identified (if possible) and sample collection procedures modified (if necessary). Additional field blanks will be collected until it is demonstrated, by clean field blanks, that the sampling protocol does not contaminate the samples collected.

**Field duplicate sample collection:** Field duplicate water and sediment samples will be collected at a frequency of at least 5% of total project sample count. Field duplicates will be collected by collecting two samples in rapid succession. The dates and locations at which field duplicates will be collected are outlined in Table 10.

The field duplicate results will be used to assess the precision of the entire data collection activity, including sampling, analysis, and site heterogeneity. If the relative percent difference (RPD) between the field duplicates is greater than 25%, the field sampling rationale and sampling techniques will be evaluated, and laboratory analytical duplicate sample results will be

reviewed. Corrective actions (e.g., modified sample collection procedures) will depend on results of the review.

Split samples: Although not included in the SWAMP guidelines, split water and sediment samples will be analyzed during one of the initial sampling events. If results from initial split-sample analyses are acceptable, analysis of split samples will be discontinued for the duration of the project unless and until questionable sample results are obtained. A split is two or more representative portions taken from one sample in the field and analyzed by two different analysts, methods, or laboratories. For the purpose of this work plan, splits will consist of water and sediment samples for selenium analyses only. Two different laboratories will be used for split analysis, as specified in section 6.

If the reported selenium concentrations are greater than the method reporting limiting and the RPD between split samples is greater than 25%, but field duplicates analyzed at a single lab showed acceptable RPD, laboratory staff will be consulted to determine methodological differences that may have led to the discrepancy. Corrective actions and the need for additional split samples will depend on results of the consultation. Pending the results of initial round(s) of split sampling, the primary analytical laboratory for these parameters may change to Brooks Rand Labs, LLC, and the laboratory for split sample analyses changed to Applied Speciation and Consulting, Inc., if it is determined that Brooks Rand Labs, LLC analyses resulted in higher technical quality data (considering accuracy, precision, and laboratory QA/QC results).

Quality assurance samples to be analyzed by the analytical laboratory include method blanks, laboratory control samples, matrix spikes, and matrix spike duplicates. The analytical laboratories will employ their own internal quality assurance (QA) measures, consistent with SWAMP, for the work they are to perform for this project to ensure the accuracy of analytical results. The standard data validation procedures documented in the analytical laboratory's QA manuals will be used to accept, reject, or qualify the data generated by the laboratory. The laboratory's QA officer will be responsible for validating data generated by the laboratory.

Applied Speciation has noted the following deviations from the SWAMP quality control guidelines for inorganic analytes in fresh and marine water and in freshwater sediment and freshwater marine sediment.

- For selenium speciation in water and sediment, the matrix-spike and matrix-spike-duplicate measurement quality objective is 75-125% recovery or mass balance obtained, unless sample matrix induces species conversion. If these objectives are not met, the matrix spike results are compared to those of the bracketing continuing calibration verifications (CCV). If species conversion was absent in the CCVs but was observed in the matrix spike, the sample matrix is deemed to induce conversion. The lab will also identify whether a mass balance was obtained for the added spike.
- An internal standard is not applicable to selenium speciation in water or sediment.
- For all selenium analyses in water and sediment, the measurement quality objective for the laboratory duplicate is  $RPD < 25\%$ , or  $\pm RL$  for samples  $< 5 * RL$ .

Upon receipt of lab reports from the analytical lab, RBI will conduct a thorough review of the results and accompanying laboratory control charts and quality control measures. The results of this review will be used to refine initial results provided by the laboratory. Data review will also include comparison of results, as they are made available, to previous sampling event results, and comparison of receiving water concentrations to discharge concentrations.

## 7.8 Reporting

Table 8 contains the deadlines for quarterly reporting, the first year report, and the final report. Quarterly reports will consist of all monitoring data collected in the quarter, along with a brief summary of any significant issues encountered in the sampling or analysis, deviations from the work plan, and actions taken or proposed to be taken to resolve these issues. The first year report will include and summarize all data collected in the first year, significant findings, and QA/QC issues, and may request changes to sampling frequency, sampling locations, or other adjustment of sampling scheme, based on first year's sampling results, consistent with section 10.b of the Order. The final report will include and summarize all of the data collected in the study, summarize significant findings regarding selenium fate, transport, modeled bioaccumulation, and any impacts to beneficial uses, describe any QA/QC issues, describe future monitoring needs, and include a description of existing or proposed actions to address any selenium impairments associated with the discharges from the quarry areas. This may include a description of treatment for selenium that is anticipated to be on-line prior to the completion of the study, and a description of treatment efficiency.

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## **Appendix A**



Photos of Field Sampling Stations



Stevens Creek near South San Francisco Bay (facing North/downstream)



Stevens Creek near South San Francisco Bay. (facing South/upstream)

Figure A 1. STE010 sampling station on Stevens Creek.



Permanente Creek crossing at Charleston Rd. (facing North/downstream)



Permanente Creek crossing at Charleston Rd. (facing South/upstream)

Figure A 2. PER010 sampling station on Permanente Creek.



Permanente Creek crossing at Rock St. near Crittenden Middle School (facing North/downstream)



Permanente Creek crossing at Rock St. near Crittenden Middle School (facing South/upstream)

Figure A 3. PER020 sampling station on Permanente Creek.



Hale Creek crossing at Mountain View Ave. (facing Northeast/downstream)

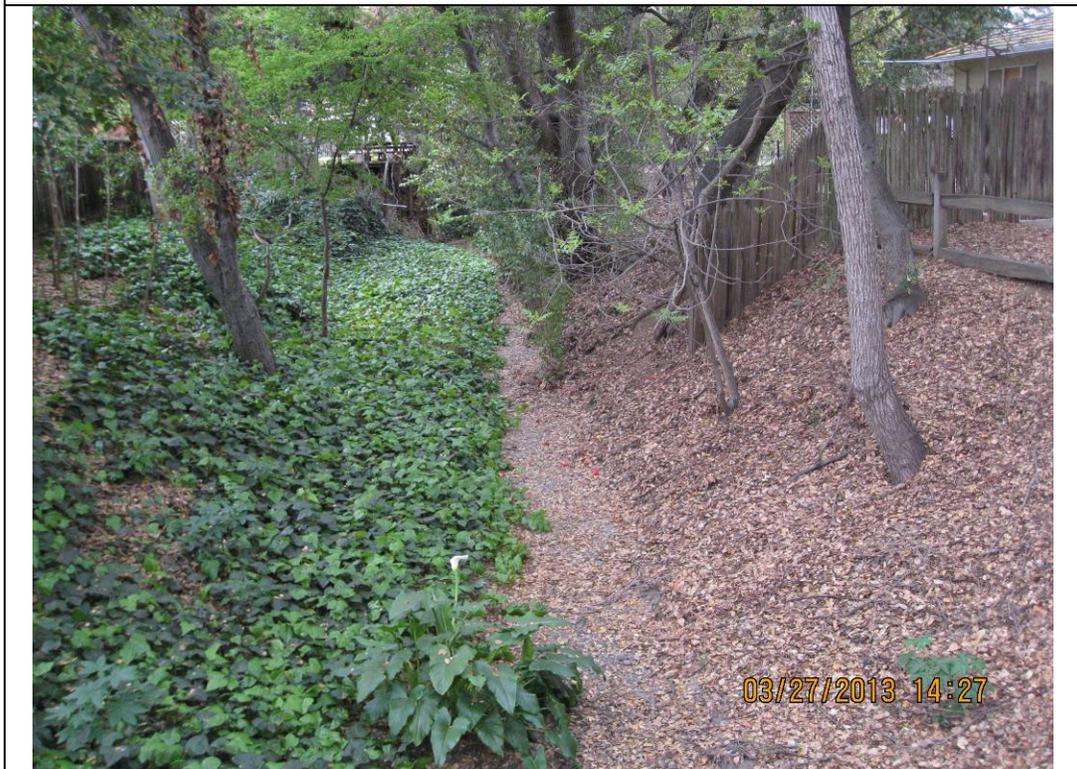


Hale Creek crossing at Mountain View Ave. (facing Southwest/upstream)

Figure A 4. HAL010 sampling stations on Hale Creek.



Permanente Creek crossing at Covington Rd. (facing North/downstream)



Permanente Creek crossing at Covington Rd. (facing South/upstream)

Figure A 5. PER035 sampling station on Permanente Creek.



Stevens Creek crossing at La Avenida St. (facing North/downstream)



Stevens Creek crossing at La Avenida St. (facing South/upstream)

Figure A 6. STE020 sampling station on Stevens Creek.

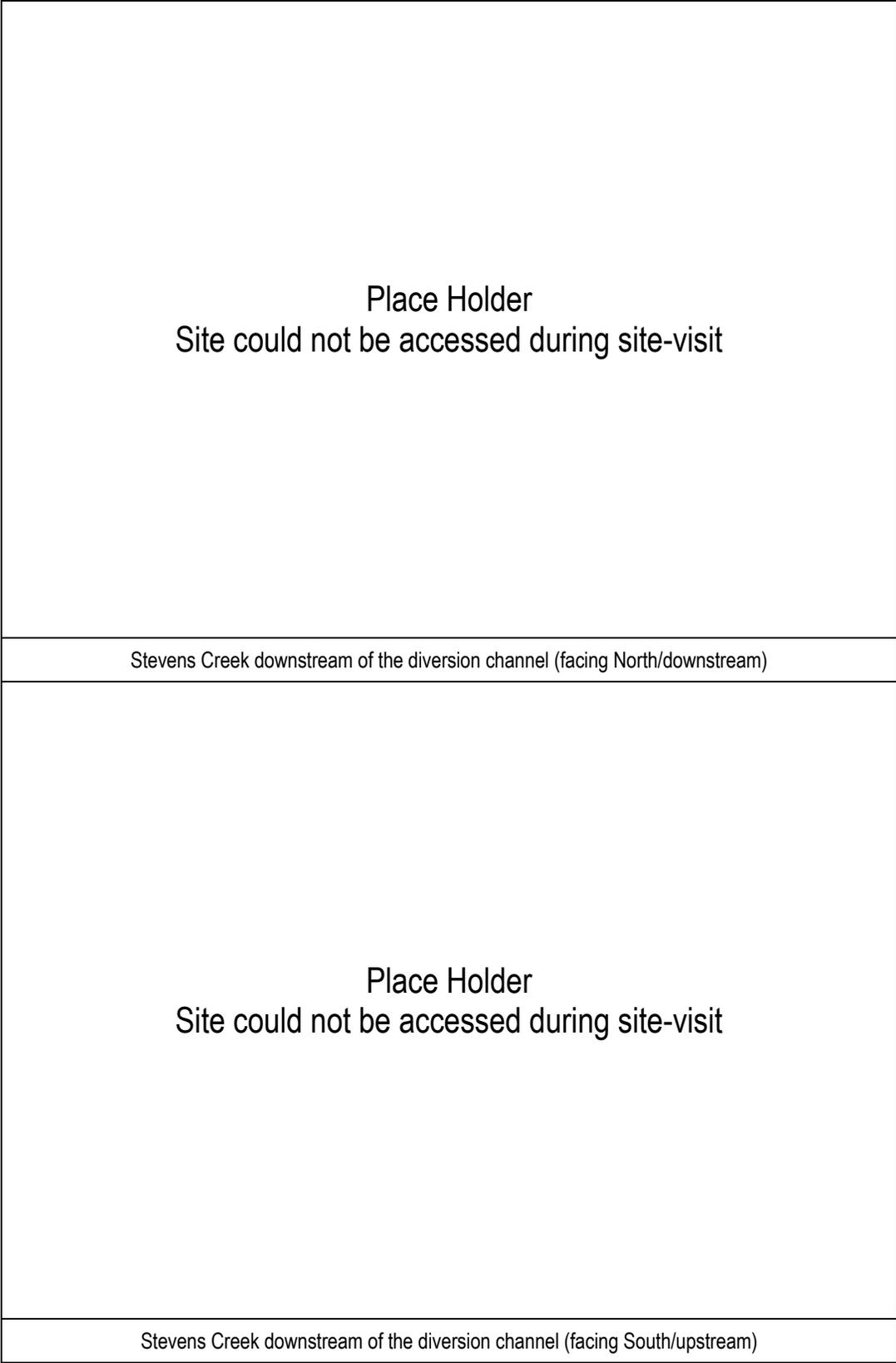


Figure A 7. STE040 sampling station on Stevens Creek.



Diversion channel near intersection of Miramonte Ave. and Berry Ave. (facing North/downstream)

Figure A 8. PER045 sampling station on Permanente Creek diversion channel.



Permanente Creek at Rancho San Antonio Open Space Preserve (facing downstream)



Permanente Creek at Rancho San Antonio Open Space Preserve (facing upstream)

Figure A 9. PER070 sampling station on Permanente Creek.

Place Holder  
Site could not be accessed during site-visit

West Branch Permanente Creek at Rancho San Antonio Open Space Preserve (facing downstream)

Place Holder  
Site could not be accessed during site-visit

West Branch Permanente Creek at Rancho San Antonio Open Space Preserve (facing upstream)

Figure A 10. PER080 sampling station on Permanente Creek.



Pond 14 located in Permanente Creek on Permanente Facility property (facing downstream)



Inlet to Pond 14

Figure A 11. Pond 14 sampling station.



Pond 13 located in Permanente Creek on Permanente Facility property (facing the pond inlet/upstream)

Figure A 12. Pond 13 sampling station.

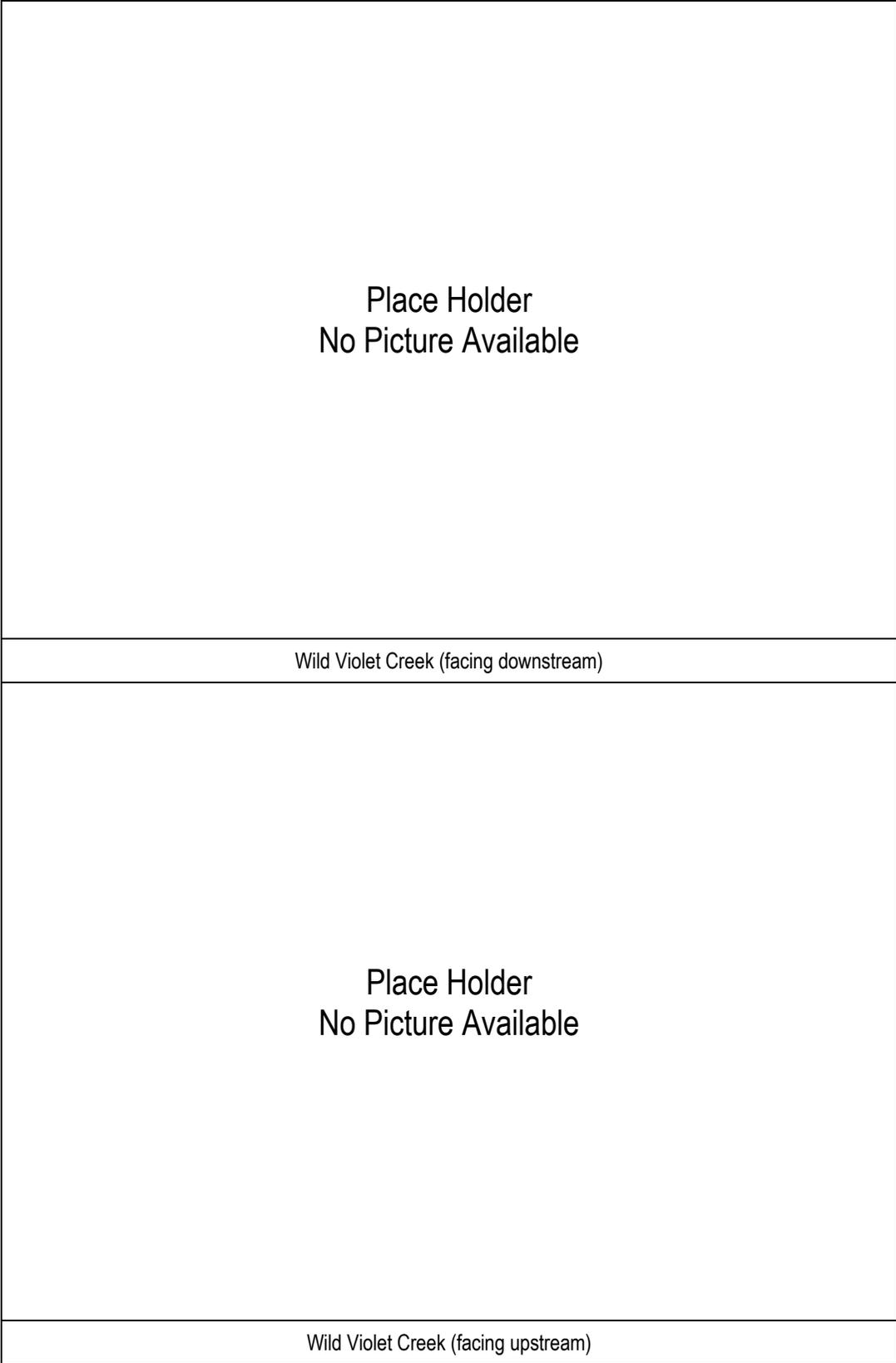


Figure A 13. WVC sampling station.

## **Appendix B**

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Example Field Sampling Data Sheets

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**Lehigh Permanente Facility Selenium Impact Assessment Study**  
**SAMPLING LOG**

DATE:		FORM COMPLETED BY:			
SAMPLING PERSONNEL:					
WEATHER CONDITIONS:					
METERS USED:	1)	2)	3)	4)	
CALIBRATED BY:					
DATE:					
GENERAL NOTES:					

Sampling Location:		Date:
Form Completed By:		Begin Time:
		End Time:
<i>In Situ</i> Measurements		
Parameter	Reading	Units
pH		std units
Temperature		°C/°F
Conductivity		µS/cm
Dissolved Oxygen		mg/L & %
Oxidation-Reduction Potential		mV
Other:		
Waterway & Sample Observations (color, clarity, odor, heterogeneity, etc.):		
Photos:		
Notes:		

