Phase II Sampling and Analysis Plan

Sediment Studies at Islais, Mission and Yosemite Creeks

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1.0 INTRODUCTION

This sampling and analysis plan (SAP) provides the overall guidelines for conducting Phase II sediment studies at Islais, Mission, and Yosemite Creeks located within San Francisco Bay. Phase II activities include two separate sampling events, scheduled for Fall 1999 and Spring 2000, and are designed to confirm and augment previous data produced in Phase I studies (conducted in Fall 1998). Phase II investigations at these creeks consist of sediment sampling and analysis to determine the nature and extent of toxicity and chemical contamination at the three subject sites. Bioaccumulation of chemicals will be evaluated in the Spring 2000 investigation only. Phase II investigations focus on the more contaminated areas within each creek and use a refined list of chemicals of concern (COC) identified in the Phase I study. The Phase II investigation also makes use of in-bay reference areas as a benchmark for determining whether the subject sites are significantly impacted.

This SAP describes the study design, field and analytical methods, and quality assurance/quality control procedures that will be used to collect and analyze sediments. Also included are approaches for data analysis and interpretation of results. This SAP follows the general approach of recent San Francisco Bay studies for the Bay Protection and Toxic Cleanup Program (BPTCP) and the Regional Monitoring Program (RMP), making use of trace analytical methods and extended analytes to identify potential contaminant sources. This study is designed to meet the following specific objectives: (1) to confirm Phase I results, which indicated that two of the subject sites (Islais and Mission Creeks) do not qualify as "toxic hot spots"; (2) to collect data to determine whether Yosemite Creek is significantly toxic and contaminated (Phase I results for Yosemite Creek were inconclusive); (3) to further define the vertical extent of contamination; and (4) to determine if the subject sites are significantly more contaminated and/or toxic than in-bay reference sites. Data collected in support of objectives (1) and (2) may be used to assist the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB) in developing corresponding cleanup plans.

1.1 Background

BPTCP survey results for Islais and Mission Creeks were summarized by the SFBRWQCB in a meeting with the City and County of San Francisco, Public Utilities Commission (SFPUC) on May 18, 1998. Results from sediment tests were presented in the BPTCP Proposed Regional Toxic Hot Spot Cleanup Plan (SFBRWQCB, December 1997) where several creek areas potentially influenced by City operated CSOs were identified as candidate Toxic Hot Spots. SFBRWQCB's assessment of Islais and Mission Creeks was based primarily on results from sediment chemistry and toxicity tests, while the assessment of Yosemite Creek was based on data collected by the U.S. Navy in support of a Phase I Remedial Investigation at Hunter's Point (PRC 1996).

BPTCP assessment of Islais and Mission Creeks was based on a limited number of sediment sampling locations (i.e., 3 to 4). At Islais Creek, moderate to high sediment concentrations of heavy metals, chlorinated pesticides and polychlorinated biphenyls (PCBs) secondarily supported the toxicity results. Sediments collected from Mission Creek were found to have high concentrations of PCBs, select chlorinated pesticides, and heavy metals at a single location measured several times. Yosemite Creek was sampled at three locations that extended from the mouth to approximately 500 meters within the creek.

These sediments were reported to have moderate to high concentrations of select metals, PCBs, and polycyclic aromatic hydrocarbons (PAHs) (PRC 1996); however, sediments located close to the main CSO were not sampled.

The SFPUC conducted Phase I sediment studies in Fall 1998 for each of the three creeks. The studies were conducted as agreed between the SFPUC and the SFBRWQCB, with the primary objective of confirming or refuting previous BPTCP results indicating that the subject sites were toxic and contaminated. Phase I results were presented to SFBRWQCB in three separate draft reports (i.e., ADL 1999a, 1999b, 1999c). Summarized report results follow.

1.1.2 Summary of Phase I Results

Phase I results were applied to BPTCP established criteria for identifying "toxic hot spots". These data indicated that neither Islais nor Mission Creek sediments qualified as toxic hot spots, using chemical criteria that were modified to correct inconsistencies that were applied in the BPTCP (see ADL 1999a, Section 1). Phase I data for Yosemite Creek were inconclusive, as the toxicity tests showed probable interference from resident predators.

1.1.2.1 Islais Creek

Phase I results were used to determine whether Islais Creek (or portions therein) qualified as a toxic hot spot using BPTCP criteria. A critical BPTCP criterion for final hot spot designation is significant toxicity coupled with evidence of "contributing chemical contamination" (Hunt et al. 1998). Although portions of Islais Creek met this criterion using BPTCP data collected in 1994 and 1997, Phase I data indicated that sediments are no longer toxic and contaminated, and therefore, the site no longer qualifies as a toxic hot spot.

A total of 18 surface samples extending from the creek origin to the mouth were collected and analyzed in the Phase I study. All 18 were analyzed for chemical contaminants and six of the 18 were analyzed for toxicity. None of the stations exhibited significant toxicity combined with elevated chemical contaminants, defined as less than 68.5% survival and an ERM quotient greater than 0.5, respectively, by the BPTCP (ADL 1999a, Section 1.2). Two stations exhibited moderate toxicity, one located near the CSO weir (Station 2N) and one located across from the Quint Street outfall (3S); however, corresponding ERM quotients were well below 0.5 (i.e., 0.27 and 0.23, respectively) (Table 1-1). Of the remaining 12 stations without toxicity results, only one station (3N) had an ERM quotient greater than 0.5 (i.e., 0.83). This quotient was less than that reported for Station 1N (i.e., 0.99), which had the highest amphipod survival of all stations (83%). Both ERM quotients were driven primarily by elevated concentrations of lead, mercury, zinc, and high molecular weight PAH, and both stations had extremely high concentrations of TOC (i.e., > 3%) (Table 1-1). Total organic carbon (TOC) tends to concentrate contaminants in sediments regardless of source (ADL 1999a, Section 4). As previously discussed, the ERM guidelines used in the BPTCP are based on sediments with an average concentration of 1.2% TOC. These guidelines would undoubtedly be significantly higher, if they included sediments with higher TOC concentrations, such as those encountered in the creeks. Toxicity results, ERM quotients and TOC concentrations are shown for Islais Creek surface sediments in Table 1-1.

Table 1-1. ERM quotients, % fines, TOC and toxicity results for Islais Creek surface sediments.

Station	ERMQ	Fines (%)	TOC (%)	Amphipod Survival (%)
1C	0.48	87.6	3.1	
1N	0.99	31.2	4.8	83.0
1S	0.35	5.4	1.2	
2C	0.21	98.3	1.8	
2N	0.27	97.2	1.9	58.5
2S	0.27	96.7	2.2	
3C	0.26	98.4	1.7	
3N	0.83	88.4	3.6	
3S	0.23	97.7	1.6	61.5
4C	0.16	97.7	1.5	
4N	0.16	98.7	1.3	
4S	0.18	98.3	1.8	70.5
5C	0.17	97.7	1.7	82.0
5N	0.16	98.9	1.7	
5S	0.19	98.3	1.3	
6C	0.13	95.2	1.5	70.0
6N	0.15	94.9	1.3	
6S	0.14	85.0	1.2	

1.1.2.1 Mission Creek

Phase I data indicated that Mission Creek sediments are no longer toxic and contaminated, although portions of the creek were identified as "toxic hot spots" using BPTCP criteria and data collected in 1994 and 1997.

A total of 13 surface stations extending from the creek origin to the mouth were sampled and analyzed in the Phase I study (ADL 1999b). All 13 were analyzed for chemical contaminants and six of the 13 were analyzed for toxicity. None of the six stations exhibited toxicity combined with elevated chemical contaminants, defined as less than 68.5% survival and an ERM quotient greater than 0.5 by the BPTCP. Contrary to previous BPTCP findings (see Section 4 in ADL 1999b), Mission Creek had good overall survival (i.e., > 73%) for all six sediments tested (Table 1-2) with a maximum survival of 85% recorded at two upper creek stations (1N and 3N), closest to the CSO. All stations tested had higher survival than the Phase I reference site at Paradise Cove (i.e., 65%). Although there was no significant toxicity at Mission Creek, eight of the 13 stations had ERM quotients greater than 0.5 (Table 1-2), and toxicity was not tested at four of these stations. However, the highest ERM quotient (1.53) was recorded at Station 2S, which was not toxic (74% survival). Elevated ERM quotients were driven primarily by elevated concentrations of lead, mercury, zinc and high molecular weight PAH, and all upper creek stations had high concentrations of TOC (i.e., > 2%). Toxicity, ERM quotients, percent fines and TOC results are shown for Mission Creek surface sediments in Table 1-2.

Table 1-2. ERM quotient, % fines, TOC and toxicity results for Mission Creek surface sediments.

Station	ERMQ	Fines (%)	TOC (%)	Amphipod Survival (%)
1N	1.11	27.8	2.9	85.0
1S	1.17	24.0	2.5	
2N	0.94	24.1	4.5	
2S	1.53	34.0	4.2	74.0
3N	0.85	92.1	4.4	85.0
3S	0.75	82.0	3.4	
4N	0.57	93.9	2.8	
4S	0.70	91.9	3.2	78.5
5N	0.22	98.2	1.5	77.0
5S	0.25	97.8	1.8	
6C	0.15	94.7	1.4	
6N	0.14	90.6	1.3	82.0
6S	0.16	93.7	1.3	
Paradise Cove		90.3	1.2	65.0

1.1.2.3 Yosemite Creek

A total of 18 surface samples extending from the creek origin to the mouth were collected and analyzed in the Phase I study (ADL 1999c). All 18 were analyzed for chemical contaminants and six of the 18 were analyzed for toxicity. All of the toxicity results were rejected due to the high probability of test interference from large predator polychaetes, which were found in at least one laboratory replicate for most of the field samples. Toxicity was performed following a modified test protocol used in the BPTCP, as required by the SFBRWQCB. Use of standard (e.g., EPA, ASTM) protocols allow for the removal of resident predator organisms by press sieving, while the BPTCP protocol does not. Toxicity testing will be performed at six stations using ASTM standard test methods for the Phase II study.

All Yosemite Creek stations had ERM quotients greater than 0.5; however, TOC and percent fine-grained sediments were correspondingly high. Percent fine-grained sediments exceeded 80% for all upper creek stations (i.e., stations 1-3), except Station 2S (75.4%), and TOC was greater than 2% for all upper creek sediments. ERM quotients, percent fine-grained sediments and TOC results are shown for Yosemite Creek surface sediments in Table 1-3.

Table 1-3. ERM quotients, % fines, and TOC results for Yosemite Creek surface sediments.

Station	ERMQ	Fines (%)	TOC (%)	Station	ERMQ	Fines (%)	TOC (%)
1N	0.87	97.0	2.3	4N	0.57	92.1	1.6
1S	0.52	97.5	2.0	4S	0.54	90.0	1.9
2N	0.73	93.3	2.4	5A	0.52	81.2	1.7
2S	1.32	75.4	2.3	5C	0.55	92.5	1.8
3N	0.72	81.7	2.6	5N	0.52	82.7	1.6
3S	0.67	91.2	2.7	5S	0.35	95.1	1.5
4C	0.63	91.5	2.4				

Note: Toxicity results were disqualified from use due to interference from resident predators

2.0 PHASE II STUDY DESIGN

The Phase II investigation of the three creeks is designed to determine the extent of environmental impact to sediments that have received and continue to receive combined effluent and stormwater discharges from SFPUC operated CSOs. Since applicable or relevant and appropriate requirements (ARARs) have not been developed for contaminants in marine sediments, assessment of environmental impact will be based on comparison of outfall sediments to suitable in-bay reference sediments. Creek and reference sediments that differ significantly in grain size and/or organic carbon will be normalized prior to comparison (inference testing) to minimize differences in chemical concentrations due to physical attributes. This approach is recommended as a modification to the existing BPTCP approach which is based on observed amphipod toxicity (i.e., > 69.5% of control survival) and exceedance of an effects-range median (ERM) summary quotient (i.e., > 0.5). Sediment quality guidelines, adopted from Long et al. (1995) ERM values, were used in the BPTCP to evaluate the extent of chemical contamination (Hunt et al. 1998). Limitations of the approach used in the BPTCP are discussed in detail in draft reports for each of the three creeks, submitted to the SFBRWQCB in June 1999 (ADL 1999a, 1999b, 1999c).

2.1 Overall Objectives and Approach

The question of whether creek sediments are impacted and pose a threat to the ecology of San Francisco Bay relative to reference sediments will be answered based on an evaluation of surface sediment chemistry, toxicity and bioaccumulation data. This weight-of-evidence approach extends the reference envelope approach, used in the BPTCP only for toxicity data, to chemistry and bioaccumulation data. The results of these tests will be applied to the decision matrix shown in Table 2-1, which presents specific actions in response to results produced for each of the three data types, ranging from consideration for remedial or preventative action to no further action at the creeks. Sediment tests will be repeated in Spring 2000 to replicate field conditions used in previous BPTCP studies, which used data collected at the end of the wet weather season (i.e., April/May). The decision matrix will be applied to Phase II combined data collected in Fall 1999 and Spring 2000, providing similar results are obtained between the two seasonal data sets, with bioaccumulation testing performed only in Spring 2000. If disparate results for chemistry and toxicity tests are produced between the two studies, additional studies may be recommended to evaluate seasonal trends, or the SFPUC may explore remedial or preventative actions with the SFBRWQCB. Table 2-1 is an abbreviated decision matrix, which presents appropriate actions for the most probable data outcomes. Unlikely outcomes such as significant bioaccumulation in the absence of elevated sediment chemistry are not shown, but will be addressed if they occur.

Table 2-1. Proposed decision matrix to assess environmental impact.

Chemistry	Toxicity	Bioaccumulation	Action
+	+	-	Consideration for remedial or preventative action
+	-	-	No further action
+	-	+	Consideration for remedial or preventative action
-	+	-	Further studies to determine cause of toxicity
-	-	-	No further action
+	+	+	Consideration for remedial or preventative action

Pluses (+) denote significantly higher values in creek sediments compared to reference sediments for any single test.
Minuses (-) denote no significant differences between creek and reference sediments.

2.1.1 Reference Site Selection and Use

The reference sites proposed for this study have been shown to represent background conditions for San Francisco Bay (Hunt et al. 1998). The six sites range in location from the south bay to the northern reaches of Tomales Bay, and are comprised primarily of fine-grained sediments (i.e., >80%) with moderate organic carbon content (i.e., approximately 1%). Five of the reference sites have been previously sampled in the Regional Monitoring Program (RMP) and/or BPTCP. A sixth reference site will be sampled at Tomales Bay, to broaden the reference range of TOC and grain size results. Tomales Bay has been used as a "fine-grained" reference site in numerous dredge material testing programs, and has a consistent record of low contamination and high bioassay survival. These reference sites will be re-evaluated to determine if they are suitable reference sites for the creeks based on the following discussion.

They are not well matched with the environmental conditions of the creeks under investigation, due to differences in grain size/mineralogy, total organic carbon (i.e., 3-4%), hydrodynamics and other conditions (e.g., temperature, depth, salinity), that may confound test results. They are proposed for use however, due to their established history within the BPTCP and RMP, and the lack of other established reference locations that may better represent creek conditions.

Sediment contaminants are frequently associated with low-energy (depositional) environments (such as the creek terminus) where fine particles accumulate. These environments are potential repositories for contaminants, irrespective of proximity to contaminant source. Despite these facts, many investigations, including the BPTCP rely on ERMs which essentially ignore TOC influences (since TOC averages 1.2% for the corresponding data set), even though depositional areas in San Francisco Bay frequently exceed 2% TOC.

Since the study and reference sites are not well-matched, sediments will be normalized to minimize effects that may be due to physical characteristics. This is a common approach that is used to correct disparities between test and reference areas that are independent of contaminant inputs. For example, sediments may be normalized using grain size or TOC, since these important characteristics are known to have a significant influence on sediment contaminant concentrations and associated toxicity (Di Toro et al. 1991; Swartz et al. 1994).

Since the main route of toxic exposure for many organisms occurs from high contaminant bioavailability in sediment pore-water (USEPA 1993), the equilibrium partitioning between the soluble porewater-phase and relatively unavailable phases associated with organic carbon, is a critical factor. For nonionic organic compounds (e.g., chlorinated pesticides, PAH, PCB) that have strong binding affinity for organic carbon, higher TOC levels portend a reduced level of bioavailability. This equilibrium partitioning approach was adopted by the EPA (1993) in the recommendation to normalize nonionic organic chemical sediment concentrations to organic carbon content. Application of these guidelines to three of the five EPA proposed compounds (i.e., three PAH) would increase sediment quality criteria 2-14 times for sediments with an average TOC concentration of 2.5%, such as those located in the west end of Islais and Mission Creeks. Total DDT was the only BPTCP "chemical" with a sediment quality criterion based on TOC concentration (i.e., 100 μg total DDT per gram organic carbon [100 $\mu g \cdot g^{-1}$ OC]) from Swartz et al. (1994). Use of this criterion substantially reduces the effective concentration of DDT in sediments with

high TOC, such as these creeks. For example, a sediment dry weight concentration of 100 $ng \cdot g^{-1}$ DDT corresponds to an organic carbon normalized concentration of 10 $ng \cdot g^{-1}$ DDT for a sample containing 1% TOC (a ten-fold reduction in DDT concentration). The same sediment sample containing 2% TOC (similar to those in the west end of the creeks) would produce a twenty-fold reduction in DDT (i.e., 5 $ng \cdot g^{-1}$ DDT).

Consistency with other proposed regulatory guidelines (USEPA 1993), as well as scientific defensibility, calls for use of criteria based on organic carbon content for all nonionic organic compounds, such as that used for total DDT in the BPTCP, especially if these data are to be used in support of biological impacts. Inorganic chemicals, such as metals, also have been shown to increase with various sediment physical attributes, most notably percent fine-grained sediment and TOC (which often co-vary).

Aluminum and iron are common elements to sediments and soils that occur in naturally high concentrations (i.e., 0.5-4%). Aluminum is mostly present as a structural component of aluminosilicate minerals, whereas iron may occur as a structural component of aluminosilicates as well as an oxide coating on mineral grains. Under natural conditions, when levels of aluminum or iron are higher in a sediment sample, concentrations of trace metals generally also are higher. Lower concentrations of aluminum, iron and metals are found for sediments composed primarily of quartz sand or shell carbonates, whereas higher metal concentrations are common to more clay-rich, fine-grained, organically-rich sediments, such as those encountered in the subject creeks. This condition is encountered even in the absence of contaminant inputs from human activity. For these reasons, and the fact that Phase I studies produced significant positive correlations between physical attributes (such as TOC and iron) and many organic and inorganic chemical concentrations (ADL 1999a), contaminant concentrations will be normalized to TOC or another proxy (e.g., iron for metals) in this study. The proxy with the strongest positive correlation with contaminant concentrations will be used in the normalization.

In summary, selection and use of appropriate reference sites is critical in determining if the study site (in this case the subject creeks) is impacted. Appropriate reference sites are not necessarily pristine, however, they should have the same loading history (e.g., dissolved water concentrations or particulate load) and possible loss (e.g. sediment burial, erosion, dredging, degradation) of contaminants as the study site, other than the release (which refers to the source of the impact) under investigation (USEPA 1997). Reference site(s) should have similar environmental features to the study site that, in addition to the release being studied, will affect assessment test results. Tests should be selected that are highly sensitive to the contaminant(s) or disturbance being assessed and insensitive to other factors. If representative reference sites do not exist or can't be found, then to the extent possible, confounding factors must be minimized when comparing data between two mismatched sites (such as the creeks and in-bay reference areas). Only then can results between the study and reference sites be compared, and the differences between them inferred to be due to creek-related inputs.

2.1 Phase II Surface Sediments

Sediment chemistry and toxicity will be measured in Fall 1999 at Islais, Mission and Yosemite Creeks, and the six reference locations. Parameters and number of stations sampled are summarized in Table 2-2.

Station locations for the three creeks are shown in Tables 2-3 through 2- and Figures 1 through 3. Reference station locations are shown in Table 2-6.

Surface sediments will be measured for trace level polychlorinated biphenyl congeners (PCB), polynuclear aromatic hydrocarbons (PAH) including alkylated homologs, chlorinated pesticides and heavy metals. Chemicals of concern identified in Phase I studies were associated with these chemical classes for each of the three creeks (e.g., > 0.5 ERM quotient). Surface sediments will also be tested for toxicity using a 10-day amphipod test. Acute toxicity will be measured with the amphipod crustacean *Eohaustorius estuarius* exposed for 10-days to whole sediment. Conventional sediment parameters will be assessed to determine whether any observed toxicity is attributable to natural products of organic degradation such as ammonia and dissolved sulfides. Modifications to the BPTCP toxicity protocol are proposed (Section 3) and include 1) exchanges of overlying water both before and during (one per day) the test to reduce ammonia, and 2) press sieving of sediments prior to test initiation to remove potential resident predators.

Sediment grain size and total organic carbon (TOC) will be measured to support interpretation of chemical and toxicity data. A list of analytical tests for surface sediments collected at each site is presented in Table 2-2. Analyte lists, method descriptions, and detection limits for each test are presented in Section 4.0. Analytical and quality control methods are in conformance with regional RMP procedures and the previously conducted Phase I study.

Sediment chemistry and toxicity tests will be repeated in Spring 2000. In addition, a pre-test for in-situ 28-day bioaccumulation test with clams will be conducted before sediments are collected for other tests at total of five locations (one at each creek, and two reference sites). The pre-test will provide data on the feasibility of conducting in-situ bioaccumulation testing at these sites. In-situ bioaccumulation testing will be conducted at all sample locations in Spring 2000 if the pre-tests are successful (defined as ≥ 70% survival for each location). Standard in-laboratory bioaccumulation testing will be performed in Spring 2000 for any test site that fails the pre-test.

Table 2-2. Numbers and types of analyses performed for surface sediments at each site.

Site	Surface Sediment Analyses	No. of Stations
Islais Creek	PCBs, pesticides, PAH, metals, toxicity, TOC, grain size	6
Mission Creek	PCBs, pesticides, PAH, metals, toxicity, TOC, grain size	8
Yosemite Creek	PCBs, pesticides, PAH, metals, toxicity, TOC, grain size	8
In-Bay Reference Area	PCBs, pesticides, PAH, metals, toxicity, TOC, grain size	6

Station transects will extend perpendicular to shore in the vicinities of selected CSOs and storm drain locations in the creek channels (see Figures 1-3). Select station locations sampled during Phase I, primarily located at creek ends, will be re-sampled for Phase II. Reference site locations will correspond with previously sampled BPTCP locations. Station locations and general site descriptions are provided in Tables 2-3 through 2-6. A description of sampling design for each creek follows.

2.1.1 Islais Creek

Six stations will be sampled within Islais Creek. These stations were previously sampled for Phase I and consist of two stations from each of the three western-most transects, extending from the main discharge CSO to the 3rd Street Bridge. Targeted stations include all Phase I stations that had less than 68.5% survival in toxicity tests, as well as all stations with ERM quotients greater than 0.5. Phase II targeted stations are shown in Figure 1 and Table 2-3. Sediment will be collected from the top 5 cm of a standard 0.05 m^2 Ponar grab, homogenized and subsampled for toxicity, PCBs, PAHs, pesticides, metals, TOC, and grain size.

Table 2-3. Phase II Islais Creek surface sediment sampling stations.

Station	Depth (ft)	Latitude (N)*	Longitude (w)*	Location
1N	9	37° 44’ 55.20”	122° 23’ 34.38”	43 m from rock pile, 94 m from S. Shore CSO, 33 m from N Shore CSO
1S	5	37° 44’ 55.74”	122° 23’ 34.68”	44 m from pipe under fwy, 32 m from S. CSO
2N	20	37° 44’ 51.30”	122° 23’ 25.38”	90 m from Rankin St. CSO, 31 m from Bulk S Shore, 236 from bridge
2S	18	37° 44’ 48.12”	122° 23’ 26.40”	30 m from Rankin St. CSO, 280 m from Bridge N.
3N	16	37° 44’ 51.54”	122° 23’ 13.45”	71 m from BPS bypass structure
3S	32	37° 44’ 49.92”	122° 23’ 17.64”	25 m from BPS Bypass structure on S. shore, 57 m from bridge

*Station coordinates shown in NAD 83 datum

2.1.2 Mission Creek

Eight sediment stations, that were previously sampled in Phase I, will be re-sampled (Figure 2) at Mission Creek extending from the main discharge CSO to the 4th Street intersection. Targeted stations include all Phase I stations that had ERM quotients greater than 0.5. There were no Phase I sediments with significant toxicity (i.e., < 68.5% survival). Sediments will be collected from the top 5 cm, homogenized and subsampled for toxicity, PCBs, PAHs, pesticides, metals, TOC, and grain size.

Table 2-4. Phase II Mission Creek surface sediment sampling stations.

Station	Depth (ft)	Latitude (N)*	Longitude (W)*	Location Description
1N	5	37º 46’ 14.28”	122º 23’ 48.66”	56 m from main CSO 24 m from north side
1S	5	37º 46’ 14.82”	122º 23’ 49.69”	56 m from main CSO 20 m from south side
2N	9	37º 46’ 17.54”	122º 23’ 46.57”	10 m from 6th St. north side CSO
2S	6	37º 46” 18.25”	122º 23’ 44.11”	20 m from 6th St. south side CSO, 190 m from main CSO
3N	13	37º 46’ 23.74”	122º 23’ 38.88”	10 m from north side CSO
3S	13	37º 46’ 22.71”	122º 23’ 37.80”	32 m from north side CSO, 16 m from south side pier
4N	13	37º 46’ 29.43”	122º 23’ 29.90”	
4S	16	37º 46’ 30.25”	122º 23’ 30.93”	39 m from north side CSO pipe hole, 5 m from S pier

*Station coordinates shown in NAD 83 datum

2.1.3 Yosemite Creek

A total of eight stations will be sampled in Yosemite Creek (Figure 3). Sediment samples will be taken from previously sampled stations extending from the end of the main creek body out to the creek mouth. Two stations each will be sampled from the north and south sides of transects 1-3. Single stations will be sampled from transects 4 and 5 (closest to the creek mouth). Surface sediments will be collected from the top 5-cm of the Ponar grab and analyzed for toxicity, PCBs, PAHs, pesticides, metals, TOC and grain size.

Table 2-5. Phase II Yosemite Creek surface sediment sampling stations.

Station	Latitude (N)*	Longitude (W)*	Location Description
1N	37° 43’ 27.60"	122° 23’ 06.97"	42 m N of S bank, 32 m S of fence on N bank, 90 m W of warehouse
1S	37° 43’ 26.95"	122° 23’ 07.42"	34 m W of end structure, 25 m N of grey warehouse, 23 m east of bank
2N	37° 43’ 25.58"	122° 23’ 01.50"	33 m S of N bank, 44 m N of S bank, 162 m E of warehouse
2S	37° 43’ 24.60"	122° 23’ 02.30"	62 m S of N bank, 15 m N of S bank, 161 m W of warehouse
3N	37° 43’ 21.94"	122° 22’ 57.36"	21 m from Griffith St. CSO, 46 m N of S bank, 346 m W of warehouse
3S	37° 43’ 21.73"	122° 22’ 57.61"	Just E of Griffith St. CSO, 21 m from cement block on S bank
4C	37° 43’ 20.77"	122° 22’ 55.57"	Mid-creek, previous U.S. Navy station
5N	37° 43’ 18.97"	122° 22’ 51.49"	45 m to N bank 216 m to old Fitch Street CSO, previous U.S. Navy station

*Station coordinates shown in NAD 83 datum

2.1.4 Reference Area

A total of six stations, five located within San Francisco Bay and one at Tomales Bay, will be sampled as reference sites (Table 2-6). Five of these in-bay sites were previously sampled and included as acceptable reference sites in past BPTCP studies. The Tomales Bay site was evaluated in the BPTCP but not used in the development of toxicity tolerance limits. It is included in this study because it is a "fine-grained" reference site that has consistently produced low toxicity and chemical concentrations in numerous dredge material disposal studies.

Table 2-6. Phase II Reference Area surface sediment sampling stations.

Station	Location	BPTCP Station	Latitude (N)*	Longitude (W)*	Location Description
1R	Paradise Cove	20005	37° 53’ 57.00"	122° 27’ 51.60"	Central San Francisco Bay
2R	Tubbs Island	20006	38° 06’ 52.20"	122° 25’ 09.60"	San Pablo Bay
3R	Island #1	20007	37° 06’ 43.20"	122° 19’ 42.60"	San Pablo Bay
4R	North Site	20013	37° 34’ 13.80"	122° 08’ 58.50"	South San Francisco Bay
5R	South Site	20014	37° 32’ 10.80"	122° 07’ 09.60"	South San Francisco Bay
6R	Marconi Cove	20009	38° 08’ 21.60"	122° 52’ 27.60"	Tomales Bay

*Station coordinates shown in NAD 83 datum

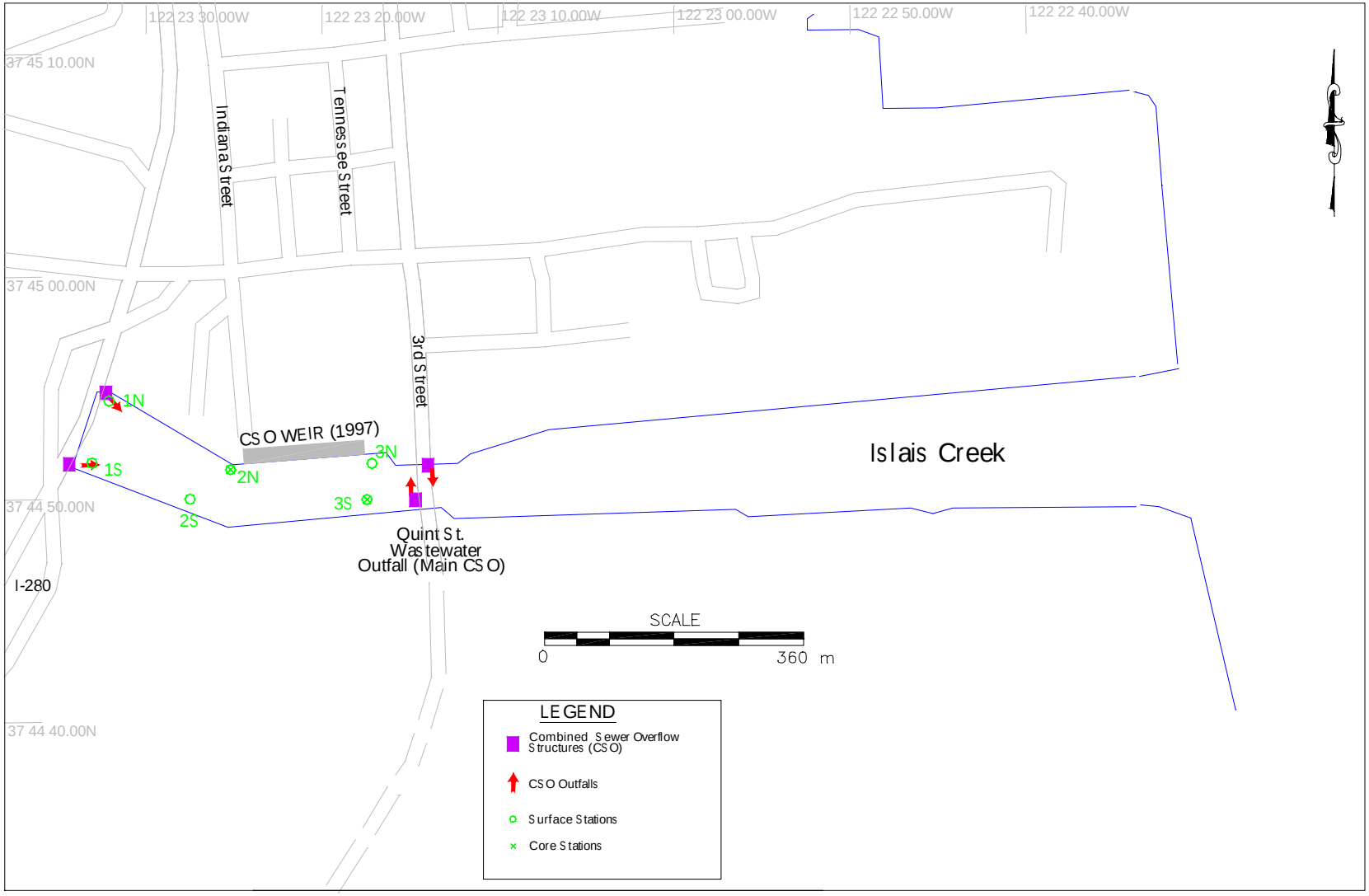

Figure 1. Phase II sampling locations at Islais Creek.

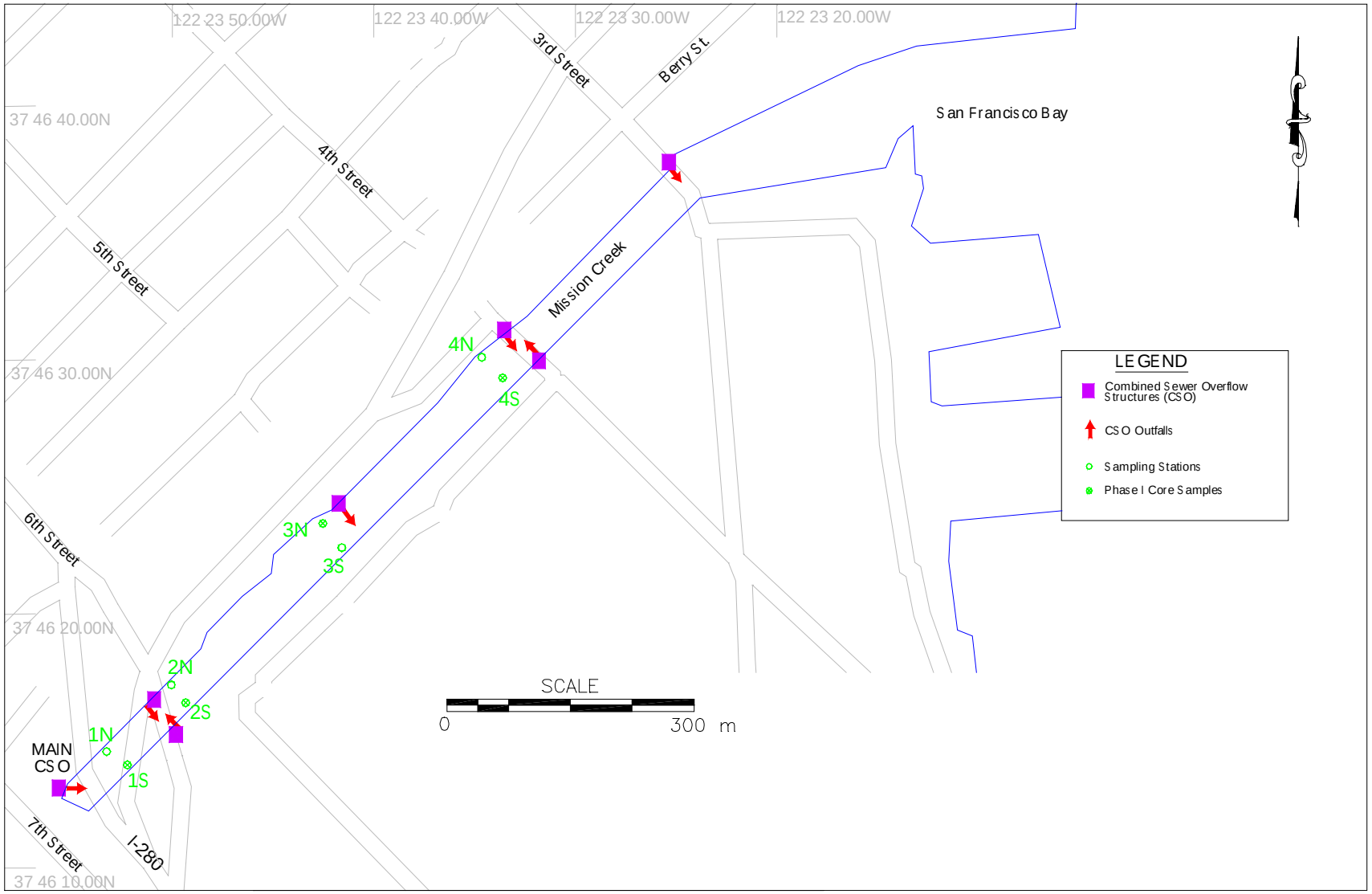

Figure 2. Phase II sampling locations at Mission Creek.

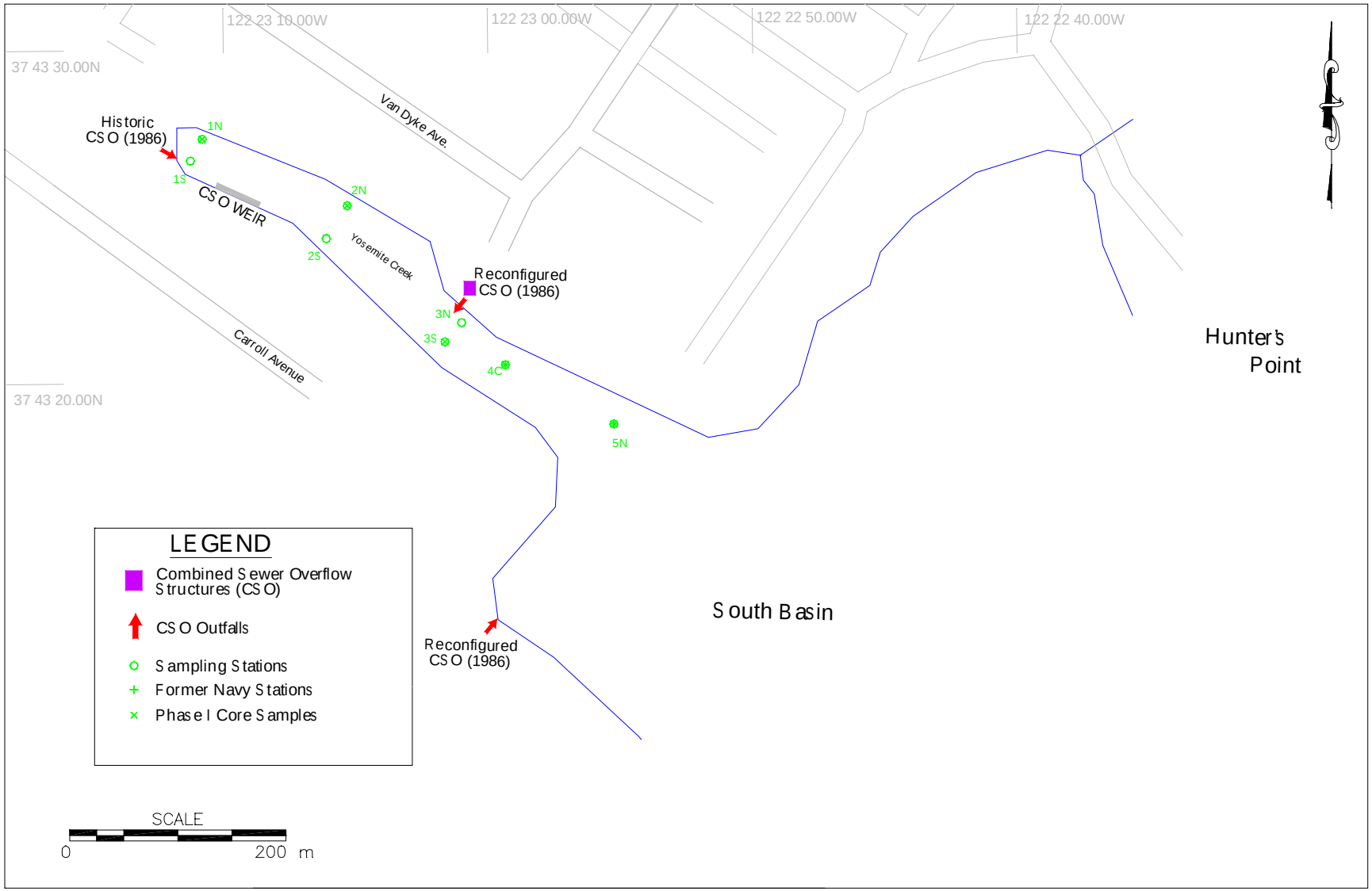

Figure 3. Phase II sampling locations at Yosemite Creek.

2.2 Phase II Subsurface Sediments

Selected subsurface sediments that were collected and archived for Phase I studies will be analyzed for Phase II. Phase I studies included collection of 5-6 subsurface cores from each creek that penetrated a maximum depth of 4 ft. The top two core sections (i.e., 0-1 and 1-2 ft) were analyzed for chemistry as part of a tiered approach in Phase I. The remaining two core sections (i.e., 2-3 ft and 3-4 ft) from the most contaminated sites within each creek will be analyzed as shown in Table 2-7. The locations of Phase I cores that will undergo additional analyses are shown for each creek in Figures 1-3. Subsurface data for each of the entire core samples will be used to determine whether significant vertical contaminant gradients exist, which if they do, support the argument that buried sediments are "in-place" and there is no significant resuspension of contaminants to the bay.

Table 2-7. Phase II subsurface sediments for bulk chemistry analysis.

Station	Depth	Analyses*	Comments
Islais Creek			
1C	2-3 ft, 3-4 ft.	PP, PAH, metals, TOC	
2N	2-3 ft, 3-4 ft.	PP, PAH, metals, TOC	
3S	2-3 ft, 3-4 ft.	PP, PAH, metals, TOC	
4S	2-3 ft, 3-4 ft.	PP, PAH, metals, TOC	
Mission Creek			
1N	2-3 ft	PP, PAH, metals, TOC	3-4 ft core not collected due to refusal*
2S	2-3 ft, 3-4 ft.	PP, PAH, metals, TOC	
3N	2-3 ft., 3-4 ft.	PP, PAH, metals, TOC	
4S	2-3 ft., 3-4 ft.	PP, PAH, metals, TOC	
Yosemite Creek			
1N	2-3 ft., 3-4 ft.	PP, metals, TOC	
4C	2-3 ft., 3-4 ft.	PP, metals, TOC	
5N	2-3 ft.	PP, metals, TOC	3-4 ft core not collected due to refusal*

*PP = pesticides and PCB congeners

2.3 Data Analysis and Interpretation

All data analyses will be performed by computer using the Statistical software SAS® (ver. 6.12) in batch programming mode.

2.3.1 Descriptive statistics

Descriptive statistics will be performed on all physical, chemical, and biological data. These statistics include computations for number of samples, means standard deviations, ranges of values, and frequencies of detectable concentrations. Computations will be performed on final data that meet data quality objectives (Section 5).

Descriptive statistics will be computed directly for chemical and physical results. Non-detect results for chemistry data will be represented as one-half of the method detection limit in all statistical analyses.

Mean values for each set of bioassay (toxicity) laboratory replicates will be used in the analysis. Replicate values for each bioassay will be tested for outliers using the Studentized Range Test (Natrella 1966). Outliers will be discarded after review by the project toxicologist, and mean values and standard deviations will be calculated using the remaining replicates.

2.3.2 Comparative statistics

Inference tests will be used to determine whether creek (test) sediments are more contaminated or toxic than reference site sediments. Prior to inference testing, chemical and biological results will be tested for normality using the Shapiro-Wilk statistic (Shapiro and Wilk 1965) to meet test assumptions. Chemistry and toxicity data may be transformed prior to analysis to address non-normality. Non-normal bioassay data may be arcsine transformed according to test protocol recommendations.

2.3.2.2 Testing of grouped stations

Tests will be performed for grouped and individual creek stations, compared to grouped reference stations (similar to a reference envelope). Grouped comparisons are made to determine whether combined creek surface sediments are different from combined reference sediments. One-tailed Student's t-test (Steel and Torrie 1960) will be performed for each of the two grouped comparisons. For each test, the equality of variance will be tested; when variances are unequal, the approximate t-statistic for unequal variance will be used. A Bonferroni adjustment for multiple testing will be applied to the resultant probabilities (Milliken and Johnson 1984).

For non-normal data, a random two-way crossed ANOVA approach may be used (Smith 1995). The model is completely random, since in this application, results may be generalized to other locations and times not in the sample from which the bounds are computed (like the reference envelop approach used in the BPTCP). Beckman and Tietjen (1989) derive two-sided tolerance intervals for a random balanced crossed ANOVA design, and Bagui et al. (1996) and Smith and Riege (1998) derive one-sided tolerance intervals for a random unbalanced crossed ANOVA design. One-sided limits that can be applied to unbalanced data sets are most appropriate for this study. One-sided intervals are appropriate for parameters where impact is associated with either an increase or decrease in the parameter value being tested (such as contaminant concentration and survival, respectively). Also, unbalanced data will result for at least one of the creek/reference comparisons (e.g., Mission Creek and Yosemite Creek have 8 stations vs. the reference area of 6).

2.3.2.3 Testing of individual stations

Individual comparisons will be made for each station within each creek using a group predictive limit (Steel and Torrie 1960), to produce a "reference envelop" for each measured parameter. Comparisons will be made for individual bioassay, physical and chemical parameters for each surface sediment. This procedure identifies potential problems (hot spots) at individual stations that might be concealed in the group comparisons. For normally distributed data, predictive limits will be calculated for each group for bioassay, physical and chemical results. Both 95% and 99% predictive limits will be calculated, representing unadjusted and Bonferroni adjusted limits, respectively. A lower predictive limit will be calculated for group survival (to identify stations with lower percent survival compared to the group);

and an upper predictive limit will be calculated for group chemistry (to identify stations with greater chemical concentrations compared to the group). The predictive interval is a modification of the confidence interval and is used when comparing individual results to a population mean.

If data fail test assumptions of normality, nonparametric tolerance interval bounds may be used (Hahn and Meeker 1991, Smith 1995).

3.0 FIELD PROGRAM

The field program will be divided into five general tasks: mobilization, navigation, surface sampling, bioaccumulation pre-tests, sample processing and demobilization. Each of the three sampling sites possesses unique qualities and problems, and as a result will require logistics specific to the creek sampled.

3.1 Equipment Mobilization

Prior to initiation of the survey, an equipment list of field materials and supplies will be prepared and reviewed by the field manager. Additionally, field notebooks and sample identification labels will be prepared. All materials and equipment will be assembled, checked against the project equipment list and inspected. The survey vessel will be notified of the schedule and inspected for readiness. Field personnel will be assigned, notified of sampling schedule and provided a summary of expected field accomplishments. Appropriate authorities (e.g., bridge keepers) will be notified of schedule and any special requirements. Receiving laboratories will be informed of the scheduled sampling and provided estimates of expected sample quantities and arrival times. All equipment will be loaded aboard the sampling vessel and setup a day prior to the sampling event, if possible.

3.2 Navigation and Station Location

A differential global positioning system (DGPS), accurate to ± 2 m, will be used to position and navigate the survey vessel. In addition to the DGPS, digital range-bearing monoculars (accurate to ± 2 m) will be used to verify that Phase II station locations coincide with previously sampled Phase I locations, or when a DGPS signal cannot be obtained (e.g., under the freeways). The following procedures will be used to navigate and locate stations.

1. The special area (e.g., CSO) will be located and defined as distance zero.
2. Using the DGPS as a guide, the distance to the first station will be traversed by the vessel.
3. The range-finder will be used to locate the first station (usually the station closest to the CSO and the south side of the channel).
4. A marker buoy may be deployed at the station and the distance from zero and the distance from shore will be measured with range-finder and recorded. Magnetic bearing will be recorded with each distance measurement.
5. Station latitude and longitude from the ship's DGPS will be recorded once the vessel is on the targeted coordinates (see Tables 2-3 through 2-6).
6. The station will be sampled as subsequently described, the marker-buoy will be recovered and the ship will move to the next station.
7. Steps 1-6 will be repeated until all stations have been sampled.

3.3 Sediment Sample Collection

Sampling will commence after the vessel is determined to be on station. Depending on the ability of the sampling vessel to maintain station position, samples may be taken by the "live boating method." Live boating requires the vessel captain to position the sampling area of the vessel (e.g., stern, or mid-ships) directly over the station marker and hold station until the sample is taken. When live boating is not possible the vessel will be positioned on station with anchors. Weather and tidal conditions will determine the number of anchors required for adequate station maintenance.

3.3.1 Surface Sampling

Surface sediment samples will be collected with a 0.05-m^2 Ponar grab sampler. The grab is constructed of stainless steel and coated with Halar to reduce contamination. A sufficient number of grabs will be taken at each station to provide surficial sediment for chemical, physical and toxicological parameters. Sampling procedures will be conducted in compliance with quality control measures established to minimize the potential for contamination in the field.

Prior to initiation of the field survey, sampling equipment that comes in direct contact with sediments will be decontaminated as follows:

- Rinse with tap water
- Wash with a non-phosphate detergent (e.g., Alconox) using a brush and rinse with deionized water.
- Rinse with methylene chloride or hexane and air dry.

During sampling, the grab sampler will be rinsed with seawater to remove visible sediments between each station. If necessary, it may be scrubbed using a non-phosphate detergent.

The quality of each grab sample will be determined by visual inspection prior to subsampling. Once the sample returns to the deck of the survey vessel, the grab will be visually inspected to ensure that there was no leakage of water or fine sediments, and that the natural surface layer of the sample was undisturbed. Any samples without overlying water or with a disturbed sediment surface will be rejected. Once the sediment grab sample is collected and approved, the sediment is sub-sampled for chemical and physical analyses. Replicate grabs will be collected and homogenized in a Halar or Teflon coated bucket.

3.3.2 Chemistry Sediment Grab Sub-Sampling

Prior to sediment subsampling, any overlying water is gently decanted or siphoned off with a pre-cleaned Teflon tube. Chemistry samples are taken using the following procedure: using a pre-cleaned 5-cm Teflon-coated scoop, the top 5 cm of sediment is removed and placed into clean Halar-coated stainless steel container. The scoop is 5 cm deep and is used to gauge the depth of the collected sample. Sediment will not be collected near the sides of the grab (distance from grab side approximately 2 cm). Collected samples are covered with aluminum foil and set aside for homogenization and sample aliquoting. The sample is homogenized with a clean Halar scoop or Teflon mixing rod. The scoop and stainless steel container used to mix the sample are cleaned between each are previously described.

Sediment Chemistry and Toxicity Sample Allocation. Homogenized sediment will be aliquoted into two 250-mL pre-cleaned and labeled borosilicate glass sampling jar for organics and archival, respectively; one 250-mL precleaned and labeled polycarbonate or polyethylene sampling jar for trace metals; and plastic jars for grain size and TOC.

All sediment samples are labeled with unique sample numbers, date and time of collection, technicians initials, preservation technique (e.g., 4°frozen) and stored on ice in coolers immediately after collection. All chain of custody, storage and transportation requirements presented in this SAP (Section 3.3.4) will be followed.

Sediment remaining in the stainless steel container (at least 2L) for toxicity analyses will be transferred using the Halar coated scoop into a large, clean plastic jar, stored and shipped on ice (approx. 4^{o} C) to the laboratory.

Upon arrival at the laboratory, sediment chemistry samples will be stored in a freezer (-20^{o}C) until initiation of sample analysis. Grain size and toxicity samples will be stored at 4^{o}C prior to analysis.

3.3.3 Field Sample Contamination

Due to the sensitive nature of the chemical analyses to be performed, every precaution will be taken against potential sources of contamination during sediment sampling operations. Representative samples of potential "field-borne" contaminants will be collected and archived for future analysis in the event that outside contamination could have occurred. These sources include airborne stack gases from vessel engines, oil slicks from fuel spills or bilge discharges, and hand-transferred oils and grease. The following guidelines will be followed when sampling:

1. Cleaning of equipment just prior to arriving on station.
2. Ensuring that the sampling equipment was never deployed or recovered through organic slicks observed on the surface of the water (sheens).
3. Closing the top access doors to the sampler when not being deployed or cleaned.
4. Covering all sampling equipment (e.g., grab sampler) when not in use.

3.3.4 Field Sample Chain of Custody, Storage, and Transportation

Immediately following collection, each sample will be labeled and chain of custody procedures initiated. Chemistry and biology samples will be aliquoted into appropriate containers and labeled with the following information:

- Sample identification
- Date
- Time
- Initials of person who collected samples
- Analysis Type (e.g., organics, metals, toxicity)
- Preservative (e.g., 4^{o} C)

The unique sample identification number will be a sequential value that is connected to sample information in the project database. Therefore every sample container will have a unique identification code that will identify data, analysis type, lab, grab number, and station ID. A separate station log will be maintained that contains sample IDs for each sample position (e.g., lat/long, water depth, and station notes such as grab quality). An Excel spreadsheet will be maintained that contains all of the sample information, location, and notes. Samples will be stored in coolers on ice prior to shipment or same-day transfer to the analytical laboratory. Samples designated for shipment will be sent "next-day" air (e.g., Federal Express). Receiving laboratories will receive faxed copies of the chains of custody and the shipper's identification numbers on the day of shipment. The Field Coordinator will contact each laboratory on the following day to validate that the samples were received in good condition.

4.0 ANALYTICAL PROGRAM

The analytical program is designed to provide detailed chemical and biological characterizations to determine the environmental condition at the study sites. The analytical approach features ultra-trace measurements of organic and inorganic compounds consistent with methods used in the San Francisco Bay RMP and the BPTCP. The following sections summarize both the analytical design and analytical procedures selected for this study. Analytical procedures are described for processing sediment samples for organic and inorganic analysis. A list of target analytes and corresponding detection limits are presented in Tables 4-2 through 4-4. Analytical procedures for biological analysis of sediment and water samples are also included.

Samples collected from the field surveys are divided and sent to respective laboratories for chemical and biological analysis. Analyses to be performed on sediments are polychlorinated biphenyls (PCB); chlorinated pesticides; polynuclear aromatic hydrocarbons (PAH); metals; grain size; total organic carbon (TOC); and 10-day acute amphipod toxicity (Table 4-1). Organic analyses will be performed by Arthur D. Little's, Inc., trace chemistry laboratory, located in Cambridge, Massachusetts. Metals, TOC and grain size will be analyzed at the SFPUC chemistry laboratory. Toxicity tests will be performed by the City's Oceanside biology laboratory. Sediment chemistry results will be reported in relation to sediment dry weight.

Table 4-1. Summary of Phase II (Fall 1999) sediment analytical methods and laboratories.

Parameter	Laboratory	Analytical Method
Chemistry		
Polynuclear Aromatic Hydrocarbons (PAH)	ADL	U.S. EPA SW-846 8270 modified using SIM
Polychlorinated Biphenyl Congeners (PCBs) & Chlorinated Pesticides	ADL	U.S. EPA SW-846 8082 modified for congener analysis
Metals	SFPUC	US EPA SW-846 6010 and 7000 series
Total Organic Carbon (TOC)	SFPUC	US EPA SW-846 Method 9060
Grain Size	SFPUC	Plumb et al. 1981
Biology		
10-day solid phase amphipod	SFPUC	ASTM E1367-92

4.1 Sediment Chemistry

4.1.1 Organic Analyses

Sediment Extraction: In summary, 30 g of homogenized sediment is serially extracted three times with a 1:1 acetone:methylene chloride solvent mixture utilizing an ambient temperature shaker table method. The procedure outlined in SOP ADL-2819 is modified for a final shaker table extraction. An orbital shaker table is set to 300RPM and after the addition of solvent and surrogates the samples are placed on the shaker table for a 1-hour final extraction. The samples are centrifuged and solvent is decanted into Erlenmeyer flasks.

The sediment samples are spiked with the appropriate amount of surrogates after the first addition of extraction solvent. The surrogates are: naphthalene-d_8, acenapaphthene-d_{10}, phenanthrene-d_{10}, and benzo(a)pyrene-d_{12} for PAH analysis; DBOFB, PCB 103, and PCB 198 for PCB and chlorinated pesticide analysis. The amount of surrogate compounds spiked corresponds to the level of contamination observed in each sample. The determination of the level of contamination is made by the person extracting the samples, in conjunction with the laboratory manager.

After sample extraction and concentration, the gravimetric weight is determined. Extracts are cleaned up on alumina column chromatography and an aliquot weighed. Additional sample cleanup and fractionation methods may be used to maintain low detection limits depending on the level of matrix contamination. The extracts are then aliquoted and submitted for GC/MS analysis for PAH target analytes, and a second aliquot is solvent exchanged in hexane and submitted for PCB/PEST target analytes by GC-ECD.

The quality control samples processed along with the sediment samples include one procedural blank and one duplicate analysis. Data quality objectives for the sediment analyses are presented in Table 5-1.

Total Extract Weight Determinations. Extract weights are performed on all extracts before alumina column cleanup and on tissue and sediment samples after alumina column following the procedure in SOP ADL-2821. The pre-alumina column gravimetric weights are used to determine lipid weights for tissue samples and if extract splits are necessary prior to alumina column cleanup for all samples.

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. Sediments will be analyzed for polynuclear aromatic hydrocarbons (PAH) by GC/MS in the selected ion mode (SIM). Approximately 200 µL of extract is submitted to analysis for PAH and steranes and triterpanes. The sample extract is injected onto a 30-m x 0.25-mm ID fused-silica capillary column with DB-5 bonded phase or equivalent. The extract will be analyzed by GC/MS SIM to determine the concentrations of parent and alkylated PAH fingerprint in the samples. Relative response factors (RRFs) of alkyl homologues will be based on the RRF of the parent compound for each alkyl homologue series. The concentration of the individual PAH will be calculated versus the internal standards, which are spiked into the sample prior to analysis. The analytes will be corrected for surrogate recoveries. The target PAH concentrations are quantified using average response factors (RF) generated from the five point calibration curve. As noted above, alkyl homologue series PAHs are assigned the response factor of the parent PAH compound.

Table 4-2. PCB congeners and chlorinated pesticides.

PCB Congeners - MDL 0.01-1 ng/g	Chlorinated Pesticides - MDL 0.1-2 ng/g
8 - 2,4'-Dichlorobiphenyl (C12)	Aldrin
18 – 2,2',5-Trichlorobiphenyl (C13)	alpha-Chlordane
28 – 2,4,4'-Trichlorobiphenyl (C13)	gamma-Chlordane
44 – 2,2',3,5'-Tetrachlorobiphenyl (C14)	cis-Nonachlor
52 – 2,2',5,5'-Tetrachlorobiphenyl (C14)	2,4'-DDT
66 – 2,3',4,4'-Tetrachlorobiphenyl (C14)	4,4'-DDT
77 – 3,3',4,4'-Tetrachlorobiphenyl (C14)	2,4'-DDE
101 - 2,2',4,5,5'-Pentachlorobiphenyl (C15)	4,4'-DDE
105 - 2,3,3',4,4'-Pentachlorobiphenyl (C15)	2,4'-DDD
118 - 2,3',4,4',5-Pentachlorobiphenyl (C15)	4,4'-DDD
126 - 3,3',4,4',5-Pentachlorobiphenyl (C15)	Dieldrin
128 - 2,2',3,3',4,4'-Hexachlorobiphenyl (C16)	Endrin
138 - 2,2',3,4,4',5'-Hexachlorobiphenyl (C16)	Heptachlor
153 - 2,2',4,4',5,5'-Hexachlorobiphenyl (C16)	Heptachlor Epoxide
170 - 2,2',3,3',4,4',5-Heptachlorobiphenyl (C17)	Lindane
180 - 2,2',3,4,4',5,5'-Heptachlorobiphenyl (C17)	Mirex
187 - 2,2',3,4',5,5',6-Heptachlorobiphenyl (C17)	trans-Nonachlor
195 - 2,2',3,3',4,4',5,6-Octachlorobiphenyl (C17)	
206 - 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (C17)	
209 - 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	

Table 4-3. Polycyclic Aromatic Hydrocarbons (PAH).

Polynuclear Aromatic Hydrocarbons (MDL 0.7-2.8 ng/g)	
Naphthalene	Fluoranthene
C_1-Naphthalene	Pyrene
C_2-Naphthalene	C_1-Fluoranthene/Pyrene
C_3-Naphthalene	C_2-Fluoranthene/Pyrene
C_4-Naphthalene	C_3-Fluoranthene/Pyrene
Acenaphthylene	Benzo[a]anthracene
Acenaphthene	Chrysene
Dibenzofuran	C_1-Chrysene
Biphenyl	C_2-Chrysene
Fluorene	C_3-Chrysene
C_1-Fluorene	C_4-Chrysene
C_2-Fluorene	Benzo[b]fluoranthene
C_3-Fluorene	Benzo[k]fluoranthene
Anthracene	Benzo[e]pyrene
Phenanthrene	Benzo[a]pyrene
C_1-Phenanthrene/Anthracene	Perylene
C_2-Phenanthrene/Anthracene	Indeno[1,2,3-c,d]pyrene
C_3-Phenanthrene/Anthracene	Dibenzo[a,h]anthracene
C_4-Phenanthrene/Anthracene	Benzo[g,h,i]perylene
Dibenzothiophene	
C_1-Dibenzothiophene	
C_2-Dibenzothiophene	
C_3-Dibenzothiophene	

Gas Chromatography-Electron Capture Detection (GC-ECD) for Pesticide and Polychlorinated Biphenyl Compounds, EPA Method 8082M. Sample extracts are analyzed at appropriate PIVs by

GC/ECD following SOP-ADL-2818-Determination of Chlorinated Pesticides and PCB Congeners by Gas Chromatography-Electron Capture Detection (GC/ECD). Extracts are analyzed on the GC/ECD using a dual column/dual detection method. A Restek, RTX-5 column, or equivalent is used as the primary column for analysis of the samples. A DB-17 column, or equivalent, is used for confirmation analysis except as noted below.

Instrument Preparation and Calibration. The GC/ECD is calibrated with a five-point calibration curve for eight select target PCB congeners from 5 to 200 ng/mL. Target analytes are identified by comparing retention times to those in the calibration standards. Retention times of all the individual congeners are determined by running either all of the target compounds individually or in smaller groups where the order of elution is known. Where co-elution occurs between one or more target compounds or where interference occurs on the RTX-5 column, the DB-17 column is used as the primary column; however, the analysts judgment factor into this decision. A new 5-point calibration is performed before any samples are analyzed.

4.1.2 Metals

Analysis of metals will be conducted in accordance with SOP MET-1A of the SFPUC Chemistry Laboratory. Prior to analysis, samples are digested following EPA method 3050. Analysis follows EPA methods 6010 and 7000 series (EPA SW-846), inductively coupled plasma spectroscopy (ICP) and atomic absorption (AA), respectively. Sediment samples will be delivered in pre-cleaned containers to the SFPUC Chemistry Laboratory and logged upon receipt. Initially, each sediment sample will be carefully homogenized with a plastic-mixing rod. An aliquot of approximately 5 grams will be transferred into a pre-weighed aluminum-weighing dish. The remaining portion will be archived for future reference and the other sample will be set aside for analysis. The wet mass will be recorded and the dishes transferred to a convection oven for drying at 104°C overnight. After cooling, the dried samples are then weighed for the determination of percent solids.

Approximately, 1g of the dried sample is transferred to a pre-weighed Erlenmeyer flask for digestion. At this point standard spiking solutions are added to the designated matrix spike samples. Internal standards are added to all samples to produce the desired final concentration. 5 ml of Double-Distilled Nitric Acid is dispensed slowly into each Erlenmeyer flask followed by 10 ml of Double-Distilled Hydrochloric Acid. The flasks are allowed to sit overnight then transferred to hotplates for refluxing at 100^{o} C. The solutions are then evaporated on the hotplates to ca. 2.0-ml. The entire contents of the flasks are then filtered to remove the undigested solids, and the filtered solution is brought up to final volume with de-ionized water for analysis. The prepared samples are then analyzed by the appropriate instrumental analytical technique: (1) ICP emission spectroscopy, (2) Cold vapor atomic absorption (AA), (3) Hydride generation AA, Flame AA, or (4) Graphite furnace AA. Target detection limits are listed in Table 4-4.

Table 4-4. Target Method Detection Limits for Metals Analysis

Metal	Minimum Detection Limit (μg /g dry weight)	Analytical Method*
Aluminum (Al)	0.2/0.01	ICP/AAGF
Arsenic (As)	0.5	ICP
Cadmium (Cd)	1.0/0.025	ICP/AAH
Chromium (Cr)	0.1/0.01	ICP/AAGF
Copper (Cu)	0.2	ICP
Iron (Fe)	0.2	ICP
Mercury (Hg)	0.3	ICP
Nickel (Ni)	0.0005	CVAA
Lead (Pb)	0.2	ICP
Selenium (Se)	1.0/0.07	ICP/AAGF
Silver (Ag)	0.025	AAH
Zinc (Zn)	0.1	ICP

AAH = Atomic absorption hydride
AAGF= Atomic absorption with graphite furnace
ICP= Inductively coupled plasma emission spectroscopy
CVAA = Cold vapor atomic absorption

4.2 Sediment Conventional Analyses

Sediment grain size will be analyzed using sieve and pipette method of Plumb et al. 1981. Results will be reported both as phi size and in millimeters covering the ranges of fine silts to gravel. Total organic carbon (TOC) will be analyzed in sediments using the EPA Method SW-846 9060, combustion followed by infrared carbon dioxide technique, and reported as a percentage of total sediment (dry weight).

4.3 Bioassay

The amphipod *Eohaustorius estuarius* will be used in a 10-day, acute, solid-phase test based on ASTM Protocol E1367-92. *Eohaustorius estuarius* is native to San Francisco Bay typically inhabiting well-sorted, fine-grained sediments similar to those found in the creek beds and is reasonably euryhaline. Mortality, reported as percent survival, is the primary effect measured.

Amphipods will be obtained from reputable suppliers and received at the SFPUC Oceanside Laboratory within 48 hours of collection. Control sediment (home sediment) will be collected concurrently with the test species. Temperature, dissolved oxygen, pH, and salinity will be measured upon organism arrival and daily during acclimation to test conditions. Acclimation will proceed at a rate no greater than 4°C and/or 4ppt salinity in any 24-hour period. If greater than 10% mortality is realized in a 24-hour period during acclimation and holding, all organisms will be discarded and new organisms will be obtained. Tests will be started within five days of organism receipt, provided acclimation rates are not violated and sediment test conditions permit.

Test sediments are run concurrently with negative (home sediments) and positive controls (reference toxicity testing). Prior to the introduction of test organisms it is important to address conditions that may produce false positive test results. When confounding conditions (e.g., high ammonia or sulfides) exist, it becomes extremely difficult to separate anthropogenic effects from natural sediment toxicity. Before toxicity tests are initiated, porewater levels of ammonia and sulfides will be measured. Ammonia levels

greater than 20 mg/L have been shown to induce toxic responses and can be mitigated through overlying water exchange. The generally accepted procedure is to exchange water overlying the test sediments from one to fifteen times prior to the introduction of amphipods (ASTM 1993). Water exchanges will be performed on all high ammonia sediment replicates prior to test initiation when interstitial water levels exceed 20 mg/L. Porewater sulfide levels greater than 100 mg/L will be reduced by aerating overlying water. Manipulations such as these constitute deviations from standard protocols and require additional "manipulation controls." Manipulations designed to reduce potential confounding factors will not be attempted without the prior approval of the project manager and principal investigator.

The acute 10-day amphipod test is summarized as follows. All test sediments will be press-sieved (through 0.5 mm mesh stainless steel screens) and picked to remove possible amphipod predators and native amphipods that may be confused with the test species. All sediments collected from Yosemite Creek will be press-sieved prior to test initiation. Prior to introduction of the test organism, test and control sediments will be added to five replicate 1-L pre-cleaned glass containers to a depth of 3-5 cm, covered with approximately 900 mL of clean seawater and aerated under test conditions overnight.

Sediment samples with ammonia porewater values greater than 20 mg/L will require water exchanges prior to the setup of all other tested sediments and the introduction of the test species. Additional replicate test chambers (five) will be setup for these samples as described above. For these samples, 80 percent of the overlying water will be siphoned off and replaced with clean seawater three times within a single 24-hour period. After the three exchanges, one replicate is sacrificed and porewater ammonia will again be measured. This process will be repeated until all high porewater ammonia levels are below 20mg/L, or 15 exchanges (five days of exchanges) have been performed. The balance of the test sediments will be distributed into test containers only after all "high" ammonia sediments have been reduced to testable conditions.

On the day of organism addition (Day-0) eighty percent of the overlying water will be removed from all test containers and replaced with clean seawater. Test containers will be randomly placed in environmental test chambers and 20 amphipods will be randomly distributed to each replicate container for a total of 100 amphipods per treatment (20 amphipods in each of five replicates). Dissolved oxygen, pH, salinity and temperature will be measured and recorded daily. Overlying water will be removed from one replicate within each test sediment type and analyzed for ammonia on a daily basis. On test Day-3, Day-6 and Day-9, 80 percent of the overlying in all test containers will be exchanged with clean seawater. After 10-days of exposure, amphipods will be carefully removed by wet-sieving, counted, placed on clean sediment and permitted to rebury. The number of amphipods that successfully rebury will be recorded. Percent survival and percent reburial will be reported for all sediment replicates examined.

The SFPUC Oceanside testing facility is limited by shelving space with a capacity for 200 1L-jars. If water quality criteria are not exceeded during this test (none were during Phase I), a minimum of 174 test jars will be set up. However, for each water quality exceedance, an additional eight test jars will be required. In the event of multiple water quality exceedances, the laboratory will not have sufficient capacity to perform all tests at the same time. In such a case, the samples will be split into two batches. Each batch will contain half of the reference samples (randomly split) and half of the test samples

(randomly split) and a full control sample. The second batch will be initiated 48 hours after the first, allowing for supply acquisition and testing area reconfiguration.

A test will be considered valid if after 10-days of exposure the average control survival is ≥90% and each control replicate has at least 80% survival. Additionally, the LC_{50} produced during the positive control test must be bounded by the 95% confidence limits of the testing laboratory's control chart mean LC_{50}.

5.0 Quality Assurance/Quality Control (QA/QC)

5.1 Chemical and Physical Analyses

All chemistry data generated by the laboratories are assembled in data packages and reviewed by the designated team member in charge of each analysis to ensure that the data quality objectives for accuracy and precision are met, that the data are generated in accordance with the Laboratory QA Plan, and data are both traceable and defensible. Data packages will also be reviewed by the task managers to ensure compliance with procedures and data quality objectives specified in the QA Plan. Data will also be reviewed for consistency with expected analyte distributions.

When data review is completed by each facility, all data sets are submitted to the Quality Assurance (QA) Officer for a formal audit in accordance with the analytical laboratory's quality assurance project plan (QAPP). A minimum of 5 percent of each data set that was generated by an automated system will be checked for accuracy. This involves tracking the final reported concentrations back to raw data. The Project QA Officer is independent of the technical organization and reporting structure. The QA Officer audits the analytical and data management components of this project. Audit reports and reviews will be submitted to the Project Manager and any problems will be resolved before the data or reports will be released. Data packages will be submitted with a complete QC report and case narratives relating any analytical problems. All project files, including electronic files such as GC/MS output files and laboratory records will be archived at the respective facilities for at least five years.

Quality assurance and control will be implemented throughout the program. The QA/QC program is design to ensure data collected is of high quality and usable for their intended purpose. Through the implementation of the QA/QC program, data quality and consistency will be maintained for comparability between laboratories. It is important for the entire project team to review the QA/QC criteria set forth in this plan. A consensus should be reached prior to any performance of the work.

The objectives of the QA/QC program is to minimized sampling errors and to assess usability of data collected for environmental monitoring purposes. The quality assurance program will have the following elements.

- Inspection and certification of sampling and laboratory equipment
- Adherence to specified sampling procedures and protocols
- Collection and analysis of field samples
- Quality control program of the analytical laboratory
- Data review
- Data reporting

Quality assurance will be implemented through the development of and adherence to this Sampling Analysis / Quality Assurance Project Plan. QA/QC samples will be collected in the sampling program to assess data quality. The sample data will be reviewed for quality and consistency. In general, accuracy shall be assessed by the analysis of standard reference materials (SRMs), spiked recoveries and laboratory intercalibration samples. Precision shall be assessed through the analysis of duplicate field

samples and SRMs. Surrogate compounds will be spiked into field and quality control samples prior to extraction.

5.2 Data Quality Objectives

Data quality objectives (DQOs) are established to ensure analytical data are of the quality necessary to achieve project objectives. The data quality objectives are designed to enhance our ability to identify and accurately quantify source specific materials. DQOs for PAH, PCB and metal analytes are summarized in Table 5-1. Data quality objectives specified in this project plan are specific to this study, and thus, supersede those referenced in SOPs.

Method detection limits (MDLs) are typically determined at the analytical laboratory annually for the organic analyses to be used in this study. MDLs for inorganic analyses are determined at the SFPUC Chemistry Laboratory. MDLs are determined based on the standard deviation obtained from the analysis of replicate (usually seven) matrix samples spiked at three to ten times the expected MDL. This approach follows guidance provided by the U.S. EPA (Federal Register, 1984, Vol. 49, No. 209, pp198-199). Method detection limits are presented in Tables 4-2 through 4-4 for each analytical group.

Table 5-1. Chemistry Data Quality Objectives

Analyte	Minimum Frequency	Data Quality Objective/Acceptance Criteria
PAH, PCB & Pesticides		
Initial Calibration	Prior to every batch sequence for GC/MS analysis and as needed for GC/FID analysis	5 point curve. %RSD ± 25% for 90% of analytes and ± 35% for 10% of analytes
Continuing Calibration	Must end analytical sequence and every 12 field samples or 16 hours, whichever is more frequent	%RSD ± 25% for 90% of analytes. %RSD ± 25% for 10% of analytes.
Sediment SRM	Every batch/every 20 field samples	Values must be within ± 30% of true value on average for all analytes; not to exceed ± 35% of true value for more than 30% of individual analytes.
Procedural Blank	Every batch/every 20 field samples	No more than 2 analytes to exceed 5x target MDL unless analyte not detected in associated samples(s) or analyte concentration > 10x blank value.
Duplicate Sample Analysis	Every batch/every 20 field samples (client requested)	RPD ≤ 30% for all analytes > 10x MDL; Mean RPD ± 30% (advisory only).
Recovery/Surrogate Standards	Every Sample	%R 35-125% for d_8-Nap, d_{12}-Bap %R 45-125% for other quantification surrogates
Instrumental SRM (SRM 1491)	One per GC/MS instrumental sequence. Not applicable for GC/FID analysis	Values must be ± 15% difference of true value for all certified analytes
Oil Standard (5mg/mL)	One per batch/every 20 field samples	Values must be ± 35% difference of accepted value, except for analytes, which are below the reporting limits.
Matrix Spike/Spike Duplicate	One set per batch of 12 to 20 field samples (per client request)	%R 35-125% RPD ± 35% for all analytes. (advisory only)
Target MDLs		PAH / PCB
	Sediment	10 ng/g / 1 ng/g
Metals		
Initial Calibration	Prior to every batch of samples	3-5 point curve and a blank. Standard curve correlation coefficient $r^2 > 0.95$ for all analytes.
Continuing Calibration	Must end analytical sequence; for flame, repeat all standards every 5 samples; for graphite furnace and ICP-MS recheck standard after every 8 samples	%D ≤ 15% for all analytes
NIST/NBS Series SRMs/CRMs	Two per batch of 20	Values must be within ± 20% of accepted values for >85% certified analytes and within ± 25% for Hg
Method Blank	One per batch of 20	No more than 2 analytes to exceed 5x MDL unless analytes not detected in associated sample(s)
Matrix Spike /Spike Method Blank	One per batch of 20	%R 75-125%
Lab Duplicate	One per batch of 20	RPD <35% for 65% analytes;

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