Work Plan & Quality Assurance Plan

for

Sediment Sampling at

Islais, Mission, and Yosemite Creeks

Prepared by

City and County of San Francisco

Public Utilities Commission SPARC

Submitted to

San Francisco Regional Water Quality Control Board

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1.0 Introduction

Data from recent surface sediment surveys at specific areas in San Francisco Bay were summarized by the San Francisco Regional Water Quality Control Board, Region 2 (SFRWQCB) in a meeting with the City and County of San Francisco, Public Utilities Commission (the City) on May 18, 1998. Additionally, results from sediment tests were presented in the Bay Protection and Toxic Cleanup Program (BPTCP) Proposed Regional Toxic Hot Spot Cleanup Plan (SFRWQCB December 1997) where several sites potentially influenced by City operated combined sewer outfalls (CSOs) were identified as candidate Toxic Hot Spots (THS). Additionally, SFRWQCB's assessment of Islais and Mission Creeks was based primarily on BPTCP 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.

BPTCP assessment of Islais and Mission Creeks was based on limited sampling (3-4 locations) of sediments for chemistry and toxicity. At Islais Creek, moderate to high sediment concentrations of heavy metals, chlorinated pesticides and polychlorinated biphenyls (PCBs) secondarily supported the bioassay findings. 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 four locations that extended from the mouth to approximately 500m within the creek. Yosemite Creek was shown to have moderate to high concentrations of select metals, PCBs, and polycyclic aromatic hydrocarbons (PAHs) at several stations near the mouth of the creek.

Following the May 18th meeting, the City decided to conduct further investigations of these three sites to quantify the extent of contamination and if possible, to identify possible sources. This work plan describes study design, field analytical methods, quality assurance and quality control, and includes approaches for data analysis and interpretation for these investigations. This work plan follows the general approach of other San Francisco Bay monitoring programs (e.g., BPTCP, RMP), and is designed to meet the following specific objectives: (1) to confirm or refute the SFRWQCB findings, which indicate that the subject sites are toxic and contaminated; (2) to further define the horizontal and vertical extent of contamination; (3) to determine the extent that CSOs contribute toxicity and/or contamination to the receiving creek beds; and (4) to collect and archive samples for possible additional analyses to support potential remediation alternatives. Additional analyses suitable for this approach would include benthic community health to benchmark recovery at the sites in the event of any remediation effort by the City. Data collected in support of objective (2) will be used to assist the SFRWQCB in developing corresponding cleanup plans, if necessary.

The basic approach uses field and laboratory methods consistent with those used in the current Regional Monitoring Program (SFEI, 1995) and in recent BPTCP programs conducted in San Francisco Bay. Consistency between these data and data generated in the City's investigation will support the primary study objective, which is to confirm or refute the SFRWQCB findings.

2.0 Program Scope and Responsibilities

The Sampling/Analysis & Quality Assurance Project Plan (S/A & QAPP) presents the overall policies, organizational structure, program scope, and data quality objectives (DQOs). Included are specific Quality Assurance/Quality Control (QA/QC) requirements, field and analytical procedures, and responsibilities for conducting sampling and analysis at select City operated (CSO) locations. The S/A & QAPP is designed to ensure the precision, accuracy, representativeness and comparability of data collected and that these data are adequate to satisfy study DQOs.

Field sampling and analytical procedures will be performed to meet the specifications of the program objectives. All analyses will be conducted by qualified City (Oceanside) and contractor laboratories. Each laboratory is responsible for maintaining strict QA/QC programs compliant with the requirements of this plan as well as analytical method requirements for instruments, preparations, and analytical procedures employed during this project. The laboratories will be required to meet data quality and deliverable needs that are outlined in this plan. Appropriate Standard Operating Procedures (SOPs) and a general laboratory QAPP will be maintained for each laboratory.

2.1 Program Scope

Sediment chemical and physical parameters and toxicity will be measured at the three sites. Trace level chemical measures in sediment will be made for polychlorinated biphenyl congeners (PCBs), polynuclear aromatic hydrocarbons (PAHs) including alkylated homologs, chlorinated pesticides, and heavy metals. Analytes used in the 1997 BPTCP program, and characteristic sewage and wastewater markers will be measured, although not all compounds will be measured at each sampling location.

PAH and TPH analysis will provide detailed information to: 1) identify and quantify contaminants of concern (e.g., benzo(a)pyrene), 2) evaluate source and type of hydrocarbon contamination (combustion versus petroleum-related), and 3) determine allocation of mixtures of petroleum contamination. Likely sources of contamination will be identified by comparing PAH distributions to a library of road-runoff samples associated with a variety of land-use activities.

PCB and chlorinated pesticides will be analyzed to: 1) determine concentrations of specific contaminants of concern, and 2) evaluate potential PCB sources (e.g., Arochlor 1242 versus Arochlor 1248).

Sewage and/or wastewater markers will be analyzed to support source determination of associated contaminants and the extent of CSO-related contamination. Linear alkylbenzenesulfonates (LABs) will be used for identifying detergent-derived chemicals, and coprostanol and epicoprostanal will be used as domestic wastewater markers.

Acute toxicity will be measured with the amphipod *Eohaustorius* sp. exposed for 10-days to whole sediment. Physical sediment qualities consisting of total organic carbon and grain size

will be measured to aid in the interpretation of results. Conventional sediment parameters will be assessed to determine whether any observed toxicity is attributable to non-chemical influences, such as ammonia and dissolved sulfides.

The monitoring program will be carried out at the three creek sites. The robust sampling design and reasonable aerial coverage will delimit the extent of contamination within each tributary. Analytical tests are based on target contaminants defined in prior studies. Sampling techniques and analytical methods are based on compatibility with prior studies, such that the results of this effort can be used in direct comparison to published RMP and BPTCP programs. An inventory of analytical tests for surface and subsurface sediments collected at each site is presented in Table 1.

1. Islais Creek

Fifteen stations will be sampled within Islais Creek (Figure 1). Sediment samples will be taken at 9 stations (3 across x 3 along) extending from the main discharge CSO to the 3rd Street Bridge. Two sets of three stations will be taken east of the 3rd Street Bridge. A total of five "distance" strata, each containing three equally spaced sampling stations located across the creek, will produce a 5 x 3 sampling grid. This experimental design will permit the examination of effects both along the length of, and across, the creek. For all 15 locations, sediment will be collected from the top 5 cm of a standard 0.1 m^2 Van Veen grab and subsampled for PCBs, pesticides, metals, TOC, and grain size. A single grab sample will be taken at each surface station from which infaunal benthic organisms will be removed and archived for later identification if necessary.

A randomly selected station from each of the five distance-strata will be sampled for toxicity testing and chemical contamination (PAH, TPH, and sewage markers listed in Table 1). At each of these "select" stations and in addition to the surface sample, gravity cores penetrating to a nominal depth of 2 feet will be used to vertically profile the creek bed. Two homogenized subsamples from each core will be collected: one from the surface (minus 5 cm) to 1 foot and one from 1 to 2 feet. Subsurface samples will be analyzed for TOC, grain size and chemistry only.

2. Mission Creek

Similar to Islais Creek fifteen stations will be sampled (Figure 2). Sediment samples will be taken at 9 stations located along and perpendicular (3 x 3) to the creek from the main discharge CSO to the 4th Street Bridge. Additionally, two sets of three stations will be taken east of the 4th Street Bridge. Five "distance" strata, each containing three equi-distance sampling stations located across the creek, will produce a 5 x 3 sampling grid. For all 15 locations, sediment will be collected from the top 5 cm of a Van Veen grab and subsampled for PCBs, pesticides, metals, TOC, and grain size. A single grab sample will be taken at each surface station from which infaunal benthic organisms will be removed and archived for later identification if necessary.

A randomly selected station from each of the five distance-strata will be sampled for toxicity testing and chemical contamination (PAH, TPH, and sewage markers listed in Table 1). At each of these "select" stations and in addition to the surface sample, gravity cores penetrating to a nominal depth of 2 feet will be used to vertically profile the creek bed. Two homogenized subsamples from each core will be collected: one from the surface (minus 5 cm) to 1 foot and one from 1 to 2 feet. Subsurface samples will be analyzed for TOC, grain size and chemistry only.

3. Yosemite Creek

A total of 15 stations will be located and sampled in Yosemite Creek (Figure 3). Sediment samples will be taken at 12 stations along and perpendicular (4 x 3) from the end of the main creek body extending out to the creek mouth. Additionally, two stations will be sampled in the southern arm, and one in the northern arm, respectively, at the creek end. Surface and subsurface samples will be collected at all 15 locations. Surface sediments will be collected from the top 5-cm of the Van Veen grab and subsurface composites will be collected to a nominal depth of 2-ft as previously described. All samples will be analyzed for a full-suite of chemical and physical measures and a single 10-day amphipod toxicity test. A single grab sample will be taken at each surface station from which infaunal benthic organisms will be removed and archived for later identification if necessary.

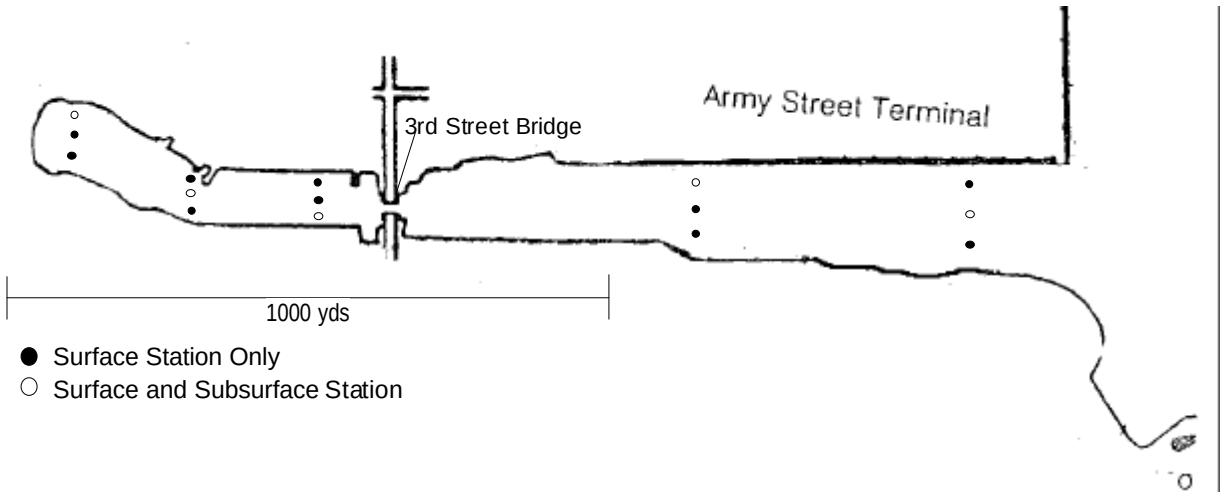

Figure 1. Approximate sampling locations for Islais Creek

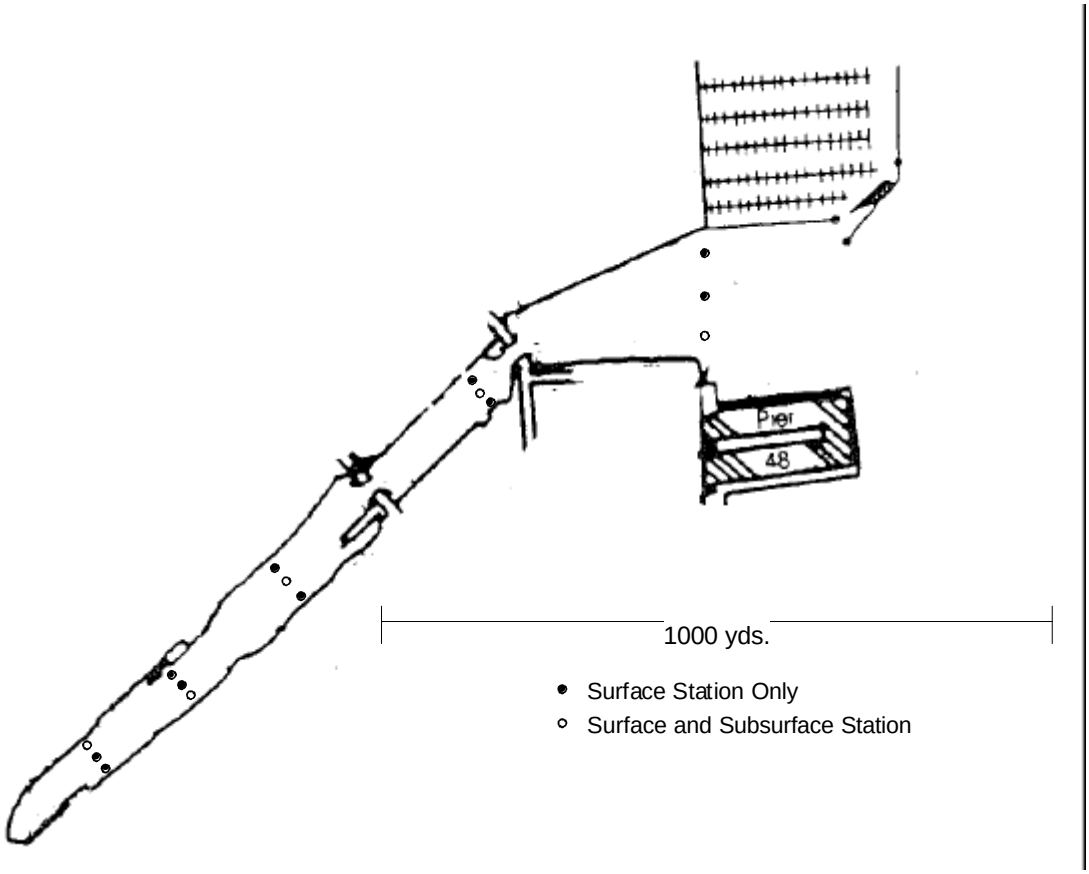

Figure 2. Approximate sampling locations for Mission Creek

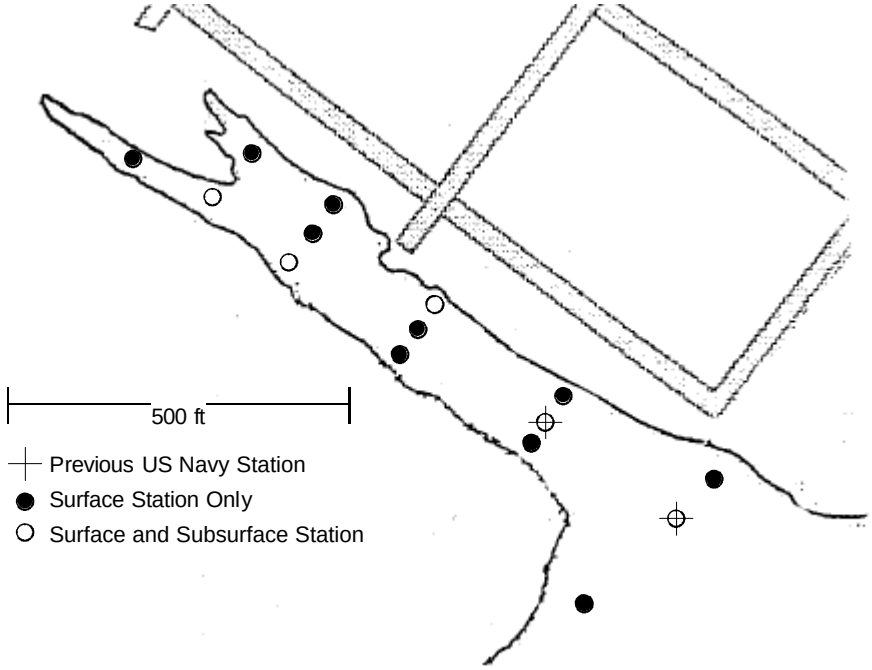

Figure 3. Approximate sampling locations for Yosemite Creek

Table 1. Numbers and types of analyses performed for each site

Site	Select Surface Sediments	No. of Select Surface Sediments	Remaining Surface & Subsurface Sediments	No. of Remaining Surface a& Subsurface Sediments
Islais Creek	PCB, pesticides, PAH, TPH, sewage markers, metals, toxicity, TOC, grain size, infauna	5	PCBs, pesticides, metals, TOC, grain size, infauna (surface)	10 surface 10 subsurface
Mission Creek	PCB, pesticides, PAH, TPH, sewage markers, metals, toxicity, TOC, grain size, infauna	5	PCBs, pesticides, metals, TOC, grain size, infauna (surface)	10 surface 10 subsurface
Yosemite Creek	NA	0	PCB, pest, PAH, TPH, markers, metals, toxicity, TOC, grain size, infauna (surface)	15 surface 15 subsurface

2.2 Roles and Responsibilities

Individuals responsible for the implementation and quality of this program consist primarily of representatives from the City and their designated contractors. The roles and responsibilities for each facility are specified below.

PUC – City & County of San Francisco

Overall responsibility for the program including performance of analytical laboratories is vested in the PUC Program Manager, the central point of contact for the program. A description of responsibilities for the program manager and primary task managers is presented below and primary contact information is listed in Table 2.

?? Program Manager (PM): The PM, Ms. Leslie Lundgren with PUC, is responsible for the overall conductance of the program and is the primary contact for SFRWQCB. The PM will work directly with the Task Managers to ensure that communications are adequate and that scope and budget control are maintained. In addition to management responsibilities, Ms. Lundgren will directly oversee the collection of field samples and will maintain close communication/coordination with support staff.

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?? Task Manager (TM): The role of the TM is to plan and implement the execution of specific tasks in order to produce the required deliverables. The task managers will manage the schedule and budget of each analytical and reporting task and the production of the deliverable(s) under that task.

?? Field Coordinator: The Field Coordinator, Ms. Arleen Navarret, is responsible for overseeing field activities and logistics. She will assign sample navigation and collection responsibilities in the field and ensure that samples are properly collected and transferred to the analytical laboratories.

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?? Chemistry Task Leader: Mr. Jim Salerno is responsible for sediment inorganic and physical analyses performed in the City's laboratory. He is also responsible for overseeing laboratories contracted for analysis of organic contaminants in sediment.

?? Biology Task Leader: Ms. Arleen Navarret is the biology task leader. Her responsibilities include oversight of toxicity tests conducted in the City's laboratory and benthic infaunal sampling.

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?? Subcontractor Contacts (SCs): The work on this project requires highly qualified subcontractors. The subcontractors will provide specific expertise and continuity to the project. The organization diagram displays subcontractor contacts. Mr. Jim Salerno will assume direct responsibility for the QA/QC programs associated with subcontracted analyses.

Table 2. Technical Program Personnel and Contact Information

Name	Title	Company	Contact Information
Ms. Leslie Lundgren	Program Manager	City & Co. of San Francisco, PUC	Ph: 415-554-9565 Fax: 415-554-9404 llundgre@puc.sf.ca.us
Ms. Arleen Navarret	Field and Biology Task Leader	City & Co. of San Francisco	Ph: 415-242-2201 Fax: 415-242-2285
Mr. Jim Salerno	Chemistry Task Leader	City & Co. of San Francisco	Ph: 415-648-6882 Fax: 415-550-9316 jsalerno@puc.sf.ca.us

3.0 Field Program

The field program will be divided into five general tasks: mobilization, navigation, surface sampling, core sampling 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. For this reason Islais, Mission and Yosemite Creeks will be treated as separate standalone sampling events, but share in common equipment and procedures.

3.1 Equipment Mobilization

The Field Task Manager will review the list of materials and supplies and provide input and procurement support, as well as onsite assistance for installation and testing of equipment. Those activities include the following:

?? Preparation of field notebooks and unique sample IDs
?? Review sampling materials and supplies list (Appendix A), comment and assist in ordering of additional materials.
?? Review workplan and safety plan with field team.

Prior to each sampling event all materials and equipment will be assembled, checked against a project specific day list and inspected. The survey vessel will be scheduled 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

Prior to occupation stations will be pre-plotted on charts of sufficient detail to permit the positioning of each station by distance and direction from special areas (e.g., CSOs) and distances from channel sides. A Global Positioning System (GPS) will be used to roughly position and navigate the survey vessel. Exact station locations will be facilitated with laser range finding monocular (accurate to ? 1 m) and digital handbearing compass (accurate to ? 2?). Stations will be located as follows:

1) the special area (e.g., CSO) will be located and defined as distance zero
2) using the GPS as a rough 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 will deployed at the stations and the distance from zero, the distance from shore will be measured with range-finder and recorded
5) station latitude and longitude will be recorded
6) the vessel will be relocated to a position approximately one quarter the way across the channel, in a direction perpendicular to the long dimension of the channel and another station marker buoy will be deployed and position recorded as 4 and 5 above
7) the vessel will be relocated to a position approximately one half way across the channel, marked with a buoy and recorded as 4, 5 and 6 above
8) the vessel will be relocated to a position approximately three quarters across the channel, marked with a buoy and recorded as 4, 5 and 6 above establishing sampling locations for three station of the first “distance strata”
9) the vessel will then be relocated to the approximate beginning of the second “distance strata” using the GPS and steps 3 through 7 are repeated
10) step 9 is repeated until all five “distance strata” and 15 stations have been located, marked and recorded.

This procedure is same for Islais and Mission Creeks, however, Yosemite Creek differs in the location of stations nearest to the end of the creek. For these three stations, it will be necessary to sight and mark each with distances and directions to permanent land based markers.

Depending on vessel availability, station location and marking may take place the day before the actual sampling of a creek. Station location is a time consuming process, but requires fewer personnel than the chemical and biological field sampling. A smaller vessel may also be used for this program task.

3.3 Sediment Sample Collection

After all stations have been marked with buoys, sampling will commence. Depending on the ability of the sampling vessel to maintain station 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 0.1-m^2 Van Veen grab sampler. The grab is constructed of stainless steel and coated with Kynar to reduce contamination. Two grabs will be taken at each station, one for chemical/physical/toxicological parameters and one for benthic infauna. Sampling procedures will be conducted in compliance with quality control measures established in Section 5.0 of this project plan. Quality control samples will be collected for each study site. Prior to deployment, the grab for the sampling of chemical/physical/toxicological parameters will be decontaminated as follows:

?? Rinse grab with seawater to remove visible sediment.
?? ? ash with soapy water using a brush and rinse with seawater. If grab has visible sediment after rinsing repeat scrub with a brush.
?? Rinse with ambient seawater.
?? If grab is visibly oiled, follow up with a final methylene chloride or hexane rinse.

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 and 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.

3.3.2 Subsurface Sediment Core Sampling

Subsurface cores will be taken from one randomly chosen station within each "distance strata," as previously described. Stations will be occupied in the same manner used in surface sampling and a simple three-inch diameter steel gravity corer will used to take samples for vertical profiling. Pre-cleaned plastic liners (butyrate or polycarbonate) will be used to reduce

contamination associated with the steel core barrel. Upon retrieval the corer will be disassembled, the liner removed, the bottom covered with wide Teflon tape and closed with a plastic cap. The outside of the plastic liner will be wiped clean with a soft cloth and inspected for penetration and completeness of sample. Core samples less than two feet in length will be discarded and the plastic tube will not be used for subsequent sampling. Core samples two feet in length, or greater, will be considered successful. Core tubes will be clearly marked as to direction (top and bottom), overlying water will be removed by siphoning and the core will be cut at the sediment surface using a non-chipping pipe cutter. The top of the core will covered with Teflon tape, capped, labeled appropriately and placed into 4?C storage. Cores will be sub-sampled, composited and distributed in controlled space at the City's Oceanside laboratory.

3.3.3 Chemistry Sediment Grab Sub-Sampling

Prior to sediment subsampling, the overlying water will be siphoned off with a pre-cleaned teflon tube. Chemistry samples will be taken using the following procedure: using a pre-cleaned 5 cm Kynar coated scoop, the top 5 cm of sediment will be removed and placed into a pre-cleaned Pyrex mixing bowl. The scoop is 5 cm deep and is used to gauge the depth of the collected sample. It is important that all personnel collecting the samples using this method be trained prior to sample collection. Sediment will not be collected near the sides of the grab (distance from grab side approximately 2 cm). Once the sediment is collected, the bowl will be covered and the sample removed to a "clean-room" on the vessel for homogenization and sample aliquoting. The sample is homogenized in a pyrex bowl with a clean Kynar scoop or Teflon mixing rod. The pyrex bowl and scoop used to mix the sample are cleaned between each use as follows:

?? Rinse bowl and scoops with seawater to remove visible sediment.
?? ? rush wash with soapy water.
?? Rinse with DIW.
?? Rinse with 5% nitric acid.
?? Rinse with DIW.
?? Rinse with methylene chloride or hexane.

Sediment Chemistry and Toxicity Sample Allocation. The upper 5 cm of sediment in the grab will be placed in a pre-cleaned (solvent rinsed followed by de-ionized water) glass mixing bowl. The sediment in the bowl will be mixed thoroughly using a pre-cleaned Kynar coated scoop or Teflon mixing rod. The homogenized sediment will then be aliquoted into one 250-mL pre-cleaned and labeled borosilicate glass sampling jar for organics (e.g., I-CHEM or equivalent); one 250-mL precleaned and labeled polycarbonate sampling jar for trace metals; and one food-grade labeled ziplock for grain size and TOC.

Sediment remaining in the glass mixing bowl (at least 2L) will be transferred using the Kynar coated scoop into a large, clean, labeled food-grade plastic bag for toxicity testing. The bag will be closed with plastic tie-wraps, placed into a second labeled food-grade plastic bag and transferred to 4?C storage.

All sediment samples will be 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 workplan (Section 3.3.4) will be followed.

3.3.4 Infaunal Sediment Grab Sampling

Surface sediments destined for infaunal collection will be obtained with a 0.1 m^2 Van Veen grab sampler. The grab is constructed of stainless steel and coated with Kynar to reduce contamination. Unlike samples taken for chemical analysis, infaunal grabs do not require elaborate clean procedures. Grabs taken for benthic infauna only need to be rinsed with seawater prior to deployment. The quality of each grab sample will be determined by visual inspection. Grabs that contain severely slumped, or mounded sediments will be discarded and re-taken. Additionally, grabs that appear to have large leakages of overlying water and fine sediments, or where the natural surface layer of the sample was obviously disturbed will be rejected.

Once the sediment grab sample is approved, the entire contents of the grab are removed. Infaunal samples will be wet sieved through nested 1.0mm and 0.5mm mesh screens on the vessel. Retained organisms and debris will be relaxed for 15 minutes in a seawater/magnesium-chloride solution followed by fixation in 10% buffered formaldehyde. Fixed infaunal samples and associated debris will be transferred into appropriately labeled containers and transferred to the Cities Oceanside laboratory, where the formaldehyde fixative will be replaced with 70% ethanol within 48 hours. Infaunal samples will be archived pending sorting and taxonomy.

3.3.5 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. A representative sample should be collected from these sources for the anticipation of future problems. 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.

3.3.6 Field Sampling Quality Control Samples

To assess the effectiveness of equipment decontamination, equipment blanks, field blanks, and field duplicates will be collected either once per day or at a frequency of 10% of the total samples to evaluate potential cross contamination levels. Additional equipment blanks should be collected if the Van Veen grab sampler contains visible oil residues. To collect the equipment blank, the grab is first decontaminated according to the procedures specified above. Then the

inside of the grab is rinsed with high-purity de-ionized water and the rinsate collected directly into a clean, pre-labeled water sample container. The rinsate equipment blank is preserved with methylene chloride (100-mL methylene chloride for a standard 2-L equipment blank) and refrigerated. Due to the background nature of many of the samples, and the ability of the laboratory to chemically identify the presence of petroleum product contamination (e.g., diesel fuel) in the samples, the background sediment samples will provide more useful equipment blank information.

3.3.7 Field Sample Chain of Custody, Storage, and Transportation

Immediately following collection, each source material and sediment sample will be labeled and chain-of-custody procedures initiated. The combined sediment chemistry samples, toxicity samples from each grab and core samples will be aliquoted into appropriate containers. These bottles and bags will be labeled with unique labels. Each label include the following information:

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

The unique station ID 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.

Upon arrival at the laboratories, the sediment chemistry samples will be stored in a freezer (-20 ^{o}C) until initiation of sample analysis. The grain size and toxicity samples will be stored at 4 ^{o}C until sample analysis. Infaunal benthic samples will be archived in 70% ethanol until needed.

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 is presented in Tables 3 and 4. Analytical procedures for biological analysis of sediment and water samples are also included.

4.0 Analytical Program Design

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 PCBs; chlorinated pesticides; PAH; TPH; metals; grain size (GS); TOC; and 10-d acute amphipod toxicity. Organic analyses will be performed by a contracted laboratory. Metals (Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Se, Zn) TOC, grain size, and toxicity will be processed by the City laboratory.

4.1 Sediment Chemistry

4.1.1 Organic Analyses

Sediment Extraction

Sediment samples are extracted per SOP ADL-2819. 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 PAH, PCB/PEST, and LAB 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/PEST analysis; l-phenylnonane for LAB. 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 case leader. The surrogate spiking amounts corresponding to the level of contamination are as follows:

Level	PCB/PEST (ng)	PAH (?g)	LAB (?g)	Coprostanol
Low	200	1.0	2.0	2.0
Mid-Low	200	2.0	2.0	4.0
Mid	NA	10	10	10.0
High	NA	100	100	100

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, LAB, and coprostanol target analytes, TPH by GC/FID, and the third 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, one MS, one MSD, and one duplicate analysis. The MS and MSD samples are spiked with approximately 500 ng of the PAH matrix spike solution, 200 ng of the PCB/PEST matrix spike solution, and 1000 ng of LAB matrix spike solution. Table 5 outlines the data quality objectives for the sediment analyses.

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 3. Polychlorinated Biphenyl and Chlorinated Pesticide Target Analytes

Compound	Surr/Rec. Standards	Compound	Surr/Rec Standards
PCB 007/9	1,A	PCB 137/176	1,A
PCB 8	1,A	PCB 138/160	1,A
PCB 008/5	1,A	PCB 141/179	1,A
PCB 015	1,A	PCB 146	1,A
PCB 016/32	1,A	PCB 149/123	1,A
PCB 018	1,A	PCB 151	1,A
PCB 18	1,A	PCB 153/132	1,A
PCB 022/51	1,A	PCB 156/171	1,A
PCB 024/27	1,A	PCB 158	1,A
PCB 025	1,A	PCB 167	1,A
PCB 28	1,A	PCB 170/190	1,A
PCB 029	1,A	PCB 172	1,A
PCB 031	1,A	PCB 174	1,A
PCB 033/53/20	1,A	PCB 177	1,A
PCB 037/42/59	1,A	PCB 178	1,A
PCB 040	1,A	PCB 180	1,A
PCB 041/64	1,A	PCB 183	1,A
PB 44	1,A	PCB 185	1,A
PCB 045	1,A	PCB 187/182/159	1,A
PCB 046	1,A	PCB 189	1,A
PCB 047/48/75	1,A	PCB 191	1,A
PCB 049	1,A	PCB 194	1,A
PCB 52	1,A	PCB 195/208	1,A
PCB 056/60	1,A	PCB 196/203	1,A
PCB 66	1,A	PCB 200	1,A
PCB 070	1,A	PCB 201	1,A
PCB 074	1,A	PCB 205	1,A
PCB 77	1,A	PCB 206	1,A
PCB 082	1,A	PCB 209	1,A
PCB 083	1,A	Hexachlorobenzene	1,A
PCB 084	1,A	cis-Nonachlor	1,A
PCB 085	1,A	gamma-Chlordane	1,A
PCB 087/115	1,A	Lindane	1,A
PCB 088	1,A	Heptachlor	1,A
PCB 092	1,A	Endrin	1,A
PCB 097	1,A	Aldrin	1,A
PCB 099	1,A	Heptachlorepoxide	1,A
PCB 100	1,A	alpha-chlordane	1,A
PCB 101/90	1,A	trans-Nonachlor	1,A
PCB 101	1,A	Dieldrin	1,A
PCB 105	1,A	Mirex	1,A

PCB 107/108/144	1,A	2,4'-DDD	1,A
PCB 110/77	1,A	4,4'-DDD	1,A
PCB 118	1,A	2,4'-DDE	1,A
PCB 126	1,A	4,4'-DDE	1,A
PCB 128	1,A	2,4'-DDT	1,A
PCB 129	1,A	4,4'-DDT	1,A
PCB 136	1,A	o,p-DDD	1,A
PCB 138	1,A	o,p-DDE	1,A
PCB 153	1,A	o,p-DDT	1,A
PCB 170	1,A	p,p-DDD	1,A
PCB 180	1,A	p,p-DDE	1,A
PCB 187	1,A	p,p-DDT	1,A
PCB 195	1,A	DDMU	1,A
PCB 206	1,A	alpha-HCH	
PCB 209	1,A	beta-HCH	
		delta-HCH	
Recovery Standard		gamma-HCH	
TCMX	A		

Surrogates	
PCB 103	1
DBOFB	2
PCB 198	3

Table 4. Polynuclear Aromatic Hydrocarbon, Linear Alkyl Benzene, and Coprostanol Target Analytes

Compound	Surrogate	Compound	Surrogate
1-Methylnaphthalene	1	Chrysene	3
2,3,5-Trimethylnaphthalene	1	C_1-Chrysene	3
2,6-Dimethylnaphthalene	1	C_2-Chrysene	3
2-Methylnaphthalene	1	C_3-Chrysene	3
Naphthalene	1	C_4-Chrysene	3
C_1-Naphthalene	2		
C_2-Naphthalene	2	Benzo[b]fluoranthene	4
C_3-Naphthalene	2	Benzo[k]fluoranthene	4
C_4-Naphthalene	2		
		Benzo[e]pyrene	4
Benzothiazole	2	Benzo[a]pyrene	4
Acenaphthylene	2	Perylene	4
1-Methylphenanthrene	2	Indeno[1,2,3-c,d]pyrene	4
Acenaphthene	2	Dibenzo[a,h]anthracene	4
Biphenyl	2	Benzo[g,h,i]perylene	4
Dibenzofuran	2		
		Phenyl decanes	5
Fluorene	2	Phenyl undecanes	5
C_1-Fluorene	2	Phenyl dodecanes	5
C_2-Fluorene	2	Phenyl tridecanes	5
C_3-Fluorene	2	Phenyl tetradecanes	5
Anthracene	3	Coprostanol	
Phenanthrene	3		
C_1-Phenanthrene/Anthracene	3	<u>Surrogates</u>	
C_2-Phenanthrene/Anthracene	3	Naphthalene-d_8	1,A
C_3-Phenanthrene/Anthracene	3	Acenaphthene-d_{10}	2,A
C_4-Phenanthrene/Anthracene	3	Phenanthrene-d_{10}	3,A
		Benzo[a]pyrene-d_{12}	4,B
Dibenzothiophene	3	1-Phenylnonane	5,B
C_1-Dibenzothiophene	3		
C_2-Dibenzothiophene	3		
C_3-Dibenzothiophene	3	<u>Recovery Standards</u>	
Fluoranthene	3	Fluorene-d_{10}	A

Pyrene	3	Chrysene-d_{12}	B
C_1-Fluoranthene/Pyrene	3		
C_2-Fluoranthene/Pyrene	3		
C_3-Fluoranthene/Pyrene	3		
Benzo[a]anthracene	3		

Gas Chromatography-Electron Capture Detection (GC-ECD) for Pesticide and Polychlorinated Biphenyl Compounds, Method 8080M. Analyze sample extracts 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). Analyze the extracts on the GC/ECD using a dual column/dual detection method. Use a Restek, RTX-5 column, or equivalent as the primary column for analysis of the samples. Use a DB-17 column, or equivalent, for confirmation analysis except as noted below.

Instrument Preparation and Calibration. Calibrate the GC/ECD with a five-point calibration curve for the individual target PCB congeners from 5 to 200 ng/mL. Identify the target analytes by comparing retention times to those in the calibration standards. Determine the retention times of all the individual congeners 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, use the DB-17 column as the primary column, however, the analysts judgment should factor in to this decision. Make and approve a new 5- point calibration before any samples are analyzed.

4.1.2 Metals

Analysis of metals will be conducted in accordance with SOP MET-1A of the City's Oceanside Chemistry Laboratory. Sediment samples will be delivered in pre-cleaned containers to the City's Oceanside Chemistry Laboratory in South San Francisco 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 C for **??** hrs. The solutions are then evaporated on the hotplates to ca. 2.0-ml. Then 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)High resolution ICP-AES, (2) Cold vapor AA, (3) Hydride generation AA, Flame AAS, or (4) Graphite furnace AA. Target detection limits are listed in Table 5.

Table 5. Target Method Detection Limits for Organic and Metals Analysis

Metal	**Detection Limit (? g metal/g sediment)**	**Lowest Level in SF Bay from SFEI Studies (? g/g)**
Ag	0.001	0.07
Al	70	11,896
As	1.6	2.00
Cd	0.00002	0.17
Cr	9.44	0.8
Cu	4.57	21.10
Fe		20,640
Hg	0.005	0.07
Se	0.025	0.22
Zn	18.9	60.77
Organic Compound	**Detection Limit (ng/g sediment)**	
PCB	0.01 – 2.0	NA
PAH	0.07 - 2.84	NA

4.2 Physical 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 and gravel. Total organic carbon (TOC) will be analyzed in sediments using a combustion technique followed by infrared detection of CO_2 (ASTM method **???**) and reported as a percentage of total sediment weight.

4.3 Toxicity

The amphipod *Eohaustorius* sp. will be used in a 10-day, acute, solid-phase test based on ASTM Protocol E1367-92. *Eohaustorius* sp. 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, making it an excellent test species. Mortality, reported as percent survival, is the primary effect measured. Failure to re-bury in clean sediment at conclusion of the 10-day exposure is used as a subchronic toxicity measure. The ability to re-bury is important and has

ecological relevance since individuals that fail to re-bury after a disturbance are prone to predation and unlikely to survive in natural habitats.

Amphipods will be obtained from historic collection sites in San Francisco Bay and received at the City's Oceanside Laboratory within 48 hours of collection. Control sediment (home sediment) will be collected concurrently with the test species. Water/sediment 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 three days of organism receipt, provided acclimation rates are not violated and sediment test conditions permit.

Test sediments are run currently with negative (fine-grained control sediments collected from Tomales Bay, California, and 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. Well know is the fact that ambient sediment conditions unrelated to sediment contaminants cause toxicity. 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 determined. Ammonia levels greater than 20mg/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. Water exchanges will be performed on all high ammonia sediment replicates prior to test initiation when interstitial water levels exceed 20mg/l. Porewater sulfide levels greater than 100mg/l can be reduced by aerating overlying water. When high levels of sulfides are present aeration will be increased. Manipulations such as these constitute deviations from standard protocols and require addition "manipulation controls." Manipulations designed to reduce potential confounding factors will not be attempted without the prior approval of the PM.

The acute 10-day amphipod test is summarized as follows. All test sediments will be dry-sieved through 1mm mesh stainless steel screens to remove possible amphipod predators and native amphipods that may be confused with the test species. Test and control sediments will be added to 1L pre-cleaned glass containers to a depth of 3-5cm, covered with approximately 900ml of clean seawater and aerated under test conditions overnight. Five replicate test chambers will be setup for each treatment twenty-four hours before the introduction of the test species (test initiation).

Sediment samples with ammonia porewater values greater than 20mg/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. Only after all "high" ammonia sediments have been reduced to testable conditions will the balance of the test sediments be distributed into test containers.

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 randomly distributed to each replicate container for a total of 100 amphipods per treatment (20 amphipods in each of five replicates). Daily measurements taken and recorded include dissolved oxygen, pH, salinity and temperature. 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.

A test will be considered valid if after 10-days of exposure the average control survival is ?90% and no control replicate exceeds 20% mortality. 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}.

4.3 Data Analyses and interpretation

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

4.3.1 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 results data that have passed QC review.

Descriptive statistics will be computed directly for chemical and physical results. Non-detect results for chemistry data will be excluded from statistical analyses. Mean values for each set of bioassay (toxicity) 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. Any test that has greater than one outlier will be repeated.

4.3.2 Comparative Statistics

Inference tests will be used to determine whether inner creek sediments are more contaminated or toxic than outer creek stations. 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.

4.3.3 Testing of Grouped Stations

Tests will be performed for stations grouped by distance strata and by long-channel strata. Grouped comparisons are made to determine whether combined locations (across or along creeks) differ. 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).

4.3.4 Testing of Individual Stations

Individual comparisons will be made for each station within a creek using a group predictive limit (Steel and Torrie 1960) established for the creek. Comparisons will be made for individual bioassay, physical and chemical parameters for each surface sediment, and for individual chemical and physical parameters for each subsurface sediment core interval. This procedure identifies potential problems (hot spots) to individual stations that might be concealed in the group comparisons. Predictive limits will be calculated for each creek 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.

4.3.5 Gradient Analysis

Linear regression will be used to search for gradients in contaminant concentrations and biological results across and along creeks. Subsurface cores will be analyzed to identify linear vertical trends in chemical concentrations only. Regressions will be performed for each creek by grouping stations to look for linear trends in chemical concentration with distance along and across the channels. Analytes that are detected in at least 50% of the samples will be included in the analysis.

5.0 Data Review and QA/QC

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). Approximately 20 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 through the monitoring of surrogate compound recoveries and the analysis of standard reference materials (SRMs), 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. Recovery internal standards will spiked into extracts prior to instrumental analyses and are used to calculate the recovery of the surrogate compounds. SRMs will be selected for matrix and analyte class analyzed. Potential analytical interference/contamination will be monitored through the processing and analysis of a laboratory procedural blank with each batch of field samples. Acceptability criteria are specified in this plan as well as SOPs to be used.

5.1 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, TPH and metal analysis are summarized in Table 6. DQOs specified in this project plan is 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 Oceanside 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 Table 5.

5.2 Quality Control

Quality control measures will be implemented in field sampling and in chemical analysis as a measure of analytical accuracy, precision, and potential contamination. The individual SOPs contain the detailed information for the quality control samples to be performed.

In the laboratory, all reagents and solvents used will be logged into a record book. Lot number, purity, and chemical descriptions will be recorded. Standards preparation will be documented and the records maintained in separate 3-ring binders. Laboratory notebooks or log sheets for all sample preparation activities will be maintained. Access to all chemicals, calibration solutions, and reference materials will be controlled. Balances used to weigh materials will be calibrated according to standard procedures (Appendix, Table A2).

Table 6. Data Quality Objectives

Element	Minimum Frequency	Data Quality Objective/Acceptance Criteria
PAH, PCBs, 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	Sediment	PAH PCB 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 > 0.99 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 ? 10% 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 85-115%
Lab Duplicate	One per batch of 20	RPD <25% for 65% analytes;

5.2.1 Organic Analyses

Data quality for organics and metals analyses must be ensured through QA program that is extensively documented through a laboratory QA Plan and SOPs. As a matter of policy and practice, Independent QA staff should be used to ensure that data quality objectives are met, QA issues are coordinated among project personnel, and that an independent audit of each data package is conducted prior to submission. The overall QA program for the project and all laboratory operations will be documented.

Upon arrival at the laboratory, all field and QC samples will be examined for possible contamination from breakage, spillage, and for acceptable shipping conditions, assessed for adequate sample volume, and checked against the accompanying sample custody sheets. Each sample received will be entered into the laboratory sample logging system and assigned a laboratory sample identification number and the sample container placed in storage according to SOP. The required chain-of-custody procedures will be completed and individual samples will be evaluated for storage, handling, and analytical instructions. Explicit sample preparation and analysis instructions and authorization will be prepared according to method specifications prior to proceeding with the analyses.

Several project-specific QC measures will be implemented in conjunction with TPH and PAH analyses in order to provide a measure of analytical accuracy, precision, and potential contamination.

As a standard procedure, every lot of solvent/reagents used in sample preparation will be analyzed and checked in duplicate by instrumental methods for potential contamination. All laboratory standards will be instrumentally checked prior to use. Standards will not be used unless approved by the laboratory manager or project manager.

All sediment field samples will be processed in batches of 15 field samples. Additionally, the sample batch will include a procedural blank, SRM (NOAA/NIST marine Sediment 1941a), a laboratory duplicate sample, matrix spike sample and a laboratory control sample. Acceptability criteria for the QC samples are specified in the data quality objectives list in Table 5. Any values below the analyte and matrix-specific MDL will be reported as non-detected (ND).

Potential analytical interference/contamination from, laboratory solvents, reagents, glassware and processing procedures, will be monitored through the processing and analysis of the matrix spike sample and the laboratory procedural blank. One equipment blank (field blank) will be analyzed to evaluate potential hydrocarbon contamination from field sampling activities. A laboratory control sample (blank spike) will be processed and analyzed with each analytical batch to observe the accuracy of the analytical procedure in recovering selected compounds within a compound class of interest. A duplicate sample will be processed and analyzed with each analytical batch to check the precision of the analysis for the matrix tested.

Quality control measures for instrumental analyses include instrument tuning criteria, initial calibrations, routine calibration checks (for approximately every 18 h of instrument run time),

and analysis of instrument reference material. For PAH analysis, an instrument check oil standard (e.g. North Slope crude oil (5 mg/l)) should be spiked with surrogates and internal standards, and analyzed with each batch of samples to check the precision of the instrument. To monitor laboratory accuracy, a matrix-specific SRM, SRM 1941a (marine sediment - certified for PAHs) will be analyzed with each batch of sediment samples. To monitor instrumental accuracy independently, SRM 1491 (a certified PAH solution containing 5 µg/L PAHs or equivalent), will be analyzed with each batch of PAH analyses.

Before instrumental analysis of sample extracts, a five-point calibration will be run for organic analyses and the linearity of the individual analyte response factors checked. Every 12 to 18 hours, or every 10 to 12 samples, a daily calibration will be run to check the stability of the instrument response. A new five-point calibration will be run if the RSD for either the initial calibration or the daily calibration fail to meet the criteria set in the SOP.

5.2.2 Metals Analysis

Data quality for metal analyses will be ensured at the City's Oceanside Chemistry Laboratory through SOPs that guide and document the overall Quality Assurance (QA) program at Oceanside. In addition, all relevant laboratory operations will be documented. However, the Project QA Officer will have the ultimate responsibility to ensure all metals data generated by Oceanside satisfies DQOs established in this project plan. Upon receipt, all field and quality control (QC) samples received will be examined for possible contamination from breakage, spillage, and for acceptable shipping conditions, assessed for adequate sample volume, and then the sample labels were matched against the accompanying sample custody sheets. Sediment samples will then be transferred to a refrigerator (4°C) for storage until analyzed. It is standard practice to use the client sample identification numbers as the laboratory sample identification numbers. These numbers will be entered into the laboratory's sample logbook. After completing the required chain-of-custody procedures and assessing if the sample set was complete, individual samples will be evaluated, and specific storage, handling, and analytical instructions will be specified. Specific analysis instructions will be prepared according to method specifications prior to proceeding with the analyses.

When needed for analysis, each individual sample will be logged out by the person requesting the sample, as well as the date, time, and room to which the sediment sample will be transported. Return of the samples to the refrigerator was also recorded.

Samples will be prepared for analysis as described in later sections with careful attention placed on minimizing contamination from environmental sources and sample carry-over (cross-contamination). According to laboratory SOP, QC measures will include instrument calibration, analysis of procedural blanks, matrix spikes, duplicate samples, and SRMs, and standard checks. Data quality objectives for the QC measurements are provided in Table 6.

Each analytical instrument (AAS or ICP) will be set up and undergo initial calibration according to manufacturer's directions and applicable SOPs. Calibration stock solutions for each instrument and matrix will be prepared from NIST-traceable trace metal or analytical-grade

material. Certified trace metal or analytical grade acids for all solutions will be used according to SOP. Records of all prepared solutions and source, including certified analyses, will be kept.

Before instrumental analysis of sediment digests by AAS or ICP, a three- to five-point calibration will be run and the linearity of the individual analyte response factors checked. The calibration solution will be re-analyzed after every 5 to 8 samples. If the relative standard deviations (RSD) for the initial calibration and subsequent calibrations were more than 10 percent but less than 25 percent, the calibration curve will be recalculated. If the RSD exceeded 25 percent, the calibration solution affected samples will be re-analyzed.

With each batch of field samples a procedural blank, a matrix spike sample, a SRM, and a sample duplicate will be analyzed to assess contamination, interference's, accuracy, and precision. A procedural blank will be processed and analyzed in order to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. Prior to sample analysis, every lot of acid to be used in analyzing sediment samples will be analyzed in triplicate to determine potential contamination. A matrix spike sample (method of additions analysis) will provide information on the extent of any signal suppression or enhancement due to the matrix. If necessary (e.g., when matrix spike results are outside the 85 to 115 percent acceptance criteria), all samples will be analyzed by methods of additions. A common method used in evaluating the accuracy of environmental data is to analyzed SRMs; samples for which consensus or "accepted" analyte concentrations exist. The marine sediment BCSS from the National Research Council of Canada will be analyzed for certified analytes in every batch of sediment. To estimate precision of the analyses, a duplicate field sample will be analyzed with each sample batch.

5.2.3 Toxicity

A 96-hour reference toxicant test will be run concurrently with each amphipod test using the same batch of test organisms. Cadmium, as cadmium chloride, will be used to produce five reference toxicant concentrations (e.g., 0.25, 0.5, 1.0, 4.0 mg Cd/L). Clean seawater will be used for control and diluent water. Reference toxicant testing coincident with the solid-phase testing will be conducted in the absence of sediment. Test containers will be randomly distributed in a constant temperature chamber, stocked with 10 amphipods each and left in the dark for 96-hours. Dissolved oxygen, salinity, pH, and temperature will be measured daily in one replicate from each treatment, and the number of live and dead organisms will be recorded daily for all containers.

At the conclusion of the test, percent survival will be calculated and an LC_{50} generated. The LC_{50} value will be compared to the in-house species specific reference toxicant database to determine whether or not the *Eohaustorius* sp. exhibited abnormal sensitivity. Tests exhibiting LC_{50} values within two standard deviations of the laboratory control chart mean are considered normal.

5.3 Laboratory Records

All laboratory operations are to be documented and placed in three ring binders. Documentation include the following:

- ?? Lot number and vendors for reagents and standards;
- ?? Preparation of stock solutions, standards, and spiking solutions;
- ?? Sample preparation;
- ?? Analytical procedures; and
- ?? Analytical instrument and conditions.

Target analyte concentrations, surrogate and matrix spike recoveries, SRM and other QC results will be summarized in a spreadsheet format. After careful checking and review by the project team, the data will be arranged in Excel, Lotus or Quattro Pro spreadsheet format. Diagnostic graphics will be generated and submitted upon request. A program database will be created to fulfill specific project requirements.

Appendix A.

Table A1. Field Equipment List

Quantity	Units	Check	Description
1	each		Stainless steel - Kynar coated modified Van-Veen Grab
2	each		Van Veen table and tub
1	each		Gravity core system (with core noses, core catchers, spare parts)
30	each		Gravity core liners (>2 feet in length)
1	each		Laser Rangefinder
1	each		Electronic Compass
1	each		DGPS system
2	each		Fiberglass measuring tape, 100 meters
18	each		Weight/line/buoy markers
1	set		Tide charts for sampling week
1	4-L bottle		Methylene Chloride - field QC samples, equipment de-con. (plus squirt bottle)
1	4-L bottle		Hexane - equipment de-con. (plus squirt bottle)
2	2.5-L bottle		Nitric Acid - acrylic core tube de-con. (plus squirt bottle)
1	20-L bottle		100% Formalin - need to make 10% solution for biological sample preservation
1	box		Arm & Hammer 20 mule team borax - equipment cleaning, de-con.
1	20 Liters		De-ionized distilled water - equipment de-con. and field QC samples (plus squirt bottle)
60	each		1-qt plastic wide -mouth jars - infauna samples
200	each		Food-grade ziplock plastic bag – TOC/grain size
120	each		250-mL I-CHEM short wide-mouth glass jars w/ labels – organic chemistry
120	each		250-mL I-CHEM short wide-mouth polyethylene jars w/ labels - metals samples
15	each		Glass jars for trip/field/equipment rinse blanks, organic analyses
15	each		Polyethylene jars for trip/field/equipment rinse blanks, metals analyses
60	item		Sample labels (waterproof) for toxicity samples (two per sample)
3	each		1.0 mm sieve buckets w/handle – infauna sample
3	each		0.5 mm sieve buckets w/handle - infauna sample
3	each		Teflon-coated stainless steel trowels
3	each		Stainless steel spoons - infauna sub-sampling
72	each		Teflon core liner w/caps (included in container table)
6	each		5-cm stainless steel spoon/spatula w/TFE coating (Fisher 14356-10) - sediment chemistry sub-sampling
2	each		Teflon tube w/siphon bulb - subsampling
2	each		Graduated container - infauna sediment volume estimate
15	each		Coolers - sample packing
0.5	Roll		Packing material, bubble wrap - sample packing
20	each		Chain of custody sheets and seal - sample shipping
2	each		Copies of Sampling/Analysis & Quality Assurance Project Plan
3	each		Copies of target station locations (lat/long and range/bearing)
3	each		Project maps

Table A2. Standard Operating Procedures (SOP)

SOP Number	Title
Field Operations Standard Operating Procedures	
ADL-1016	Documentation and Field Reporting Requirements for Marine Sampling
ADL-1017	Sample Labeling and Chain of Custody Requirements
ADL-1018	Operation of the Van-Veen Grab Sampler
ADL-1019	Collection and Handling of Subtidal Sediment Chemistry Samples From the Van-Veen Grab Sampler
ADL-1021	Collection and Handling of Chemistry Quality Control
Standard Operating Procedures for Organic Analyses	
ADL-1013	Marine Sciences Sample Receipt and Log-in
ADL-2823	Extraction of Semivolatile Hydrocarbons from Sediment for Shoreline Soil Samples
ADL-2827	Determination of Polynuclear Aromatic Hydrocarbons and Selected Heterocyclic Compounds by Gas Chromatography/Mass Spectrometry in the Selected Ion Monitoring Mode
ADL-2828	Determination of Saturated Hydrocarbons by Gas Chromatography-Flame Ionization Detection
ADL-5802-01	Standard Operating Procedure for Cleaning and Preparing Laboratory Glassware and Teflon Jars
ADL-5814	Operation and Maintenance of the Fisher Model 361 Orbital Shaker
ADL-5809	Operation and Maintenance of the Marine Science Unit Top Loading Balances
ADL-5806	Operations and Maintenance of the CAHN 29 and CAHN 31 Electrobalances
ADL-5028	Maintenance and Operation of the Flame Ionization Detector (FID)
ADL-5036	Procedure for Injection Port Maintenance for the HP 5890A Gas Chromatograph in the GC/MS Facility
ADL-6010	Procedure for GC Data Storage and Tape Archiving*****
ADL-6013	Marine Chemistry Sample Analysis-Data Handling and Reporting
Standard Operating Procedures for Metals Analyses (Oceanside Laboratory)	
MET-1A	Determination of Trace Metals in Sediments
Standard Operating Procedures for Toxicity Tests	
ASTM-E1367-92	10-day Static Acute Toxicity Test Using Amphipods
Standard Operating Procedures for Physical Analyses	
	Grain Size Analysis
	Total Organic Carbon Analysis

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