Regional Monitoring Program

for Water Quality in San Francisco Bay

2020 Bay Margins Sediment Study

Cruise Plan

San Francisco Estuary Institute
4911 Central Avenue
Richmond, CA 94804

1. Introduction

This report details plans associated with sediment sampling for the Bay Margins Sediment Study for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Bay margins (i.e., mud flats and adjacent shallow areas of the Bay) are productive and highly utilized by biota of interest (humans and wildlife). This study will provide a spatially-distributed characterization of surface sediment contamination and ancillary characteristics within San Pablo Bay, Suisun Bay, and Carquinez Strait margin areas. This study builds on two previous studies to characterize surface sediment contamination in Central and South Bays.

The specific objectives of the sampling effort are:

1. Measure sediment parameters (pH, ORP - oxidation reduction potential) at 40 sites.
2. Collect sediment samples from 40 sites ("standard margins samples") for analysis of:
    - Sediment grain size
    - Sediment quality parameters (% solids, total solids, TN, TOC)
    - Mercury and methylmercury
    - Trace metals (Ag, Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Se, Zn)
    - PCBs (209 Congeners)
3. Collect sediment samples from 40 sites for "standard margins archives":
    - Poly- and perfluoroalkyl substances (PFAS)
    - Labile non-PFAS emerging contaminants
    - Non-PFAS organics
    - Trace metals
4. Collect sediment samples from 40 sites for add-on studies:
    - PFAS
    - Pesticides
    - Halogenated azo dyes
5. Collect duplicate sediment samples from 10 sites for interlaboratory comparison between Eurofins and ALS
    - Sediment grain size
    - Sediment quality parameters (% solids, total solids, TN, TOC)
6. Collect sediment samples from five sites for add-on studies:
    - Quaternary ammonium compounds (QACs)

2. Key Personnel and Approvals

The personnel and work assignments for this cruise are shown in Table 1. These key personnel have indicated their approval of the Cruise Plan by adding their initials and date in the far right column.

Table 1. Key Personnel for 2020 RMP Margin Sediment Cruise

Name	Affiliation	Duties	Cell	Initial and Date to Indicate Approval of Plan
Marco Sigala	SJSURF	Project Manager	831-771-4173	MS 9/2/2020
Jamie Yin	SFEI	Project Manager	831-465-4704	JRSY 9/3/2020
Melissa Foley	SFEI	RMP Manager	831-566-7816	MMF 9/2/2020
Jay Davis	SFEI	RMP Lead Scientist	530-304-2308	JD 9/2/2020
Don Yee	SFEI	RMP QA Officer	510-508-2995	DY 2020/09/03
Adam Wong	SFEI	RMP Data Manager	530-400-5192	AW 9/4/2020
Rebecca Sutton	SFEI	RMP Senior Scientist (CECs)	510-701-7050	RAS 7/8/2020

3. Cruise Schedule

The cruise schedule is shown in Table 2. The schedule is for planning purposes only, and may be revised during sampling operations to reflect weather conditions, tide restrictions, equipment performance, or other factors. Any sites that cannot be sampled at the scheduled time will be rescheduled later in the cruise, if possible.

Table 2. Anticipated Cruise Schedule for 2020 RMP Sediment Cruise

Date	Time	Activity
Aug 31-Sep 4*		Tentatively scheduled as Sample Week ~13 stations
September 14-18*		Tentatively scheduled as Sample Week ~13 stations
Sep 28-Oct 2*		Tentatively scheduled as Sample Week ~13 stations
**Due to Moss Landing Marine Labs being closed due to the pandemic, sampling is delayed from the original planned start date of July 2020.*		

4. Sampling Procedure

At each station, samples/data will be collected in the following order:

1. Two to seven sediment grabs for pH, oxidation-reduction potential (ORP), and chemistry samples. Use of each grab is outlined in the Chemistry Sample Handling and Processing Protocol section below.

2. Field observations should also be noted for each site (e.g, wind speed, wave height, weather).

Sediment samples will be collected and processed following the procedures in the following subsections.

Sample Equipment and Cleaning

Intertidal sampling in San Francisco Bay will be conducted from an 18' Boston Whaler equipped with frame and hydraulics for deploying a 0.1 m^2 modified Van Veen sediment grab. The grab is constructed entirely of stainless steel and the jaws and doors are coated with Kynar™ to improve chemical inertness. A plastic scoop will be used to remove surface sediments and fill containers. Sample jars intended for PFC and PFAS analyses or archives will be used to directly scoop sediment from the center of the grab sample. Sediment will be scooped directly into sample jars that must be frozen in the field (mercury and methyl mercury), attempting to subsample the full 0-5 cm depth into each jar as much as practicable to within ~75% full. A non-brightly colored polycarbonate bucket will be used to store a composite sample for all other standard margins samples (TN, TOC, grain size, PCBs, trace metals, archives) and add-ons (pesticides, halogenated azo dyes, QACs).

All sampling and handling will be conducted using clean techniques. Prior to sampling, all sampling equipment will be thoroughly cleaned. Equipment that is pre-cleaned includes the Van Veen grab, sample scoops, compositing (or storage) buckets, foil, polycarbonate coring devices, and wash bottles. The grab will be cleaned with detergent and pressure washed at the lab. Other equipment is washed, with a detergent and deionized water solution, and rinsed three times with deionized water in lab pre-cleaning, which can be substituted with ambient water in the field. Equipment is next rinsed with 1.0% solution of hydrochloric acid (or equivalent), followed by a rinse with methanol. All equipment, besides the grab, is stored in clean Ziploc™ bags (including pre-cleaned polycarbonate scoops) until used in the field. It is critical that sample contamination be avoided during collection. Sample scoops will be re-cleaned in the lab between uses as needed; other equipment used at different sampling stations should be re-cleaned in the field between uses.

Sample containers will be purchased pre-cleaned directly from a supplier, provided pre-cleaned by the analytical or archive agency, or purchased uncleaned from a supplier and cleaned in the lab (Attachment C).

Sampling personnel should wear nitrile gloves whenever taking or processing samples to avoid contact contamination (and for personal protection). In addition, airborne contamination is avoided by keeping sample containers, sample scoops, and compositing buckets covered when not in use. Do not allow the sample to contact clothing, textiles, or other objects that may be dyed to avoid potential contamination with halogenated azo dyes. Alcohol-based sanitizing and disinfecting products are recommended as

needed; avoid using QAC products (i.e., Lysol disinfecting sprays, Clorox wipes) to limit risk of QAC contamination, particularly on the day(s) when these samples are collected.

Sediment Collection and Sediment Field Measurement Protocol

The A-frame at the side of the vessel will be used for deploying the Van Veen grab. If water depth is insufficient to reach the sampling location by boat, sediment samples will be collected by hand using 4" polycarbonate sediment cores. The quality of grab samples will be ensured by requiring each sample to satisfy a set of criteria concerning the depth of penetration and disturbance of the sediment within the grab. In this way, each sample will normally contain the top 5 cm of sediment within the area of the grab jaws. Grab samples will be rejected for the following conditions:

- There is a rock or shell fragment wedged between the jaws of the grab allowing the sample to wash out.
- The sample surface is significantly disturbed.
- The sample is uneven from side to side, indicating that the grab was tilted when it penetrated the sediment.
- The surface of the sample is in contact with the top doors of the grab, indicating over-penetration of the grab and possible loss of material around the doors.

The total number of grabs or cores taken will be recorded by field personnel on the field datasheets.

At least one pH measurement from each site will be recorded from a grab or exposed sediment (i.e., if site is approached from land and cores will be taken) by submerging a pH probe into the sediment (or a mini-core from a grab) to a depth of approximately 4 cm and allowing it to equilibrate until stable, up to 10 minutes. pH probes should be checked against pH standards each day before sampling and recalibrated if the measured value varies by more than 0.05 units from the expected value. ORP measurements will be made in a mini-core taken either from a grab or exposed sediment at a depth of 2.5 cm according to the RMP Short Sediment ORP measurement SOP (**Attachment A**). As time allows additional pH and/or ORP measurements may be helpful due to heterogeneity of these parameters at a small scale. Field measurements of pH, ORP, and other parameters will be recorded on the Field Data Sheet (**Attachment B**).

Sediment samples will be collected to a depth of 5 cm and composite samples will be taken until at least 2.5 L of sediment is collected (3 L needed from a subset of sites). Multiple deployments of the grab or hand cores will be composited together to obtain the required volume and to average out ultra fine-scale spatial variation. Sediment grabs showing prior disturbance (e.g., from immediate/recent prior grabs at the same site) should be retaken from an undisturbed area. Hand collected core samples should composite material from a 2-3 m radius (rather than collecting only contiguously adjacent hand cores).

Chemistry Sample Handling and Processing Protocol

After the overlying water has been drained off the grab sample, several sub-samples will be collected directly from the first and second grab. All samples that are directly collected into sample jars should attempt to representatively include all of the top 5 cm (e.g., rather than just scraping off the top 1cm) as

much as practicable (e.g., perhaps not possible with small vials), unless otherwise specified for a given sample. Some of these subsamples will be field frozen. The composite samples should include roughly equivalent volumes of sediment from at least three grabs. The subsamples to be collected and the order in which they should be collected are:

- Grab 1 - Half of the grab will be used for the ORP core and disturbed. Use the other side for Hg/MeHg (4 oz jar), and LOST (60 ml jar).
- Grab 2 - Collect 5 PFC cryovials (PFLT, PFST) first by hand-dipping the containers directly into the grab. Collect the PFAS sample next (two jars). Then collect the 3 POLT Teflon tubes. The POLT Teflon tubes must be collected after the PFLT and PFST cryovials and PFAS sample to avoid cross contamination by PFAS in the Teflon. The remaining sediment will be scooped into the polycarbonate composite bucket.
- Rest of the grabs - Any undisturbed sediment will be scooped into the clear (to prevent contamination of azo dye samples) polycarbonate bucket for the composite samples. Composite samples from the bucket will be filled in the laboratory.

Attachment C contains the details for how each field-filled sample should be collected. Important points are reiterated below:

- The mercury sample must be collected and field frozen on dry ice within 20 minutes of sample collection. If the 20 minute time limit is not met, add a note in the collection information with the amount of time that passed between collection and freezing.
- The archive samples intended for labile non-PFC emerging contaminants (LOST) and non-PFC organics or trace metals (POLT) must also be field frozen on dry ice.
- The samples for perfluorinated analysis (PFAS) and archives (PFLT, PFST) will be collected from the center of the grab, avoiding contact with the edges of the Van Veen or sediment core that may have been in contact with the grab. For PFLT, PFST, and PFAS samples, the sample container will be used to collect the sample directly into the container. The sampler should wear clean nitrile gloves and, IF NEEDED, should wipe off excess sediment on the top rim and grooves of the vial with gloves or a kimwipe to allow for a good seal.

The remainder of the sediment will be collected and stored at 4ºC in a polycarbonate bucket in a cooler. This sediment will be homogenized and subsequently sub-sampled to the appropriate laboratory specific containers in the lab within seven days following collection. **See Attachment C for details.**

The sample groups and total sediment volume that will be collected at each site, as well as the location of field duplicates and field blanks, are summarized in **Attachment D.** The number of sample containers that need to be filled with sediment from each site (as designated in Attachment D), the volume of sediment required for each container, and sample handling, storage, and shipping requirements are listed in **Attachment C.**

PFAS sample bottles should be filled to between 50-75% as sediment volume allows. All other sample bottles should be filled to 75% of total capacity unless otherwise specified, to allow room for expansion on freezing, as needed. Sample containers for MeHg/Hg will be double-bagged in ziploc bags, others

(especially glass) may be bagged in ziploc to avoid contamination and then bubble wrap bagged or placed in their original shipping box with cardboard separators to reduce potential container breakage.

Sediment QA/QC Sample Collection

The number of field duplicates and field blanks to be collected for each analyte group at each site are designated in **Attachment D, Table 1.** Attachment C lists the container types for which field duplicates and bottle/field blanks must be collected.

Field duplicates will be collected at two sites, SUB025 and SPB039. For field duplicates, separate sediment composites will be collected and composited from different sets of grabs than the primary sample for the site (two composites each site). Field duplicates will be collected from a second set of grabs sampled immediately after the first set of grabs are sampled.

Duplicate samples for grain size and TN/TOC will be collected at ten sites for an interlaboratory comparison (see **Attachment D** for details). The duplicate samples should be collected from the same composite sample immediately after the first grain size and TN/TOC sample.

If needed, extra volumes will be collected at one station for grain size (see **Attachment C** for details). The extra sample volume will be collected using the same method as field samples; for analyses using composited sediment subsamples, the extra volume should be subsampled from the same material post-compositing.

Blanks will be collected using several methods. For the mercury/methylmercury, PCB, short term archive samples (PFST, LOST, POST, TMST), PFAS, pesticides, and dye samples, two spare bottles will be retained with the set of samples to act as bottle blanks for container type. These containers have been purchased 'pre-cleaned' from ESS Vial or VWR, or provided by NIST. Bottle blanks will not be opened and will be kept with other RMP samples in case container contamination issues arise. These bottles do not need to be brought into the field. They can remain in the lab during the cruise. These containers should be clearly labeled as bottle blanks, and noted on the COCs for the analytical labs to not analyze unless later requested.

Field blanks will be conducted at SUB025 and SBP039 prior to sample collection. For samples directly collected from the grab into final containers in the field (mercury/methylmercury), field blanks will be brought into the field and handled similarly to field sample containers. Bottles will be placed in the same general location as field sample bottles and opened while (or shortly before or after, for about the same period of time) the field sample bottles are being filled, while taking care not to contaminate the blank bottles with any splashes of stray water or sediment materials. For sample bottles from composites (azo dyes and pesticides), "field" blank bottles will also be opened to air in the same vicinity and time while the sample jars are open for composite subsampling in the lab. These containers should be clearly labeled as field blanks and noted on the COC for the analytical lab to not analyze unless later requested.

5. Laboratories

Contact information for the laboratories and archive agencies receiving samples from the sampling event, as well as the field contractor, is shown in Table 3.

Table 3. Contact Information for laboratories and contractors for the 2020 Bay Margins Sediment Study

Agency	Role	Contact	Shipping Address	Phone / Email
Laboratory Contacts				
Eurofins	Grain size, TOC, TN	Michele Castro	Eurofins Calscience, LLC 7440 Lincoln Way Garden Grove, CA 92841	949-870-8766 MicheleCastro@EurofinsUS.com
ALS	Grain size, TOC, TN	Mark Harris	1317 South 13th Ave Kelso, WA 98626	360-577-7222 mark.harris@alsglobal.com
Brooks Analytical Lab	Mercury	Amy Goodall	18804 North Creek Parkway, Suite 100 Bothell, WA 98011	206-632-6206, ext. 110 amy@brooksapplied.com
SFPUC	Trace metals	Austin Lau	1000 El Camino Real, Millbrae, CA, 94030	650-871-3011 alau@sfwater.org
SGS AXYS	PCBs	Sean Campbell	SGS AXYS Analytical Services, Ltd. 2045 Mills Road Sidney, British Columbia V8L5X2	250-655-5838 Sean.Campbell@sgs.com
Dr. William Arnold, University of Minnesota	QACs	William Arnold	William Arnold Department of Civil, Environmental, and Geo-Engineering University of Minnesota 500 Pillsbury Dr. SE Minneapolis, MN 55455	952-693-8603 arnol032@umn.edu
Archive Agency Contacts				
NIST	Long-Term Archives	Amanda Moors	NIST Hollings Marine Laboratory 331 Ft. Johnson Rd. Charleston, SC 29412	843-762-8953 amanda.moors@nist.gov
AMS	Short-Term Archives	Paul Salop	Applied Marine Sciences 4749 Bennett Dr., Ste. L Livermore, CA 94551	925-373-7142 salop@amarine.com
Field Contractor (equipment shipping)				
San Jose State University Research Foundation (SJSURF)	Field Contractor	Marco Sigala	Marine Pollution Studies Lab Moss Landing Marine Laboratories 7544 Sandholdt Rd. Moss Landing, CA 95039	831-771-4173 msigala@mlml.calstate.edu

6. Sampling Sites

Forty sites will be targeted in 2020. Coordinates for all RMP sampling sites are shown in Attachment D and Figure 1.

Site Access and Selection

The list of the 40 target sampling sites is shown in Attachment D, Target Sites. Sites are distributed among margin areas in three regions: San Pablo Bay, Suisun Bay, and Carquinez Strait. There are 27 target sites in San Pablo Bay, 11 target sites in Suisun Bay, and 3 target sites in Carquinez Strait, each of which were selected through a probabilistic site selection scheme.

Target analyte groups will be collected at all sites, with the exception of QACs (collected at SUB025, SUB027, SUB021, SUB026, SUB020) and sediment interlaboratory comparison samples (collected at SPB028, SPB032, SPB036, SPB040, SPB044, SPB048, CAR08, SUB018, SUB022, and SUB026). "Standard" margins samples, including analyses for mercury, PCBs, trace metals, PFCs, PFAS, pesticides, azo dyes, ancillary parameters, and archives will be collected at the 40 probabilistic sites.

Field teams will navigate to the coordinates for the target sites within the accuracy of the shipboard GPS. However, the field team can move around within 50 meters of the planned site to find a suitable location with target habitat nearby if any of the following logistical problems prevent sampling at the planned site coordinates:

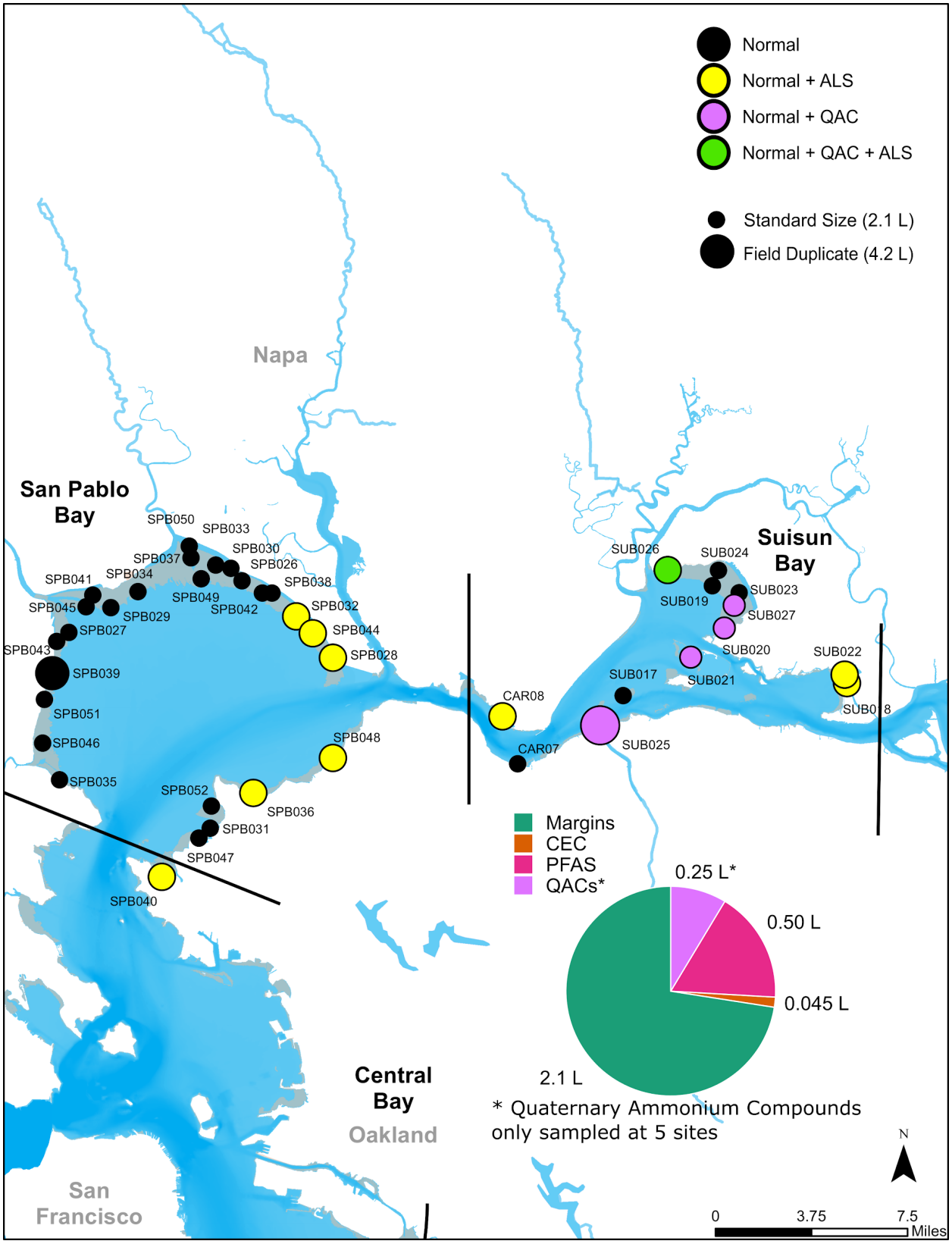
- Access/safety: The site cannot be accessed safely; OR
- Substrate: The substrate at the site is too coarse to collect a cohesive sample, is rocky shoreline, is covered with dense aquatic vegetation, or is shell hash; OR
- Upland area (above MHW): The planned site is in a salt marsh or upland area; OR
- Deep subtidal area: The planned site is deeper than 1 ft below MLW.

For sites that need to be relocated within the 50 meter allowable radius, the sample should be collected at the expected water depth for the original site to avoid biasing (e.g., biasing by always going to the deepest allowed depth). The expected water depths for the target sites are shown in Attachment D.

Sites that are not at their expected depth but are still within acceptable habitat and depth range (MHW to 1 foot below MLW) will be sampled at the target coordinates.

If no suitable locations are found within 50 meters, the site will be rejected as not possible to sample. The next available site in the respective overdraw lists in Attachment D Overdraw Sites will be added in its place depending on the region.

Figure 1: 2020 RMP Margins Sediment Cruise Target Sampling Sites. The 40 target sites are symbolized based on approximate sample volume needed to be collected.



7. Sample Labeling

The sample ID system used for the Bay Margins cruise for analytical samples is as follows:

YYRMPMC-STA#-AGX-rep#

Where:

YY = Year (for 2020, YY = 20)

RMPMC = Project (RMP Margins Cruise)

STA# = Station ID (e.g., SPB026 through SPB052)

AGX = Acronym for analyte group. See **Attachment C** for acronyms (acronym is 2-4 letters)

Rep# = Replicate number

The sample ID system used for the Bay Margins cruise for archive samples is as follows:

YYRMPMC-STA#-AGXAARep#

Where:

YY = Year (for 2020, YY=20)

RMPMC = Project (RMP Margins Cruise)

STA# = Station ID (e.g., SPB026 through SPB052)

AGX = Acronym for analyte group. **See Attachment C for acronyms.**

AA = Archive type (when applicable). (ST = short term, LT = long term)

Rep# = Replicate jar number for each analyte group

Notes on assigning Rep#: The replicate number should be increased sequentially as needed to characterize a field replicate and duplicates. For example, for mercury samples, there is only one container to be filled for each sample. The Rep# will be 1 for the primary sample and 2 for the field duplicate. In contrast, for PFLT archive samples, there are two containers to be filled for each sample. The Rep# will be 1-1 and 1-2 for the primary sample and 2-1 and 2-2 for the field duplicates. For field blanks, use “FieldBlank”, and for bottle blanks, use “BottleBlank”.

Every container will be labeled with a unique sample ID following this system. The sample ID will be recorded on a field data sheet (**Attachment B**).

8. Sample Handling and Custody

Chain of custody records will be maintained throughout the course of the sampling effort. For each set of samples being shipped to a laboratory or archive, SJSURF will initiate a COC form, include the original form with the sample shipment, and provide a copy/scan of the form to SFEI at the time of the shipment.

Field sample handling, storage, custody, and shipping information are outlined for each sample type in **Attachment C**. A summary of key points is reiterated below:

- SJSURF will store all standard margins samples, CEC samples (PFAS, pesticides, azo dyes, QACs), and archives and ship them to their respective laboratory or agency destinations at the end of the field season.

Agencies should be notified prior to any shipment, and the contacts listed in Table 3 should be included in any FedEx shipment notifications. The laboratories will provide Analytical Services Request (ASR) templates prior to field sampling, which will then only need to be filled in with the sample date.

Attachment A

RMP short sediment ORP measurement SOP (revised 2015-05 for margins)

The method is modified to take a single reading at 2.5 cm depth rather than at three depths in the standard RMP method. Steps for taking a picture were also made optional.

Oxidation/reduction potential (ORP) readings are taken at each station from a grab core or direct insertion in exposed sediment. Additional readings can also be taken, time permitting. Instrument ORP readings are offset from true "Eh" readings by an amount specific to the particular electrode type: the Sentix ORP (platinum) probe for the WTW meter is ~-210mV relative to true Eh (hydrogen electrode); Eh= ORPreading + 210mV (at 20^{o}C). DO NOT make a correction to the ORP reading in the field; record what you read.

Materials:

ORP meter and electrode (Oakton ORP Testr 10)

Clear coring tube, ~5 cm diameter or larger, ~5 cm height

Watch or timer to track probe equilibration time

Collection method:

1. Push the core tube into the grab, let the crew collect the rest of the material.

2. Dig a tool or fingers under to help lift it out

3. Once out, place on a jar lid or other flat surface (to prevent core sliding out of the tube).

Measurements:

1. Make a note in the field log of depth below the surface of any transitions or notable features in the core or surrounding grab (e.g., gray below 4 cm, fine shell fragments throughout). Optionally, take a picture of core/grab/in situ sediment cross section.

2. Push the ORP probe, to **2.5cm** depth.

    a. If the probe hits something hard like shell, rock, or wood fragment, do not force through, as the probe tip may break. If close to target depth (e.g., > 2 cm), keep that location. If a long way from target depth, note the depth of the obstruction, and pull out the probe. For exposed site sediment, just insert at another point.

    b. In a core, there is less space to relocate so use a wire or skinny screwdriver to poke at locations to find a way around the object, but do not poke all the way to the target depth (or you may expose that point to air).

c. If a clear path is found with test wire/screwdriver, insert the probe along that path. If near the core edge, be sure the ORP probe orifice (small hole in the probe side about 0.5 cm from the tip) is facing toward the core center.

3. Note time/set timer. Record reading after the sensor has equilibrated, about 5-8 min. Record raw ORP, **NOT** Eh conversion.

4. If ORP > 0 in anoxic (black/sulfidic) sediment, the probe may be broken. Switch probe.

5. Dump core, rinse probe in site water, re-cap, and get ready for the next station, or take another reading from the same station if there is enough time.

6. Clean well, rinse/store with DI water in cap at the end of the day.