Regional Monitoring Program
for Water Quality in San Francisco Bay

2023 Bay Prey Fish and Near-field / Margins Sediment Sampling and Analysis Plan

RMP

Prepared by

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1. Introduction

This is a sampling and analysis plan for the Bay Status and Trends (S&T) Prey Fish and Near-field / Margins Sediment monitoring for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). Bay margins are defined by the RMP as extending from Mean Higher High Water (MHHW) to 1 foot below Mean Lower Low Water (MLLW). These mud flats and adjacent shallow areas of the Bay are productive and highly utilized by biota of interest (humans and wildlife). Near-field stations are located near watershed inputs in the Bay. Prey fish are a key matrix to monitoring the status and impacts of contaminants, especially near margin areas where they have shown strong contamination signals in previous RMP studies. This monitoring design provides a spatially-distributed characterization of contaminant concentrations in fish and sediment found within the margins of Central Bay, South Bay, and Lower South Bay. This study builds on previous S&T efforts to characterize surface sediment contamination across the Bay while piloting routine monitoring of prey fish. Additional samples outside of S&T will be collected for special studies. A subset of samples will be archived for potential future analysis of emerging contaminants or other analyte groups.

The specific objectives of the sampling effort are:

1. Collect prey fish samples from 12 areas for analysis of:
    - Per- and polyfluoroalkyl substances (PFAS) for SGS AXYS
    - Ancillary tissue parameters (solids, lipids) for SGS AXYS
    - PCBs for SGS AXYS (2 stations in San Leandro Bay PMU only [prey fish were sampled for PCBs at the SS/RC PMU in 2022 so they don't need to be sampled again in this year])
    - Short term archives (as available) for AMS
    - Long term archives (as available) for NIST
2. Measure sediment parameters (pH) at 38 (24 M, 14 NF) stations.
3. Collect sediment samples from 24 margins stations for analysis of:
    - PFAS for SGS AXYS
    - Bisphenols for SGS AXYS
    - Sediment grain size for ALS
    - Sediment quality parameters (% solids, total solids, TN, TOC) for ALS
    - QACs for UMN (1 station)
4. Collect sediment samples from 24 margins stations for short term archives for AMS.
5. Collect sediment samples from 5 margins stations ("Repeat stations") for long term archives for NIST.
6. Collect sediment samples from 14 near-field stations ("standard near-field samples") for analysis of:
    - PFAS for SGS AXYS
    - Bisphenols for SGS AXYS
    - Sediment grain size for ALS
    - Sediment quality parameters (% solids, total solids, TN, TOC) for ALS
    - QACs for UMN (3 stations)
7. Collect sediment samples from 14 near-field stations for short-term archives for AMS.
8. Collect sediment samples from 6 near-field stations for long term archives for NIST.

2. Key Personnel and Approvals

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

Table 1. Key Personnel for 2023 Prey Fish and Margin Sediment Sampling Plan

Name	Affiliation	Duties	Cell	Initial and Date to Indicate Approval of Plan
Marco Sigala	SJSURF	Field Collection Lead	831-595-3448	MAS 9/5/2023
Autumn Bonnema	SJSURF	Fish Processing Lead	831-771-4175	
Amy Kleckner	SFEI	RMP Manager	415-531-3390	AK 9/5/2023
Jay Davis	SFEI	RMP Lead Scientist	530-304-2308	JD 9/6/2023
Don Yee	SFEI	RMP QA Officer	510-508-2995	DY 2023/09/05
Adam Wong	SFEI	RMP Data Manager	530-400-5192	
Rebecca Sutton	SFEI	RMP Senior Scientist (CECs)	510-701-7050	RAS 9/5/2023

3. Sampling Schedule

The sampling 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.

Table 2. Anticipated Sampling Schedule for the 2023 Prey Fish and Sediment Study

Date	Time	Activity
August 21-25, 2023*		Tentatively scheduled period for Sampling
September 5-8, 2023*		Tentatively scheduled period for Sampling
September 11-15, 2023*		Tentatively scheduled period for Sampling

4. Sampling Procedures

Prey Fish

There are 12 total stations planned for prey fish sample collection (**Figure 1**). At each fish sampling station, samples/data will be collected as follows:

1. At each station, three samples of 30 fish each should be collected (90 total fish per species). The primary target species will be topsmelt, based on what was successfully collected in previous studies (Yee et al. 2021). If Mississippi silverside are observed instead of topsmelt, they will be collected.

    a. At nine stations (only sampling one of the two stations in each of the three PMUs [Richmond Harbor, San Leandro Bay, SS/RC]), a composite of 20 staghorn sculpin will be collected.

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

Fish sampling stations overlap with or span near-field and margin sediment stations but are likely to differ depending on where fish are present.

This study is a pilot to evaluate the feasibility and usefulness of adding prey fish to S&T biota monitoring. The species collected encompass benthic and pelagic species, including topsmelt, Mississippi silverside, and staghorn sculpin. Collections are prioritized at locations where other S&T monitoring is occurring, particularly for sediment and sport fish, to best compare species and matrices. In addition, stations near pathway inputs or key habitats for sport fish and birds were prioritized.

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

<u>Sample Equipment and Collection</u>

Fish will be collected by the Marine Pollution Studies Laboratory (Marco Sigala, lead) using nets appropriate for each area, including beach seines, minnow traps, otter trawls, gill or cast nets

The coordinates of the actual sampling stations will be determined using a handheld or shipboard global positioning system (GPS) and reported on field sheets. Other pertinent information will also be recorded, including the sampling method, device, depth, and descriptive location. For samples collected over an area, an extent or rough polygon of the area of capture will be reported.

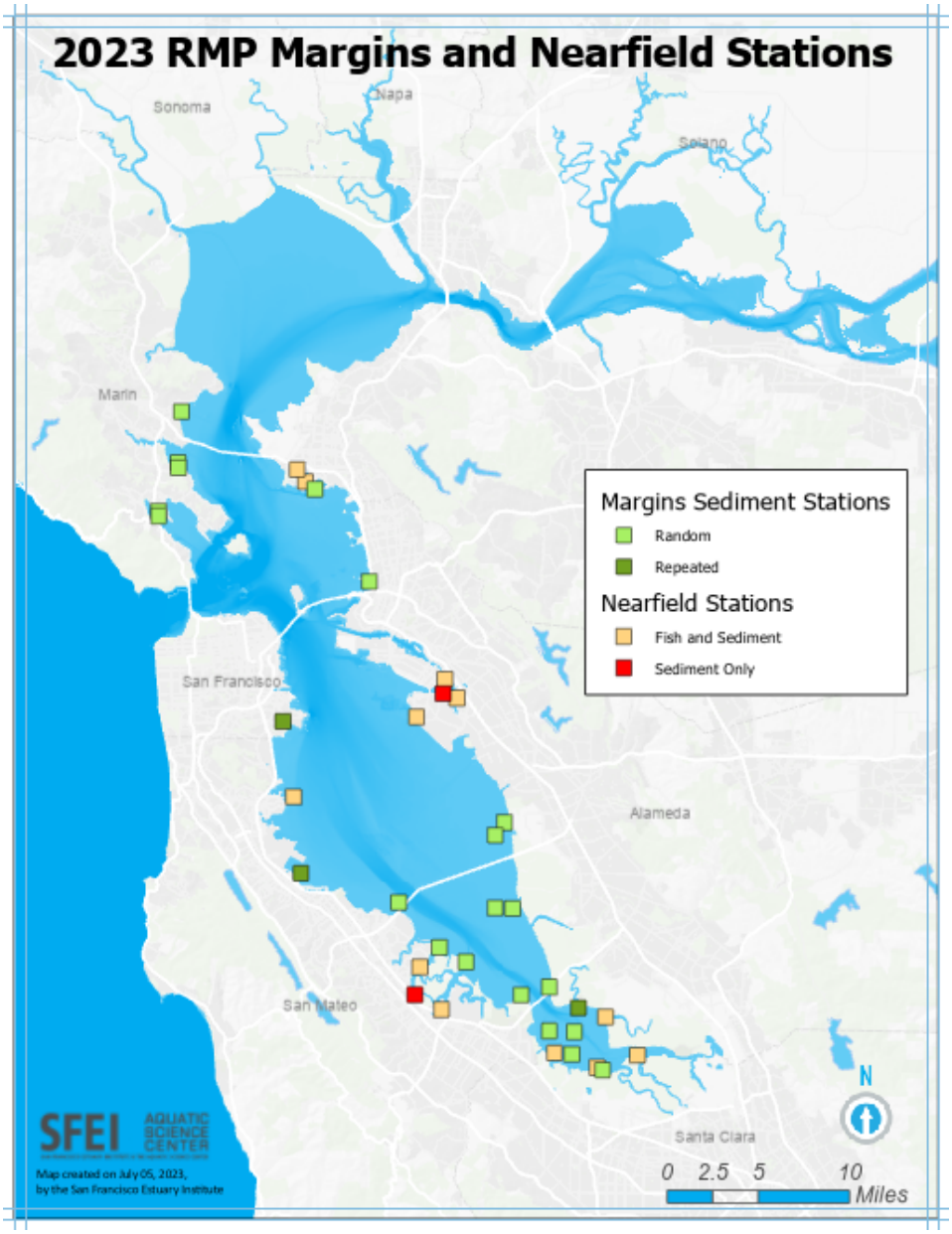

Figure 1. 2023 S&T Target Prey Fish, Near-Field Sediment, and Margins Sediment Sampling Locations

Sample Handling and Processing Protocol

This study involves **PFAS Contamination Risk**. Nitrile gloves are essential; latex is prohibited. Do not use “non-stick” aluminum foil; regular aluminum foil is acceptable. Avoid touching gloves with materials that are waterproof (e.g., waterproof clothing and shoes, including but not limited to Coated Tyvek®, Gore-Tex®, ScotchgardTM, and RUCO®; waterproof paper and notebooks such as Rite in Rain®) or greaseproof (e.g., food packaging materials, including food wrap, paper towels, aluminum foil), because these materials may contain PFAS. Avoid touching gloves with first aid adhesive wrappers. Avoid touching gloves to your face or exposed skin, as some personal care products and sunscreens may contain PFAS. Avoid regular and thick sized

markers of any brand (fine and ultra-fine are acceptable), sticky notes, and plastic clipboards. Avoid anti-fogging lens spray, wipes, or solutions for glasses or safety goggles. Avoid new (unwashed) clothing, and any clothes recently treated with fabric softeners, fabric protectors, insect resistance and water/stain/dirt-resistant chemicals.

Prey fish will be analyzed using “whole body” tissue and as a 20-fish (sculpin) or 30-fish (topsmelt and silverside) composite. Generally, a composite of 20 topsmelt has provided about 30-50 g of analyzable sample with more collected in this effort to cover all analyses and any remaining for archives.

The target size range for inclusion in a sample composite is: topsmelt (60-90 mm TL), silversides (40-80 mm TL), and sculpin (100-150 mm TL) (Greenfield and Allen 2013, Jahn 2018). Topsmelt larger than 90 mm may not be age-0, and should be avoided if possible, given an apparent shift to herbivory in age-1 fish (Jahn 2018).

Fish will be placed on a PFAS-free pre-cleaned measuring board and the smallest and largest fish will be measured for total length to provide a size range. Individual fish will be measured for total length and weighed in the field. Length measurements will be conducted on a fish measuring board that does not require calibration. No other field measurements will be taken. When possible, sex, parasites, and body anomalies will be noted on the field sheet.

In the field, fish will be wrapped whole in aluminum foil (dull side towards fish; do not use foil labeled “non-stick”), placed in a clean labeled bag, and then chilled on wet ice. While on wet ice, MPSL staff will check on the samples periodically to ensure that they are appropriately protected and there is sufficient wet ice. At the end of the day, MPSL staff will freeze samples with dry ice.

At the end of each sampling week, MPSL staff will transport the samples on dry ice to MPSL-MLML where they will then be stored at -20^{o}C until dissection and homogenization. Frozen tissue samples have a 12 month hold time from the date of collection. If a hold-time violation has occurred, data will be flagged appropriately in the final results. The study is planned to be completed well before the 12 month hold time. All samples will be accompanied by a chain of custody form (COC) (provided by MPSL). The COC form will include the sample unique ID, site name, collection date, sample type, analysis required, and other remarks. COC information will be sent in digital form to SFEI.

MPSL-MLML (Autumn Bonema, lead) will perform dissection and homogenization of the samples before sending to SGS-AXYS for PFAS, PCBs, and tissue ancillary analysis (lipid and solids) or to AMS for the short-term archives, or to NIST for the long term archives.

All field sheets should be scanned and sent to SFEI, along with a brief sampling report that describes the stations sampled, weather conditions, gear used, fish caught, and any deviations from this SAP.

Near-Field and Margins Sediment

Order of Sample Collection

Samples collected directly from VanVeen grab (small uncoated stainless steel scoops may be used as needed to fill containers)

1.1. Measure pH in each grab (~2.5cm depth)
1.2. PFAS samples directly out of grab for SGS AXYS
1.3. Short-term archive for PFAS directly out of grab
1.4. Bisphenols directly out of grab
1.5. Short term archive for bisphenols

Fill order for samples collected from composite bucket

1.6. Total Nitrogen for ALS
1.7. TOC/TS for ALS
1.8. Sediment for grain size determination for ALS
1.9. Collect short-term archive from composite
1.10. QACs for UMN (select stations)

Field replicate samples of the same sample type should be collected at designated sites from separate grabs. For field replicates for analytes collected as a surface scrape directly from the grab, a scrape from separate grab will be used. For the field replicate samples for analytes collected from composites, grabs for a separate composite for the field replicates will be collected into a separate bucket.

Field blanks for PFAS and bisphenols will be collected by opening the sample jar provided by SGS AXYS (containing Ottawa sand) during the onboard filling process and closing it up again. This should occur near the Van Veen grab for field samples collected directly. For QACs, which are composite samples, an empty field blank container must be opened onboard the vessel during the process of sediment collection, and then is opened again during the compositing process.

Sample Equipment and Collection

The top 5 cm of sediment will be collected from the sediment stations listed in Table 4 and 5, which are also visualized in **Figure 1**. Stations in and around channels were placed using Google Earth imagery, but may not be exact as fixed structures within Google Earth vary in location among historical images. For channel stations, locations are intended to be the central axis for that distance along the channel, with samples for sediment composites collected in a cross-channel transect, or an array around those central points, in an attempt to characterize the sediment at a location that are accessible to fish at different times in the tidal cycle.

Near-field and margins sampling will be conducted from a 25' Boston Whaler equipped with frame and hydraulics for deploying a 0.05 or 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 scoop and bucket used to remove and composite sediments are constructed of polycarbonate material. In areas where sampling from the boat is not possible, overland access to the site and direct scooping from the target depth of surface sediment may be used.

The a-frame at the side of the vessel will be used for deploying the Van Veen grab. 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 taken will be recorded by field personnel on the field datasheets.

Sediment samples for chemistry will be collected to a depth of 5 cm and sediment grabs will be taken until at least 2.5 L of sediment is collected. Multiple deployments of the grab 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. Excess sediment should be kept on the boat until collection for the station is done where possible, unless there is sufficient flow to ensure that discarded sediment is not redistributed to areas later collected in subsequent grabs for the same station (e.g., by always heading up the current for later grabs).

Sediment will be stored at 4^{o}C in a polycarbonate bucket in a cooler. Sediment for chemical and sediment quality analysis will be homogenized and subsequently sub-sampled to the appropriate laboratory specific containers in the lab within 7 days following collection. The number of sample containers that need to be filled with sediment from each site, the volume of sediment required for each container, and sample handling, storage, and shipping requirements are listed in **Appendix A.**

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, 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 by ambient water in the field. Equipment is next rinsed with 1.0% solution of hydrochloric acid (or equivalent), followed by a rinse with methanol or petroleum ether, followed by another set of three rinses with deionized water (or ambient water in the field).

All equipment besides the grab is stored in clean Ziploc™ or trash bags until used in the field. It is critical that sample contamination be avoided during collection. New pre-cleaned equipment should be used for each station where possible. Equipment that cannot be changed at different sampling stations such as the grab should be re-cleaned in the field between uses.

- Rinse equipment with station water.

- Scrub with dilute Micro detergent, rinse with station water.
- Only sediment not contacting surfaces of the grab should be collected; leave 1-2 cm contacting the edge uncollected..

Sampling personnel should wear nitrile gloves whenever taking or processing samples to avoid contact contamination (and for personal protection). In addition, airborne contamination should be avoided by keeping sample containers, sample scoops, and compositing buckets covered when not in use.

Sampling Protocols

1. PFAS
    a. This study involves **PFAS Contamination Risk**. Nitrile gloves are essential; latex is prohibited. Do not use “non-stick” aluminum foil; regular aluminum foil is acceptable. Avoid touching gloves with materials that are waterproof (e.g., waterproof clothing and shoes, including but not limited to Coated Tyvek®, Gore-Tex®, ScotchgardTM, and RUCO®; waterproof paper and notebooks such as Rite in Rain®) or greaseproof (e.g., food packaging materials, including food wrap, paper towels, aluminum foil), because these materials may contain PFAS. Avoid touching gloves with first aid adhesive wrappers. Avoid touching gloves to your face or exposed skin, as some personal care products and sunscreens may contain PFAS. Avoid regular and thick sized markers of any brand (fine and ultra-fine are acceptable), sticky notes, and plastic clipboards. Avoid anti-fogging lens spray, wipes, or solutions for glasses or safety goggles. Avoid new (unwashed) clothing, and any clothes recently treated with fabric softeners, fabric protectors, insect resistance and water/stain/dirt-resistant chemicals.
    b. Collect samples directly from the center of the grab, avoiding contact with the edges of the Van Veen that may have been in contact with the grab. Small uncoated stainless steel scoops can be used to collect the small NIST samples. For larger samples, the container will be used to collect most of the sample directly into the container; the same scoops can be used to complete sample collection. The sampler should wear clean nitrile gloves and, IF NEEDED, should wipe off excess sediment on the top rim and grooves of the container with gloves or a kimwipe to allow for a good seal. Fill all containers 80% full. Place on wet ice (no blue ice) onboard the vessel, and freeze with dry ice at the end of each day. Store frozen.
2. Bisphenols
    a. Collect samples directly from the center of the grab, avoiding contact with the edges of the Van Veen that may have been in contact with the grab. Small uncoated stainless steel scoops can be used to collect the small NIST samples. For larger samples, the container will be used to collect most of the sample directly into the container; the same scoops can be used to complete sample collection. Place on wet or blue ice onboard the vessel, and freeze with dry ice at the end of each day. Store frozen.
3. Archives, Ancillary, QACs
    a. This study involves **QACs Contamination Risk.** Avoid using QAC products (i.e., Lysol disinfecting sprays, Clorox wipes; alcohol-based antimicrobial products are acceptable). Avoid touching gloves with clothing that has been washed/dried with fabric softeners or dryer sheets. Cleaning sampling equipment with Liquinox is

not recommended due to presence of lauramine oxide; Alconox is the preferred alternative.

b. Sediment is collected and placed on wet or blue ice onboard the vessel, and stored chilled until compositing. Collect the samples from the bucket after the sample has been homogenized. Sample bottles can be filled using the polycarbonate scoops. Fill all containers 80% full. Ancillary samples (grain size, TOC, TN) should be kept and shipped chilled. All others freeze after compositing. Store frozen. Be careful to not smudge the label.

5. Laboratories

Contact information for the laboratories and archive agencies receiving samples from the sampling event is shown in Table 3.

Table 3. Contact Information for laboratories for the 2016 SS/RC Bay Study. See Appendix A for details of the target parameter and methods.

Matrix/Analyte	Lab / Company / Agency	Contact	Shipping Address	Phone / Email
Laboratory Contacts				
Sediment TOC, grain size, TN	ALS	Howard Boorse	1317 South 13th Ave Kelso, WA 98626	360-577-7222 Howard.Boorse@alsglobal.com
Fish Tissue & Sediment/ PFAS Target (both), PCBs (tissue), bisphenols (sediment)	SGS-AXYS	Sean Campbell	SGS-AXYS Analytical Services Ltd. 2045 Mills Road Sidney, BC V8L 5X2	250-655-5834 scampbell@axys.com
Sediment/ QACs	UMN	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				
Fish tissue, Sediment (Short-term)	AMS	Paul Salop	Applied Marine Sciences 4749 Bennett Dr., Ste. L Livermore, CA 94551	925-373-7142 salop@amarine.com

Fish tissue, sediment (long term)	NIST	Amanda Moors	NIST Hollings Marine Laboratory 331 Ft. Johnson Rd. Charleston, SC 29412	843-762-8953 amanda.moors@nist.gov

6. Sampling Stations

Sampling stations are located in multiple locations throughout Central Bay, South Bay, and Lower South Bay, including Richmond Harbor, San Leandro Bay, Redwood Creek/Steinberger Slough, South Bay near airports, and Lower South Bay. There are 12 prey fish sampling stations (for chemistry and ancillary analysis) and 38 sediment sampling sites (24 margins and 14 nearfield). Fixed nearfield sediment sites were selected deterministically to cover areas corresponding to loading areas of interest for water nearfield sampling. Fixed ambient margins sites were selected to include at least one repeated from the prior margins pilot study for each of the major Bay segments (Suisun, San Pablo, Central, South, and Lower South, but excluding Carquinez and Extreme Lower South Bay (Southern Sloughs)), and near WRMP priority sites (SBWT01 and LSBCP01). For allocation of random sites, Central Bay and Lower South Bay have approximately the same surface area, but double the number of sites was allocated to Central Bay due to greater urban density and interest in potential historical contamination sources. The remainder of ambient samples were allocated roughly proportional to margins area within each segment. The following tables list the sampling locations.

Table 4. Coordinates for 2023 S&T Prey Fish and Near-field Sediment Sampling Stations. All coordinates are listed in WGS-84 datum.

Station Code	Subembayment Location	Latitude	Longitude	SiteType
CB1_NF	Central Bay	37.7583	-122.221	Fish and Sediment
CB2_NF	Central Bay	37.74341	-122.209	Fish and Sediment
CB3_NF	Central Bay	37.91319	-122.365	Fish and Sediment
CB4_NF	Central Bay	37.92252	-122.373	Fish and Sediment
SS1_NF	South Bay	37.52919	-122.241	Fish and Sediment
RC1_NF	South Bay	37.49555	-122.218	Fish and Sediment
SOSL15_NF	Lower South Bay	37.45178	-122.062	Fish and Sediment
SOSL40_NF	Lower South Bay	37.46212	-122.022	Fish and Sediment
LSB1_NF	Lower South Bay	37.49194	-122.054	Fish and Sediment
LSB02_NF	Lower South Bay	37.46282	-122.105	Fish and Sediment
SB1_NF	South Bay	37.72784	-122.249	Fish and Sediment
SB2_NF	South Bay	37.66243	-122.37	Fish and Sediment

CB5_NF	Central Bay	37.74685	-122.223	Sediment Only
SS2_NF	South Bay	37.50697	-122.245	Sediment Only

*Prey fish stations sites are named by their nearest sediment station, but actual sampled areas may differ and collected fish be assigned to the nearest actual sediment site(s)

Table 5. Coordinates for 2023 S&T Margins Sediment Sampling Stations. All coordinates are listed in WGS-84 datum.

Station Code	Subembayment Location	Latitude	Longitude	Margins SiteType
LSB01	Lower South Bay	37.49877	-122.082	Repeat Site
LSB12	Lower South Bay	37.47974	-122.086	Random Site
LSB13	Lower South Bay	37.46193	-122.088	Random Site
LSB14	Lower South Bay	37.48016	-122.111	Random Site
SB051	South Bay	37.60175	-122.362	Repeat Site
SB077	South Bay	37.54515	-122.222	Random Site
SB078	South Bay	37.50824	-122.139	Random Site
SB079	South Bay	37.57717	-122.167	Random Site
SB080	South Bay	37.51516	-122.111	Random Site
SB081	South Bay	37.64523	-122.159	Random Site
SB082	South Bay	37.53385	-122.195	Random Site
SB083	South Bay	37.5802	-122.263	Random Site
SB084	South Bay	37.57711	-122.149	Random Site
SB085	South Bay	37.63488	-122.168	Random Site
SOSL17	South Bay Sloughs	37.44983	-122.057	Random Site
CB01	Central Bay	37.72218	-122.382	Repeat Site
CB41	Central Bay	37.92596	-122.493	Random Site
CB50	Central Bay	37.96663	-122.491	Random Site

CB51	Central Bay	37.88702	-122.512	Random Site
CB54	Central Bay	37.90732	-122.355	Random Site
CB55	Central Bay	37.88336	-122.511	Random Site
CB56	Central Bay	37.83465	-122.299	Random Site
SBWT01	South Bay	37.59232	-122.162	Repeat Site
LSBCP01	Lower South Bay	37.46372	-122.051	Repeat Site

7. Sample Labeling

The sample ID system used for the S&T prey fish, near-field sediment, and margins sediments for analytical and archive samples is as follows:

23RMPXX - STA - M# - ZZZY

Where:

23RMP = Cruise Year

XX = Project (PF for Prey Fish, NF for Near Field, and MC for Margins)

STA = Station Code (see Tables 4 and 5)

M = Matrix (S for sediment, T for tissue)

= Replicate number

ZZZ = Analyte Code (see Appendix A)

Y = Unique aliquot or jar number (archived and field replicate samples only)

Appendix A