

REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY sfei.org/rmp

Water Year 2024 RMP Near-Field Water Sampling and Analysis Plan

Prepared by:

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1. Introduction

This report details plans associated with the pilot near-field water sampling for the Regional Monitoring Program for Water Quality in San Francisco Bay (RMP). The RMP recently reviewed the Status & Trends (S&T) Program and added a pilot effort to quantify contaminants of emerging concern (CECs) in Bay water in areas near ("near-field" of) expected loading pathways during or shortly after storm events and during the dry season. For the first year of the pilot (Water Year 2022), the near-field design included three targeted, near-field stations and four ambient Bay stations. Subsequent years added a fourth near-field station. Samples will be collected at these stations during or shortly after two storm events, and once in the dry season. The analytes that are being measured include bisphenols, organophosphate esters (OPEs), PFAS, TOP, and a suite of stormwater CECs.

2. Key Personnel and Approvals

Oversight of the 2024 sampling is done by SFEI senior managers shown in Table 1. These key personnel have indicated their approval of the Sampling and Analysis Plan (SAP) by adding their initials and date in the far right column.

Personnel participating in the sampling are shown in Table 2. SFEI staff will be responsible for oversight of sampling operations, compliance with the SAP and quality assurance guidelines, maintenance of the sample field log, chain-of-custody procedures, and sample collection.

Contact information for participating laboratories is shown in Table 3.

Name	Affiliation	Duties	Cell	Initial and Date to Indicate Approval of Plan
Amy Kleckner	SFEI	RMP Manager	415-531-3390	AK 11/14/23
Jay Davis	SFEI	RMP Lead Scientist	530-304-2308	
Don Yee	SFEI	RMP QA Officer	510-508-2995	DY 2023/12/11
Rebecca Sutton	SFEI	RMP Scientist (CECs)	510-701-7050	RAS 11/20/23

 Table 1. Approvals of Sampling and Analysis Plan

Name	Affiliation	Duties	Cell
Alicia Gilbreath	SFEI	Prep and field sampling	530-400-3950
Amy Kleckner	SFEI	Field sampling	415-531-3390
Beth Ebiner	SFEI	Field sampling	909-646-0914
David Peterson	SFEI	Field sampling, shipping	608-628-3998
Diana Lin	SFEI	Field sampling	714-932-8085
Don Yee	SFEI	Field sampling	650-530-0603
Ezra Miller	SFEI	Field sampling	505-239-6931
Jen Hunt	SFEI	Field sampling	510-290-8390
Jennifer Dougherty	SFEI	Prep, field sampling, shipping	650-814-3403
Kayli Paterson	SFEI	Field sampling, shipping	541-598-6285
Kyle Stark	SFEI	Field sampling	540-333-4874
Lawrence Sim	SFEI	Field sampling	818-606-8467
Lilia Mourier	SFEI	Field sampling	650-892-4216
Martin Trinh	SFEI	Prep, field sampling, shipping	864-913-8237

Table 2. Personnel for wet weather sampling

Table 3. Laboratory Contact Information

Lab / Company	Name	Phone	email	Shipping Address
SGS-AXYS	Sean Campbell	(250) 655-5834	sean.campbell@sgs.com	2045 Mills Road Sydney, BC, Canada V8L5X2
UW	Ed Kolodziej / Melissa Gonzalez	(253) 254-7030 x8009	<u>koloj@uw.edu</u> melisg07@uw.edu	Center for Urban Waters Attn: Melissa Gonzalez/Ed Kolodziej 326 East D St. Tacoma, WA 98421

Table 4. Combined Site-Parameter List and Handling Instructions

3. Sampling Plan

3.1. Sample Process Design - Land-based sampling

Sampling will be conducted from shore. The objectives of the sampling effort are to collect the following:

Collect Real-time Data on Field Parameters

- 1. Real-time data for salinity and temperature.
- 2. Document current and recent weather conditions at each site.

Collect Water Samples - Total Fraction (Unfiltered water samples)

- 3. 4 stations (1 blank per event, 1 field replicate per season, 1 MS per season, 1 method dup per season) for analysis of Bisphenols (SGS AXYS)
- 4. 4 stations (1 blank per event, 1 field replicate per season, 1 MS per season, 1 method dup per season) for analysis of OPEs (SGS AXYS)
- 5. 4 stations (1 blank per event, 1 field replicate per season, 1 MS per season, 1 method dup per season) for analysis of PFAS (SGS AXYS)
- 6. 4 stations (1 blank per event, 1 field replicate per season, 1 MS per season, 1 method dup per season-wet season only) for analysis of stormwater CECs (UW)
- 7. 4 stations (1 blank per season, 1 field replicate per season, 1 method dup per season, -wet season only) for analysis of TOP (SGS AXYS)
- 8. 4 stations (1 replicate per event and 1 blank per season) for analysis of SSC (SFEI)

3.2. Sample Process Design - Boat-based sampling

Sampling is conducted from the *R/V Peterson* during regularly scheduled USGS cruises. The objectives of the sampling effort are to collect the following:

Collect Real-time Data on Field Parameters

- 1. Real-time data for salinity and temperature (RMP CTD or shipboard logging, or USGS CTD casts).
- 2. Document current and recent weather conditions at each site (observational field sheets).

Collect Water Samples - Total Fraction (Unfiltered water samples)

- 3. 4 stations (1 blank per season, 1 field replicate per season, 1 MS per season, 1 method dup per season- during dry season Lab QC samples can be batched with land-based samples) for analysis of for analysis of Bisphenols (SGS AXYS)
- 4. 4 stations (1 blank per season, 1 field replicate per season, 1 MS per season, 1 method dup per season- during dry season Lab QC samples can be batched with land-based samples) for analysis of for analysis of OPEs (SGS AXYS)
- 5. 4 stations (1 blank per season, 1 field replicate per season, 1 MS per season, 1 method dup per season- during dry season Lab QC samples can be batched with land-based samples) for analysis of for analysis of PFAS (SGS AXYS)
- 6. 4 stations (1 blank per season, 1 field replicate per season, 1 MS per season, 1 method dup per season-wet season only) for analysis of stormwater CECs (UW)
- 7. 4 stations (1 blank per season-wet season only) for analysis of TOP (SGS AXYS)
- 8. 4 stations (1 replicate per event and 1 blank per season) for analysis of SSC (USGS/SFEI)

3.3.Sampling Methods

Field Parameters

Salinity

For the nearfield stations, salinity should be at least > 15 ppt (half seawater) or ideally > 20 ppt (\sim 2/3 seawater). If the sampling occurs during an extended period of high precipitation, the salinity may not rise to the target range despite tidal mixing, so collection can occur after at least two high tides after at least 0.25" of rainfall has occurred in the event, and preferably during a time in which the watershed is showing a lower stage (at least partially back to baseflow). This ensures there has been enough mixing of stormwater with Bay water.

If these conditions are not met, the field crew should check in with Don Yee (mobile: 650-530-0603) to determine the next steps.

Alternatively, YSI Hand-Held Field Meter (for land-based sampling only)

Field parameters (temperature, conductivity, and salinity) will be collected using a YSI water quality meter or an equivalent calibrated handheld meter. The YSI meter should be calibrated for conductivity at the start of each day, and calibration results recorded on the station field sheet. When recording field readings, the sampler should ensure that the YSI electrode is fully submerged and not surrounded by any bubbles.

The following steps describe the YSI deployment and data management process (see manufacturer instructions for other models):

Programming the YSI

- 1. Hit 'Esc' to go to menu
- 2. Arrow down to "Logging Setup"
- 3. Go to 'edit site list' delete old stations or just add in new stations
- 4. Enter sites then press enter to store the site
- 5. Hit 'esc' to get out of the menu

Calibrating the YSI

- Calibrate the YSI once per day at the beginning of the day prior to sampling (within ~24 hours of sampling start)
- Rinse the probe and calibration cup with DI water in between calibrations. Make sure the calibration cup is dry before adding a new calibration solution.
 - o Specific Conductance
 - fill the calibration cup ¹/₃-¹/₂ full with 12,800 uS/cm standard (enough to submerge both the metal tip probe with no trapped air pocket in the side port – note that the port assembly has substantial volume and may overflow the cup if it is overfilled)

- submerge the probe in the calibration cup, and allow the meter reading to equilibrate
- hit 'esc' to go to menu, go to 'calibrate,' and choose 'Specific Conductance' (NOT 'Conductivity')
- set the calibration standard to 12.8 mS/cm, and press enter to calibrate
 - If no 12.8 mS/cm standard available, YSI is capable of calibrating to any manually entered target value (25 or 50 mS/cm or 1413 µS/cm can work as well, but generally use a standard close to your measurement range if there are options)
- o DO (optional)
 - Rinse out calibration cup with DI, dump and add ~5mm DI to cup
 - Screw on cup extremely loosely (just enough to catch threads)
 - Calibrate to DO % saturation
- o pH (optional do not bother if probe marked as faulty)
 - Choose 2 point calibration (pH 7 & 10)
 - Fill cup ¼ with each standard, rinse with DI between solutions

Running the YSI

- 1. hit 'esc' to go to the menu
- record salinity, spec. cond., temperature, DO, pH (if calibration passed), site code, and sampling date/time on the YSI field sheet, usually requested near start or middle of time on station
- 3. go to logging setup menu and set the logging interval to 5 minutes
- 4. go to 'start logging' and press enter
- 5. select site from site list and press enter
- 6. screw the metal cage onto the probe sensor assembly
- 7. lower the probe sensor assembly to 1 m below the water surface, and fix cable to the railing to keep the probe at that depth for the duration of the time on station
- 8. to stop logging go to 'stop logging' and hit enter

Lab Parameters

Sample labeling

- 1. Assemble bottle kits
 - a. Each bottle needs a label. Use an extra fine Sharpie to write on waterproof labels. On each label, write the sample ID and the target analyte to match what's on the field sheet.
 - b. Apply the labels to the correct bottle type and cover with a piece of packing tape. Place in a cooler.
 - c. Once all bottles are in the cooler, double-check labels and bottle types. Place the field sheets inside.

d. Using duct tape, label the outside lid of the cooler with the name of the kit: "[Project] - [Bottle Numbers]", i.e., "ST-100s"

SFEI staff will print out and provide sample labels to sampling personnel prior to arrival on station. The sample ID naming convention is as follows:

24-ST-xxx

where xxx is a three-digit number assigned by the sample tracking and labeling application.

PFAS, Bisphenols, OPEs, and TOP samples need to be bagged after collection. Labels are dropped inside the bag, or attached to the bottle only if an *extra fine point sharpie* was used to write the sample ID on the label. Labels should be attached directly to bottles without bags, and the site code and analyte should be written on the bottle lid. Labels should have packing tape applied over it.

Blank sample collection

For Stormwater CECs, blanks will be taken at the beginning of the day, before any other sample collection. The clean bailer will be rinsed 3x with MilliQ water (provided by UW), then filled with MilliQ water, which will be transferred to the field blank sample container. The field blank for SSC should be filled from the bailer as well; add more (cheaper) DI water as needed to obtain ~250 ml for the SSC sample.

Field blanks for Bisphenols, OPEs, TOP, and PFAS will be collected at the same time as field samples are collected. Collecting field blanks for these samples involves opening pre-filled containers while the field sample is being poured into the collection bottles (only when sample bottles are open). *Check blank containers and ensure they have not been overfilled by labs*; if so, pour out some of the blank water to ensure sample integrity for later freezing.

Land-based monitoring includes one field blank per storm event (two storm events per year, as well as a dry season event), while boat-based monitoring includes one field blank per season, for a total of four field blanks.

Sample Collection

<u>Sample bottles for Bisphenols, OPEs, TOP, and PFAS should NOT be rinsed.</u> Bottles should be filled no higher than 80% to prevent breakage when samples are frozen. See <u>Table 4</u> for a list of sample bottles by parameter and bottle handling instructions.

To limit procedural contamination during sample collection, some common products must be avoided while samples are being collected.

Nitrile gloves are essential; latex is prohibited. 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. The eating area should be separate from the sampling area. 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.

Sample bottles for stormwater CECs SHOULD be rinsed 3x with site water. Bottles should be filled <u>completely</u> (no headspace); <u>DO NOT FREEZE</u>.

Sampling Methods

Sampling at the land-based stations should be conducted within two tidal cycles of the end of a storm event. Sampling via the R/V Peterson will ideally be conducted within two weeks of a storm event, cruise schedule permitting. Stormwater CECs should not be collected on Friday or Saturday unless prior arrangements have been made with UW staff.

Organophosphate esters, bisphenols, TOP, PFAS, SSC, stormwater CECs

Only remove the cap with clean hands in nitrile gloves. Bottles have been pre-cleaned by the respective laboratories.

Water samples will be collected by deploying a stainless steel bailer over the side of the structure/vessel via a cotton rope. A stainless steel painter's pole will be used to keep the bailer away from the side of the vessel during deployment and retrieval. The bailer will be deployed once as a site water rinse and then will be used to fill sample containers. Sample containers will be handled with nitrile gloves.

1. Bisphenols

Collect site water using the stainless steel bailer. Fill the 500 mL wide-mouth amber glass container 80% with site water. A 1 L amber glass container may be used instead of the 500 mL container. If using a 1 L container, fill it <500 mL with site water.

2. Organophosphate esters(OPEs)

Collect site water using the stainless steel bailer. Fill the 1 L amber glass container 80% with site water.

3. *PFAS*

Collect site water using the stainless steel bailer. Fill the 500 mL HDPE container 80% with site water.

4. SSC

Collect site water using the stainless steel bailer. Fill the 250mL HDPE bottle with a maximum of 200-250 mL of water (other bottle sizes and materials may be used, but keep collected volume to <250 mL even if using larger bottles, as oversized samples may be hard to filter. On extremely turbid samples consider even smaller volumes).

5. Stormwater CECs

Collect site water using the stainless steel bailer. Remove the cap with clean hands in nitrile gloves. Rinse 1L amber glass container 3x with site water, then fill completely (no headspace).

6. *TOP*

Collect site water using the stainless steel bailer. Fill the 60 mL HDPE container 80% with site water.

Between stations, the bailer will be cleaned by scrubbing with a horse hair brush and Alconox detergent, then multiple DI rinses, then two methanol rinses, and then two UHPLC grade water rinses.

Field blanks for stormwater CECs will be collected prior to any sample collection. The clean bailer will be rinsed 3x with DI water, then filled with lab-supplied DI water, which will be transferred to the field blank sample container. The field blank for SSC can be filled from the bailer as well.

Field blanks for PFAS, TOP, Bisphenols, and OPEs are collected by opening a container of lab-supplied water during the collection of a field sample, dumping out some blank water so the container is only filled to about 80%, then closing the container.

Completed water samples are chilled in coolers with wet ice or ice packs (1 to 5°C). Bisphenols, OPEs, TOP, and PFAS samples may be frozen prior to shipping (wet ice preferred, rather than blue/chemical ice packs) for best preservation of sample. Stormwater CECs are NOT to be frozen and must be shipped overnight on ice (wet ice or ice packs) as soon after collection as possible.

4. Sampling stations

WY2024 target sampling stations are shown in Figures 1-5 and listed in <u>Table 5</u>. All coordinates are in NAD83 datum.

4.1 Station directions (land-based near-field)

San Leandro Bay: Pedestrian Bridge over Damon Slough. Parking at Damon Slough Staging Area on Oakport St., just south of the intersection with 66th Ave, Oakland 94621.

Redwood Creek: Access is via the Marine Science Institute, 500 Discovery Parkway, Redwood City, 94063. Please notify MSI when sampling is likely to occur (<u>marilou@sfbaymsi.org</u> and <u>jesus@sfbaymsi.org</u>)

Palo Alto: Baylands Sailing Station, parking lot at the end of Embarcadero Road, Palo Alto 94303. Walk to the end of the dock to sample.

Stevens Creek: Pedestrian Bridge over Stevens Creek. Parking is available in the Google parking lot off North Road, Mountain View. If salinity is too low, walk out on the trail towards the Bay until you can sample safely in higher saline water.

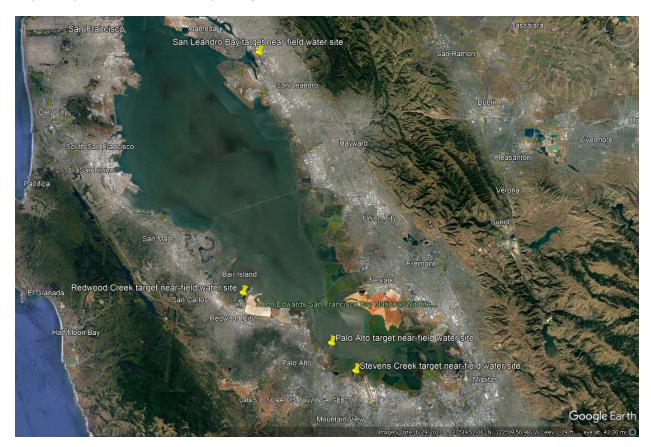


Figure 1. WY 2024 Near-field sampling locations. These are accessed via land.

Table 5. Location of WY2024 RMP Target Sampling stations. Coordinates are in theNAD83 datum. The goal is to navigate to within 100 meters of these coordinates.

Region	Site Code	Site Type	Target Latitude	Target Longitude
LSB	NMS34	Target/Ambient	37.495	-122.098333
LSB	NMS33	Target/Ambient	37.508333	-122.121667
SB	NMS31	Target/Ambient	37.528333	-122.158333

СВ	NMS23	Target/Ambient	37.728333	-122.336667
LSB	SC001	Target/Near-field	37.430169	-122.068303
SB	RC001	Target/Near-field	37.505517	-122.217375
SB	PA001	Target/Near-field	37.457750	-122.101161
СВ	SLB001	Target/Near-field	37.752083	-122.209553
		-		-



Figure 2. Stevens Creek sampling location (SC001)

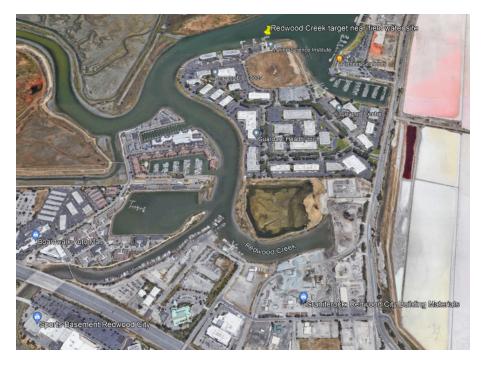


Figure 3. Redwood Creek sampling location (RC001)



Figure 4. Palo Alto sampling location (PA001)



Figure 5. San Leandro Bay sampling location (SLB001)

4.2 Bay Stations

For the wet season, Bay samples will be collected on USGS cruises from stations 23, 31, 33, and 34 (Figure 6). These are the USGS stations closest to the target near-field (land-based) stations.



Figure 6. Location of WY2024 USGS Bay Stations.