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

Water Year 2023 RMP Near-Field Water Sampling and Analysis Plan

Prepared by:

Amy Kleckner, Rebecca Sutton, Don Yee, Alicia Gilbreath, and Martin Trinh
San Francisco Estuary Institute
4911 Central Ave
Richmond, CA 94804

Contribution No. 1142

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, and a suite of stormwater CECs.

2. Key Personnel and Approvals

Oversight of the 2023 wet season 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.

Table 1. Approvals of Cruise Plan

Name	Affiliation	Duties	Cell	Initial and Date to Indicate Approval of Plan
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	
Rebecca Sutton	SFEI	RMP Scientist (CECs)	510-701-7050	RAS 9/5/2023

Table 2. Personnel for wet weather sampling

Name	Affiliation	Duties	Cell
Alicia Gilbreath	SFEI	Prep and field sampling	530-400-3950
Don Yee	SFEI	Field sampling	650-530-0603
Diana Lin	SFEI	Field sampling	714-932-8085
Martin Trinh	SFEI	Prep, field sampling, shipping	864-913-8237
Ezra Miller	SFEI	Field sampling	505-239-6931
Melissa Foley	SFEI	Field sampling	831-566-7816
Jen Trudeau	SFEI	Field sampling	510-290-8390
Lilia Mourier	SFEI	Field sampling	650-892-4216
David Peterson	SFEI	Field sampling, shipping	608-628-3998
Kyle Stark	SFEI	Field sampling	540-333-4874

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	koloj@uw.edu melisg07@uw.edu	Center for Urban Waters Attn: Melissa Gonzalez/Ed Kolodziej 326 East D St. Tacoma, WA 98421
Enthalpy	Jennifer Christmann	O: (916) 673-1520 M: (916) 995-5171	Jennifer.Christmann@enthalpy.com	Enthalpy Analytical 1104 Windfield Way El Dorado Hills, CA 95762
Eurofins West Sacramento	Chanell Slaughter	(925) 596-1576	Chanell.Slaughter@et.EurofinsUS.com	Eurofins West Sacramento 880 Riverside Parkway, West Sacramento, CA 95605
UMN	William Arnold / Anna Mahony	(612) 625-8582	arnol032@umn.edu mahon445@umn.edu	Department of Civil, Environmental, and Geo-Engineering University of Minnesota 500 Pillsbury Dr. SE Minneapolis, MN 55455

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 storm, 1 field replicate per season, 1 MS per season, 1 method dup per season) for analysis of OPEs (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 bisphenols (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) for analysis of stormwater CECs (UW)
7. 4 stations (1 replicate per season and 1 blank per event) for analysis of SSC (SFEI)
8. 1 station (1 laboratory duplicate, 1 MS, dry season only) for analysis of PFAS (Eurofins West Sacramento)
9. 1 station (1 laboratory duplicate, 1 MS, dry season only) for analysis of PFAS (Enthalpy)
10. 1 station (1 blank, dry season only) for analysis of quaternary ammonium compounds (UMN)
11. 4 stations (1 blank, 1 field replicate, dry season only) for analysis of TOP (SGS AXYS)

3.2. Sample Process Design - Boat-based sampling

Sampling will be collected from the nearest ambient stations sampled in the RMP Status and Trends (S&T) Program in seasons in which the RMP is collecting water samples. In other periods, 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 event, 1 field replicate per season, 1 MS per season, 1 method dup per season) for analysis of for analysis of OPEs (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 for analysis of bisphenols (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 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) for analysis of for analysis of stormwater CECs (UW)
7. 4 stations (1 replicate 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 (~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 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. Bring an SFEI salinometer as back up.

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 new calibration solution.
    - Specific Conductance
        - fill the calibration cup ⅓-½ 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)
    - 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
    - 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
2. 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 a thin 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 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-300s"

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:

23-ST-xxx

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

For double bagged samples (PFAS, OPEs, bisphenols), labels are dropped inside the outer bag, and ***extra fine point sharpie*** (important for PFAS) is used to write the site code on the label on the outer bag. Labels should be attached directly to bottles without bags, and the site code and analyte should be written on the bottle lid. Stormwater CECs bottles (no bag) should have labels applied directly to the bottle.

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, PFAS, and TOP 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.

The field blank for QACs is collected by pouring DI water into a single sample container during sample collection (fill to 75%). Note that the QAC field blank is a single container (1 L), while field samples consist of 3 containers (3 L total).

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

Sample bottles for bisphenols, OPEs, PFAS, TOP, and QACs should NOT be rinsed. Bottles should be filled no higher than 80% to prevent breakage when samples are frozen. See Table 4 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 on the vessel.

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.

Do not use QAC-based antimicrobial products (i.e., Lysol disinfecting sprays, Clorox wipes). Alcohol-based hand sanitizer is acceptable. Avoid touching gloves with clothing that has been washed/dried with fabric softeners or dryer sheets.

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

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.

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

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, 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 2/3rds full with site water (minimum sample size 300 mL).

2. ***Organophosphate esters***
   Collect site water using the stainless steel bailer. Fill the 1 L amber glass container 80% with site water. (During the dry season sample collection, a single 1 L amber glass container will be used for both bisphenols and OPEs analysis.)

3. ***PFAS***
   Collect site water using the stainless steel bailer. Fill the 500 mL HDPE container 80% with site water. (During the dry season sample collection, multiple samples will be taken as part of an interlab comparison study.)

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.

7. ***QACs***
   Collect site water using the stainless steel bailer. Fill **three** 1 L polycarbonate containers 75% 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, 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 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, OPEs, and bisphenols are collected by opening a container of lab-supplied water during collection of a field sample, dumping out some blank water so the container is only filled to about 80%, then closing the container.

The field blank for QACs is collected by pouring DI water into a single sample container during sample collection (fill to 75%). Note that the QAC field blank is a single container (1 L), while field samples consist of 3 containers (3 L total).

Completed water samples are chilled in coolers with wet ice or ice packs (1 to 5^{o}C). Bisphenols, OPEs, PFAS, TOP, and QACs 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

2023 target sampling stations are shown in Figures 1-5 and listed in Table 5. 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 (marilou@sfbaymsi.org and jesus@sfbaymsi.org)

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 available in 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. 2023 Near-field sampling locations. These are accessed via land.

Table 5. Location of 2023 RMP Wet Season Target Sampling stations. Coordinates are in the NAD83 datum. The goal is to navigate to within 100 meters of these coordinates.

Region	Site Code	Site Type	Target Latitude	Target Longitude	Depth (ft)
LSB	NMS34	Target/Ambient	37.495	-122.098333	
LSB	NMS33	Target/Ambient	37.508333	-122.121667	
SB	NMS31	Target/Ambient	37.528333	-122.158333	
CB	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	
CB	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) (red balloon designates location)

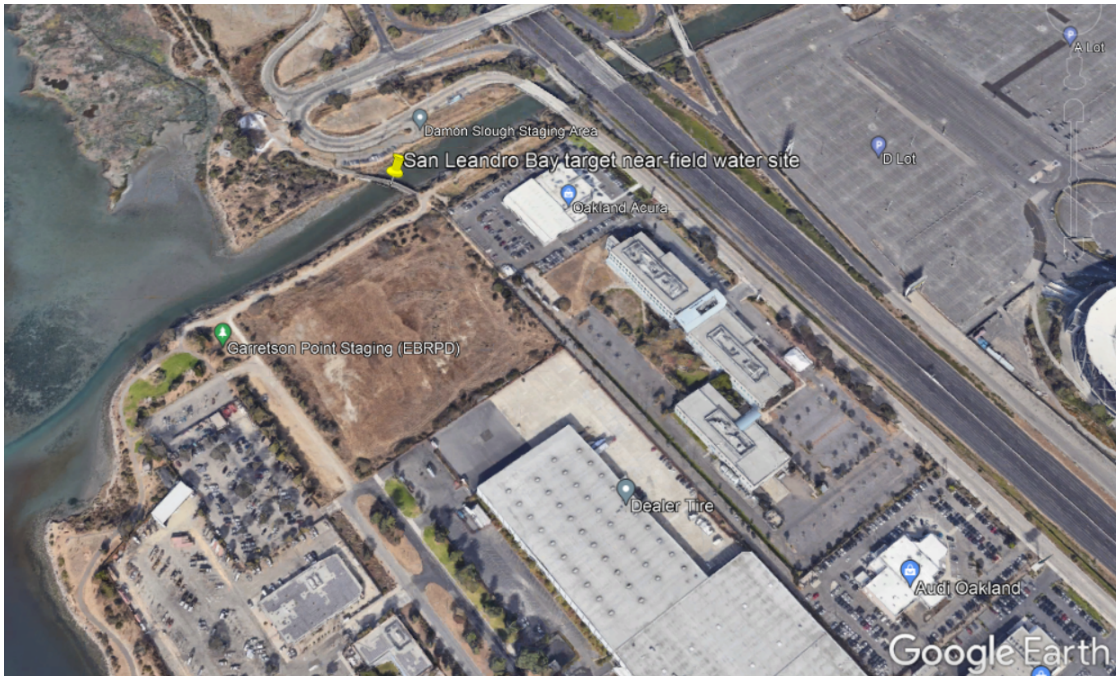

Figure 5. San Leandro Bay sampling location (SLB001)

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.

For the RMP S&T dry season water cruises, stations will vary between years, except for RMP fixed historical stations (Figure 7). Stations nearest to the targeted USGS stations and/or the near-field stations will be selected from among RMP S&T water stations for each year. Historical station BA30 will be used for 2023 (and likely future S&T years) because it is close to USGS station 33, and the other S&T stations in 2023 nearest the wet season targeted USGS stations have been selected (Table 6).

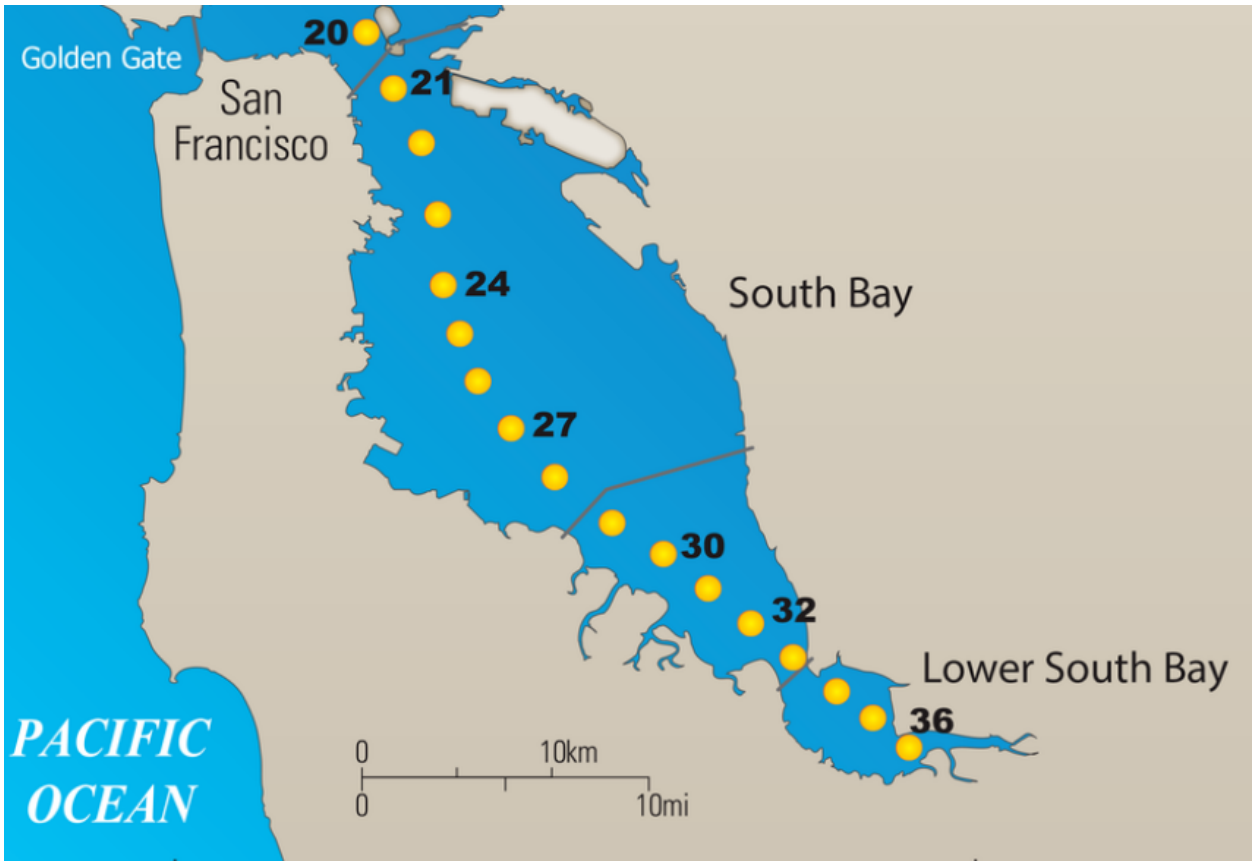

Figure 6. Location of 2023 USGS Bay Stations.

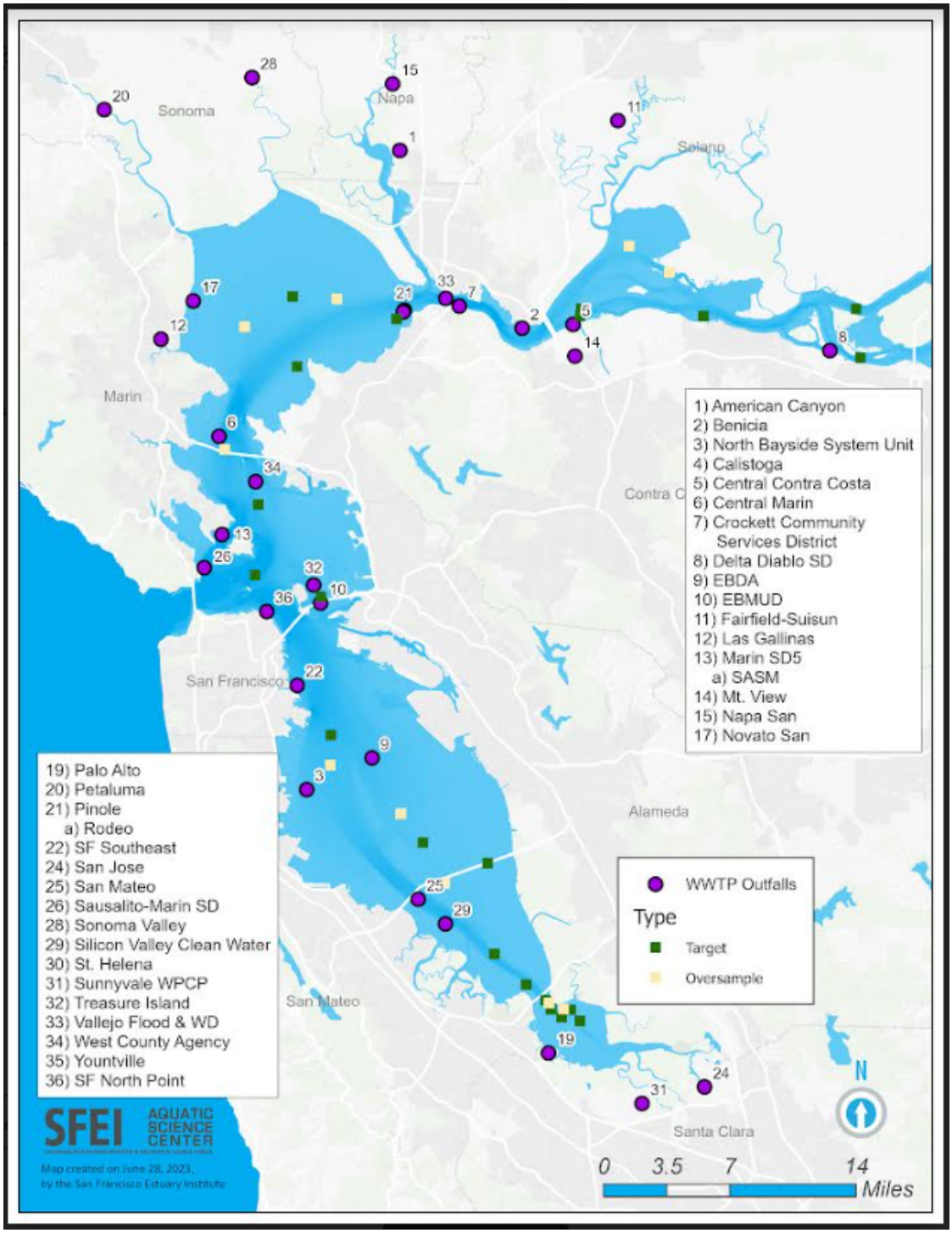

Figure 7. Location of 2023 RMP S&T Bay Stations

Table 6. Location of 2023 RMP Dry Season Bay Target Sampling stations. Coordinates are in the NAD83 datum. The goal is to navigate to within 100 meters of these coordinates. Dry season and wet season near-field (land-based) stations are identical so are not re-listed here.

Region	Station Code	Station Type	Target Latitude	Target Longitude	Depth (ft)	USGS/ NMS nearby
CB	CB056W	Random	37.7109171	-122.3366612	12+	NMS23
SB	BA30	Historic	37.51375	-122.1346166	NULL	NMS33
SB	SB082W	Random	37.53781718	-122.1673059	12+	NMS31
LSB	LSB089W	Random	37.49465708	-122.0966843	12+	NMS34