2019 RMP North Bay Selenium Monitoring Sampling and Analysis Plan

Contribution #969

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1. Introduction

In 2016, the State Water Resources Control Board approved a selenium TMDL for North San Francisco Bay. The TMDL established a target concentration of 11.3 ug/g dw in white sturgeon muscle tissue as the basis for evaluating impairment (SFBRWQCB 2015). Following discussions surrounding the North Bay TMDL, the San Francisco Bay Regional Water Quality Control Board asked the RMP Selenium Workgroup to develop a robust monitoring design for North Bay.

The goal of the monitoring is to identify leading indicators of change to allow prompt management response to signs of increasing impairment. At the 2016 technical workshop, participants reached a consensus that monitoring sturgeon, clams, and water are all needed to answer management questions. Recommendations for long-term monitoring of these three matrices are detailed in the North Bay Monitoring Design document (Grieb et al. 2018).

The USGS conducted monthly clam monitoring at multiple locations in North Bay for over 20 years, but USGS funding for this work ended in 2016. In 2019, the RMP will resume clam monitoring following a modified monitoring design optimized for early detection of changes in selenium trends in clams. These efforts will continue the long-term monitoring of *Potamocorbula amurensis.* Grieb et al. (2018) also recommended monitoring dissolved and particulate selenium in the water column. Long-term monitoring of water and sturgeon tissue in North Bay will be added to the clam sampling to track interannual trends and changes in sources or environmental processes influencing food web selenium exposures in North Bay.

Potamocorbula amurensis and water samples will be collected from two long-term USGS monitoring locations in northern San Francisco Bay. Samples will be collected and processed by SFEI and Applied Marine Sciences (AMS) aboard the *R/V Questuary*. Sampling will take place over six months each year in two key three-month periods: July-September and December-February. White sturgeon (*Acipenser transmontanus*) samples will be collected by DFW during their tagging efforts aboard the *New Alosa*. These efforts occur during DFW's fall tagging cruises (Sept - Oct). Non-lethal muscle plug samples will be collected from the epaxial muscle of each fish, just in front of the dorsal fin (Figure 5). Brooks Applied Labs (BAL),CalTest Analytical Laboratory (CalTest), and the UC Davis Stable Isotope Lab will be the analytical partners for this work. Stable isotope analysis will be used to identify spatial and temporal relationships within a food web, as well as potential sources of selenium. BAL will analyze dissolved and particulate selenium in water; clams, and sturgeon samples; and CalTest will conduct ancillary analyses on dissolved water samples.

The purpose of this Sampling and Analysis Plan is to clearly document the sampling design, methods, and responsibilities; and to facilitate coordination among project partners.

2. Key Personnel and Approvals

Table 1. Key Personnel and Approvals of Sampling and Analysis Plan

Contact	Role	Phone/Email	Plan Approval Date
Jay Davis	RMP Lead Scientist	jay@sfei.org 510-746-7368	1/31/20
Melissa Foley	RMP Manager	melissaf@sfei.org 510-746-7345	7/13/19
Don Yee	RMP QA Officer	don@sfei.org 510-7467369	7/11/19
Amy Franz & Adam Wong	RMP Data Services	ds@sfei.org 510-746-7394	7/26/19
Nina Buzby	Environmental Analyst	ninab@sfei.org 510-746-7393	Primary author
Robin Stewart	Research Hydrologist USGS Water Mission Area	arstewar@usgs.gov 650-329-4550	7/11/19
Paul Salop	Senior Scientist, Principal - Applied Marine Sciences	salop@amarine.com 925-373-7142	7/30/19
Andrew Danos	Environmental Scientist CA Department of Fish and Wildlife	andrew.danos@wildlife.ca.gov 209-992-2591	
Elizabeth Madonick (Lauren Blaiwes, Jenna Saeedi)	Brooks Applied Labs Client Services Manager	elizabeth@brooksapplied.com 206-753-6127	7/30/19
Todd Albertson	Caltest Analytical Laboratory President	Todd_Albertson@CaltestLabs.com 707-258-4000	7/30/19

3. Sampling Equipment

Clams & Water

The following is a list of recommended sampling equipment needed for clam and water sampling efforts. Equipment and materials should be prepared 2-3 days prior to sampling cruises.

- Sample containers and labels
- Clam dredge
- YSI Sensor (calibrated)
- CTD and Niskin bottle
- Peristaltic pumps (charged), power supply, and tool kit (below)
    - Weights and zip tie-tubing
    - Floats and fishing line
    - Sink for water collection
    - Table
    - Ring stand and clamps
    - Bungee cords
    - Curled tube holder
    - Sampling poles (x2)
    - Trash bags
- Pre-cleaned tubing, 3' peristaltic tubing, Materflex® size 24 attached to 15' Teflon (1 per samping event)
- Voss 0.45-um Capsule Filters (2 per samping event)
- Vacuum pump and filtration glassware (Millipore columns, flasks, tubing)
    - Metal ring stand & clamps
    - Forceps
    - Graduated cylinder
    - Kim wipes
- GE Healthcare Whatman brand, 47mm Nuclepore Polycarbonate Track-Etched Membrane filters (0.4 µm pore size)
- Deionized water
- Blank water provided by analytical partners
- Carboys for oyster water collection
- Calipers
- Coolers & ice
- Gloves
- Zip ties
- PPE and foul weather gear
- Sunscreen
- Containers for liquid and solid waste
- Dolley

Sturgeon

The following is a list of required sampling equipment that should be handed off to DFW field staff at the beginning of tagging efforts. Equipment and materials should be prepared on the Friday prior to each beginning-of-the-week ice drop.

- 5mm biopsy punches (1 per station)
- 60-100, 2 mL Nalgene cryovials
    - 25 pack
    - 500 pack
- Metal forceps & scissors

- Ziplock bags
- Orca cooler (small, green)
- Dry ice
- Nitrile gloves
- Kim wipes
- Miscellaneous supplies (pens, sharpies, duct tape)

Sampling containers and transport/shipping storage for each matrix are specified in the following table. Per recommendations from USGS contributors to previous monitoring, storage containers should not be made of glass. All tubing, filters, glassware, and plasticware should be pre-cleaned according to BAL trace metal standards. Prior to shipping BAL will run deionized water through the cleaned tubing and filter, preferably using a peristaltic pump, and then run this blank sample to ensure no contamination.

Table 2. Sampling Containers

<table>
<tr><td></td><td>Collection Container)</td><td>Shipping</td><td>Post-processing</td></tr>
<tr><td>Sturgeon</td><td>2mL Cryovial
(1 per fish, 2 plugs)</td><td>N/A</td><td>N/A</td></tr>
<tr><td>Clam - Total Se</td><td rowspan="2">2.5L Plastic wide mouth bottle
(2 per sampling event)</td><td>Ziploc freezer bag (AMS-BAL)</td><td>N/A</td></tr>
<tr><td>Clam - Isotopes</td><td>Full details (BAL-UCD)</td><td>Glass Vial</td></tr>
<tr><td>Water - Dissolved</td><td colspan="2">1L HDPE plastic bottle (2 per sampling event)</td><td>N/A</td></tr>
<tr><td>Water - Particulate</td><td colspan="2">1L HDPE plastic bottle (2 per sampling event)
Polycarbonate filter in 15mL centrifuge tube</td><td>N/A</td></tr>
<tr><td>Chl-A</td><td colspan="2">1L plastic amber bottles
(9 per sampling event)</td><td>N/A</td></tr>
<tr><td>SSC</td><td colspan="2">500mL clear plastic bottles
(6 per sampling event)</td><td>N/A</td></tr>
<tr><td>TOC</td><td colspan="2">40mL amber VOAs (triplicate)
(6 per sampling event)</td><td>N/A</td></tr>
</table>

4. Clam & Water Sampling Design

Concurrent clam and water sampling will be conducted at the two primary USGS long-term monitoring stations: 4.1 near the confluence of the Sacramento and San Joaquin Rivers, and station 8.1 at the mouth of the Carquinez Strait in Suisun Bay (Figure 1). These locations were

chosen to allow for continuity of the pre-existing long-term dataset on clam selenium concentrations at such locations (Stewart et al. 2013). Samples will be collected and processed by staff with SFEI and Applied Marine Sciences (AMS) aboard the *R/V Questuary*.

Table 3. Field Staff for Clam and Water Sampling

Name	Affiliation	Phone (cell)	Comments
Nina Buzby	SFEI	(415)-336-6485	
Don Yee	SFEI	(650) 530-0603	Only on first cruise for cross training
Clifton Herrmann	AMS	(916) 612-8718	
Paul Salop	AMS	(925) 373-7142	

Figure 1. Clam and water USGS sampling locations. Station 4.1 (blue) -near the confluence of the Sacramento and San Joaquin Rivers 38° 03.427' N 121°56.691'W (11.6 m, depth). Station 8.1 (red) - at the mouth of the Carquinez Strait in Suisun Bay 38°01.900' N 122°08.416' W (14.3 m, depth).

Sampling will occur in two three-month blocks for a total of six sampling events each year. Based on the recommended sampling design (Grieb et al. 2018) and tissue lag-time literature (Beckon and William, 2016), the sampling periods will proceed sturgeon muscle plug collection and spawning by 2-3 months. Sturgeon spawning occurs in the spring, while plug collection will occur in the fall (Table 3; Section 5). The planned three-month sampling periods for water and clams are therefore June-August and December-January (Table 3). After each sampling effort, any SFEI field staff will record any/all hours spent on the water in the navigable waters log (Appendix C).

After all field efforts are complete (Feb 2020), AMS will prepare a Field Report. The Field Report will contain a Cruise Description and Sample Collection Spreadsheet in CEDEN format (more details in Section 10). The Cruise Description will provide information on cruise participants, schedule, field conditions, coordinates of sample locations, and problems for each cruise.

5. Sturgeon Sampling Design

Sturgeon samples will be collected by the CA Department of Fish and Wildlife aboard the *New Alosa*, during their fall (Aug-Oct) sturgeon tagging efforts. The main point of contact for CA DFW is Andrew Danos (see Table 1), with whom SFEI should be in contact 1-2 months prior to sampling and throughout the collection process. The design accounts for total selenium analysis of muscle plugs from 60 individuals, though initial collections can amount to more. Each fish will require 2-3 muscle plugs to provide sufficient mass for analysis.

SFEI will provide sample field-storage materials (e.g. cooler, ice, sample containers) and data sheets. SFEI will also pick-up samples from the *New Alosa* periodically throughout the tagging efforts, at the convenience of DFW staff. At the end of sampling, SFEI will process and ship all muscle plug samples to BAL for analysis.

Table 3. Water, clam and sturgeon sampling timeline

	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr
Water & clams		x	x	x				x	x	x		
Sturgeon					x	x					x	x
					Plug Collection						*Spawning*	

6. Collection Methods

Water and clam sampling will be a concurrent effort. The vessel used for collections should have enough deck space to accommodate a peristaltic pump setup, CTD, and clam dredge. The

vessel should also have hydraulics to deploy and retrieve the sampling dredge. Duplicate clam and water samples will be taken at whichever station appears to have a greater abundance of clam samples.

While at clam/water sampling stations, a CTD cast will be made along with Niskin bottle grabs to collect at-depth water for clam storage and depuration. A total of approximately 30L of source water should be collected between the two stations and stored on wet ice. Three additional water samples will be taken for the analysis of chlorophyll-A (Chl-A), total organic carbon (TOC), and suspended sediment concentration (SSC); further details below.

A general order of operations while at each sampling station is outlined below (more details can be found in the following sections).

1. *Simultaneous steps:*
    a. *CTD cast*
    b. *Rinse peristaltic pump with site water (~1 minute)*
    c. *Ancillary parameter collections via peristaltic pump (Chl-A, SSC, TOC)*
    d. *Niskin bottle grabs (depth water collection for clams)*
2. *Particulate water sample collection*
    a. *Niskin grabs can continue during this step*
3. *Particulate vacuum filtration (see section 7)*
4. *Purge filter cartridge*
    a. *Collect purged water in carboy for depuration water*
5. *Dissolved water sample collection (includes in-line filter)*
6. *Clam Collections (repeat as needed)*
    a. *Begin clam sampling line, deploy dredge*
    b. *Record start lat/long and end lat/long*
    c. *Sort and collect clam individuals (~100 individuals > 8 mm)*

<u>Clams</u>

During each sampling event approximately 100 clams will be collected from each site using a clam dredge or benthic ponar grab (Figure 2). Dredge lines should begin approximately 50 meters upstream of the station location and continue 100 meters downstream, through the station point. Latitude and longitude of dredge start and end points will be recorded for each sampling line. Depending on location and time of year, collection efforts can vary between 15 minutes to 2 hours per station. Cruise coordinators should plan accordingly.

Figure 2. Clam sampling equipment (left - clam dredge, right - benthic ponar grab)

Contents of each dredge/grab will be poured into a plastic container (e.g. cooler) and rinsed to remove excess mud/debris. Field staff will sort through the contents for *P. amurensis* (Figure 3) larger than 8 mm, making sure to collect extra clams if the majority of the grab contains smaller individuals. This species is more triangular in shape and tends to have an “overbite”, meaning one shell is larger than the other (Figure 3). Clams will be placed into containers with water collected from the same depth and location. Sourcing this water can be done following the CTD cast with a Niskin bottle as described above. Clam storage containers should be non-glass jars with wide mouth openings. Clams should be kept at a constant temperature (10°C) to prevent overheating (Brown & Luoma 1995). Clam sample containers can be stored in a wet ice cooler with sufficient aeration until they can be transferred to the depuration tank.

Figure 3. *Potamocorbula amurensis* individuals (and shells)

<u>Water</u>

At each station the peristaltic pump line should be flushed with site water for approximately 1 minute without any filtration attachments, and an additional three minutes of flushing when an in-line filter is attached (further details below). The sample containers should then be rinsed with site water three times and filled completely.

Two 1 L grab samples should be collected at each station, from 3 ft below the surface. One of the grabs will provide material for dissolved phase samples and will require in-line filtration (0.45 um pore size); the other will be used for particulate samples. The motivation for separate water collections is to avoid the issue of possible cross contamination (e.g., filtrate becomes contaminated by a small hole in the filter or incorrect placement). BAL will provide pre-cleaned teflon tubing (at least 15 ft.), Masterflex® size 24 peristaltic tubing, and Voss 0.45-um Voss capsule filter cartridges for these collections.

The pump sampling setup will involve securing the teflon tubing to a sampling pole (Figure 4a) and float/weights that allow for sample collection from the appropriate depth (Figure 4b). The pump outflow will be directed to a ring stand setup either with (Figure 4d) or without (Figure 4c) an inline filter cartridge. The sampling container (1L HDPE bottle) and sink will be underneath the outflow for water collection.

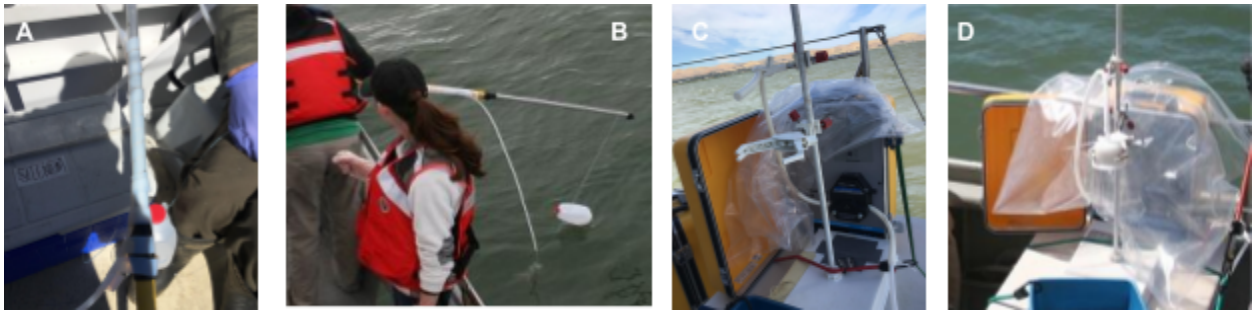

Figure 4. Water sampling setup. A - tube attachment, B - inflow, C - outflow side view, D - outflow front view

Since dissolved phase grabs may take longer with in-line filtration tubing, particulate phase samples (collected through regular tubing) should be collected before the dissolved grab. After particulate phase samples are collected, the three additional samples for ancillary parameters (Chl-A, TOC, and SSC) will be collected in 1L plastic, 500mL plastic, and amber 40mL VOAs, respectively. VOAs should have minimal headspace (no more than one small air bubble). For the first round of sampling these ancillary parameter samples should be collected in triplicate (duplicate for SSC) at each station.

All water samples should be stored in coolers with blue/wet ice until shipment or pickup. Ancillary parameter samples will be retrieved by CalTest staff the following day and selenium samples will be shipped to BAL on the following day, for same day delivery.

Sturgeon

Prior to each tagging season, SFEI personnel will communicate with DFW about expected sampling protocol (e.g. provide SAP documents, practice with fillets).

A detailed version of the plug sampling protocol can be found here: https://docs.google.com/document/d/1j8Mmwy3sWC0cZtiGnHyZf3nFLRox9aPcAfU1Vq7Xyno/edit#

In addition, an SFEI staff member should participate in the first tagging cruise to demonstrate sampling procedures while in the field. It is also recommended that a designated DFW staff member(s), and not cruise volunteers, conduct the sampling the sampling to ensure quality of sample plugs.

Two muscle plugs will be taken from each fish using a disposable 5 mm biopsy punch. The number of samples that will be analyzed in 60, however obtaining plugs from more than 60 individual fish will allow for more flexibility and discernment during the sample processing process. Plugs should be taken from the epaxial muscle near or slightly in front of the dorsal fin, offset from the midline (Figure 5a). The sturgeon skin will be rinsed with DI water prior to sampling. The biopsy punch should be inserted into the muscle tissue using a twisting motion and removed with a scooping motion (Figure 5b). Thin forceps (metal or plastic) should be used to remove the tissue plug from the biopsy punch as completely as possible (i.e. prevent tissue mangling) and place it in a 2 mL long-term storage cryovial (Figure 5b). The ideal length of a muscle plug is approximately 10 mm (Figure 5c). Forceps will be rinsed with DI water and wiped with a kimwipe between use on samples from different fish.

All plugs taken from the same fish can be stored in the same cryovial. Cryovials pre-labeled with the Organism ID, and space to mark the sampling date will be provided by RMP staff. The RMP will also provide DFW staff with field sheets to record other collection information including sampling date, time, tag number, fork length, total length, fish condition (live/weak/dead), and life stage (adult/juvenile) [see Appendix C]. Cryovials will be frozen in dry ice cooler in the field (-4 C) and transferred to a commercial freezer (-20 C) once a week during the sampling season.

Figure 5a. Location of muscle plug collection

Figure 5b. Muscle plug removal process

Figure 5c. Biopsy punch and example muscle plugs

7. Sample Processing

Clams

Literature shows a residence time for gut material of approximately 24 hours in *Potamocorbula* (Decho & Luoma, 1991), therefore, clams should be allowed to depurate for approximately 48-72 hours. Applied Marine Sciences (AMS) will set up and maintain the depuration tank using a composite of filtered Bay water from the two clam collection locations, chilled via recirculation to maintain a stable 10°C temperature. AMS will then measure and sort all clams into individual mesh pouches by size, with an additional mesh separation between stations, and place them into the depuration tank. After the depuration period, AMS will reorganize the clams into five size classes or “bins”. Starting with bins of 1 mm difference (e.g. 11, 12, 13, 14, 15, 16, 17 mm), clams can be combined with adjacent bins (e.g. 11-12, 13-14, 15, 16, 17 mm) to meet the limit

of 5 classes. If necessary, clams *only* greater than 15 mm can be combined with bins 2 mm difference (e.g. 11-12, 13-14, 15, 16, 17-19). Each size class will make up one of the five composite samples per collection site. If five size classes cannot be created with all collected clams (e.g. 11, 12, 14, 15 mm), more abundant bins can be split and then combined to meet the 5 composite target (e.g. 11-12, 12, 14, 15 mm). Clams will be shipped by AMS to BAL within two days of finishing depuration (see section 8 for more details).

Once received from AMS, BAL will dissect and homogenize clams from each size class by removing the soft tissue from the shells and placing the tissue into a pre-weighed vial for drying. Since shells can break easily during dissection, it is recommended to only shuck a small number of frozen clams at a time. A wet weight will be recorded before the samples are oven dried at 50°C. The samples should be oven dried at < 40°C until they maintain a constant weight (approximately 3 to 4 days; Brown & Luoma 1995). A dry weight will then be recorded and samples will be analyzed for Se concentrations. It is critical that drying isn't done at temperatures higher than 40℃ as selenium will volatilize. Drying temperature will also be recorded as well as moisture content.

Once dried and processed, the Se Lab will split composite samples and ship subsamples to the UC Davis Stable Isotope Facility for carbon, nitrogen, and sulfur (C, N, and S) isotope analysis. Each composite should produce two subsamples for isotope work - one for C and N analysis and another for S. Suggested elemental content for each isotope are as follows: 15-40 µg S, 20-150 µg N, and 200-2000 µg C. Samples should contain at least 8-10 mg of tissue and be stored in glass vials and shipped to UC Davis SIF. If total sample mass does not meet minimum selenium digestion mass-needs (100 mg), then no isotope subsampled should occur.

Water

Particulate filtration should begin onboard the boat. For particulate sampling details see Section 7. Samples will be filtered through 0.4um Nuclepore Polycarbonate Track-Etched Membrane filters using a portable vacuum pump. The entire filter apparatus is shown in Figure 3 and consists of the pump and glass millipore filter columns. The order of glass column aspects, with and without a filter is shown in Figures 4a and 4b. Filters should be handled using clean metal forceps and placed in the middle of the glass column (Figure 4c).

Prior to any sample filtration, the entire filtration setup should be rinsed/run with DI water without a filter, and then again with a sacrificial filter in place. Blank particulate samples can be created in a similar manner by filtering aliquots of DI water through 0.4 um polycarbonate filters. The apparatus should be rinsed between samples from different stations, and the filter forceps should also be rinsed with DI water.

Two aliquots (200-500 mL) should be filtered through each of the two Millipore glass filter columns and polycarbonate filters for the particulate samples. Aliquots should be measured using a graduated cylinder and recorded - smaller aliquots allow for duplicates. When filtering,

the vacuum should run until no liquid remains on the filter. Do not overdry the filter or it may get stuck to the glass column. The filter should then be removed, folded into quarters, placed in a centrifuge, and stored on ice.

Figure 6. Particulate water sample filtration setup

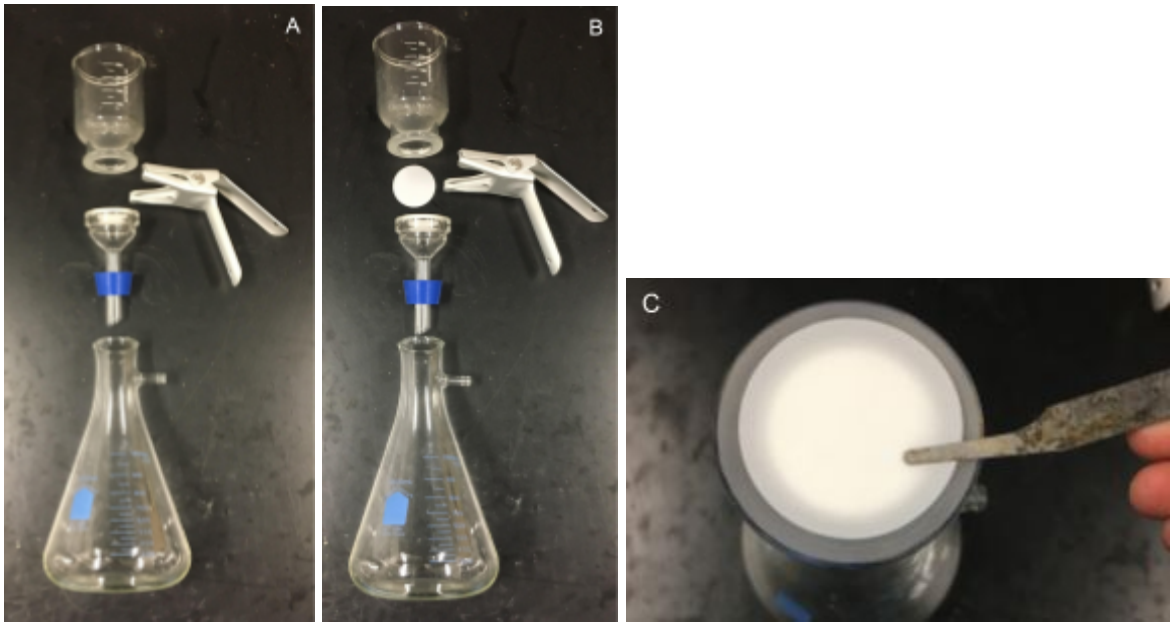

Figure 7. Column installation order with (a) and without filter (b), and (c) filter placement.

Sturgeon

Muscle plug samples will be stored in cryovials and stored at -4°C in a dry ice cooler in the field. Each cryovial should contain all muscle plugs taken from each individual fish (2-3 plugs). Samples will be transported at least once every week back to SFEI, where they will be stored in a commercial freezer at -20°C until the end of the sampling season. Muscle plug samples should be stored at -80°C whenever possible, and should not be stored at -20 C for longer than 3 months.

At the end of DFW tagging efforts sturgeon plugs will be processed at SFEI following previous USGS processing methods, also used in 2015-2017 Sturgeon Derby Studies (Sun, et al., 2019). The objective of plug processing is to remove the skin and lipid layer from the muscle plugs, leaving only fish muscle tissue remaining. The tissue, skin, and lipid can usually be differentiated by color and texture; dark grey skin, more opaque/pink lipid layer (Figure 6). Skin removal should be conducted while the plugs are still frozen, on a clean dissection tray, and under sufficient lighting to aid in differentiating between the layers of tissue. Dissection tools can be a sharp scalpel or dissection scissors; all tools should be cleaned with ethanol between samples. When no obvious lipid layer is apparent, the skin and muscle tissue should be separated approximately 1-2 mm below the skin. When the lipid layer appears mixed with muscle tissue, it should not be removed to preserve muscle tissue for analysis.

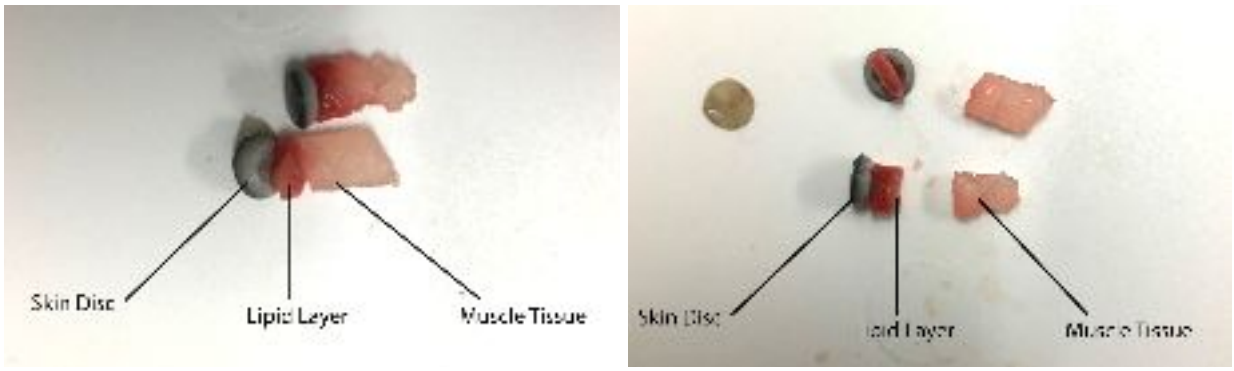

Figure 8. Muscle plugs before (left) and after (right) skin and lipid layers removal

After skin and lipid layer removal, wet tissue weight should be obtained and recorded. The ideal amount of tissue needed for analysis is between 150-200 mg, with 100 mg as an absolute minimum. Any notes about the condition of the plugs and/or anomalies should also be noted to serve as a record to refer back to if any abnormal results arise.

8. Shipping

Shipping COC template is located in the shared drive or google drive at:

- S:\Programs-Official\CleanWater\Projects\Bay_RMP\6_Special Studies\Selenium WG\Selenium North Bay Special Study\COCs
- https://drive.google.com/drive/folders/1tz7ZRvK6gVOAamT-nRCptoFlvXBOhES-

Copies of completed COCs should be saved here. For CalTest pickups, scan CalTest COC form and save to the folder as PDF.

All shipped samples will be accompanied by a chain of custody form (COC) provided by SFEI, AMS, or BAL. The COC form will include the Organism ID, site name, collection date, sample type, analysis required, and any other significant notes.

Table 4. Shipping Contact Information

	Contact	Address	Shipment Speed
BAL	Lauren Blaiwes	18804 North Creek Pkwy #100, Bothell, WA 98011	FedEx Standard Overnight or Same-Day
UC Davis SIF		UC Davis Stable Isotope Facility Dept. Plant Sciences 387 N Quad, Room 1210 PES Davis, CA, 95616	FedEx Standard Overnight
SFEI	*Nina Buzby*	*4911 Central Avenue, Richmond, CA 94804*	*N/A*
AMS	*Clifton Herrmann*	*4749 Bennett Dr # L, Livermore, CA 94551*	*N/A*
CalTest	*Todd Albertson*	*1885 N Kelly Rd, Napa, CA 94558*	*N/A*

Clams

Original samples will be shipped by AMS to BAL. The clams will be frozen (ideally at -80°C; Kleckner et al., 2010), separated into baggies of size class and station, and packed on ice. SFEI will provide AMS with labels for clam composites with site, date, and size range information (e.g. STN41_2019-0627_13-14). Clams should be shipped within two days of finishing the depuration process, and sent via next-day or overnight shipping.

Stable isotope sub-samples will be shipped by BAL to UC Davis SIF. As stated in Section 7 - samples should contain at least 8-10 mg of tissue and be stored in glass vials. Full shipping details are provided on the UC Davis website (Appendix A).

Water

Selenium water samples will be shipped by SFEI to BAL. Samples will be shipped in coolers on ice via same-day or next-day shipping (same day should be reserved for Thursday cruises, to avoid weekend delays).

Ancillary parameter samples (Chl-A, TOC, SSC) will be picked up from SFEI by CalTest staff the morning after field efforts. Until pickup, samples should be refrigerated or kept on ice.

Sturgeon

Muscle plugs will be shipped in cryovials by SFEI to BAL at the end of DFW's sturgeon tagging efforts. Samples will be shipped on dry ice via FedEx overnight service.

9. Analytical Methods

The analytes of interest for each matrix, the corresponding lab, and analytical method associated with these analyses are outlined in Table 5.

Table 5. Analytical Methods and Reporting Information

	Analyte(s)	Method	MDL (µg/L)	Lab
Sturgeon	Total Selenium	Tot rec. Se Analysis by ICP-QQQ-MS EPA 6020, Mod. with EPA 3050B digestion Total Solids (for dw correction)	1.50E-01	Brooks Applied Laboratories
Clam	Total Selenium	Tot rec. Se Analysis by ICP-QQQ-MS EPA 6020, Mod. with EPA 3050B digestion	4.22E-02	Brooks Applied Laboratories
	^{13}C, ^{15}N, and ^{34}S isotopes*	Elemental analyzer interfaced to a continuous flow (IRMS)		UC Davis Stable Isotope Facility
Water	Dissolved Se	EPA Method 1640, Mod. with Column Separation and Analysis with ICP-QQQ-MS	4.00E-02	Brooks Applied Laboratories
	Particulate Se	Tot rec. Se Analysis by ICP-QQQ-MS EPA 6020, Mod. with EPA 3050B digestion		
	SSC (ancillary)		1 mg/L	CalTest Analytical Laboratory
	TOC (ancillary)		1 mg/L	
	Chl-A (ancillary)		0.5 ug/L	

*Sulfur isotope analysis will be conducted separately from carbon and nitrogen samples.

The analytical methods for clam tissue analysis employed by BAL have been vetted for comparability to past USGS data through an intercomparison (IC) study. The lab's selenium results compared to historical concentrations showed a mean percent recovery of 99% (99% for clams and 118% for sturgeon fillets). For greater details on stable isotope analytical methods see Appendix A.

10. Quality Assurance Measures

General RMP QA/QC protocols can be found in the 2019 Quality Assurance Program Plan for the Regional Monitoring Program for Water Quality in San Francisco Bay (Yee et. al., 2019). QA/QC samples will be analyzed at a rate of a minimum of one laboratory blank and laboratory control sample per batch (or per 20 samples for larger batches), and one laboratory duplicate, one matrix spike, one matrix spike duplicate, and one certified reference material for every 20 samples (with at least one per reporting year). This frequency indicates, for example, a lab batch of 10 samples would still require at least one lab blank, while a set of 35 field samples requires 2 or more CRMs even if these samples were all reported as a single dataset.

Reference materials used by BAL are documented in performance results provided by BAL during the 2019 Selenium Intercomparison study. See Appendix B for more details. UC Davis Stable Isotope facility ensures that samples are interspersed with replicates of at least two different laboratory standards. These laboratory standards are previously calibrated against NIST Standard Reference Materials (Appendix B).

11. Reporting & Data Management

To support staggered funding efforts for this multi-year effort, data management efforts in 2019 will be minimal, with the majority of the work occurring in 2020.

12. References

Beckon, William N. 2016. “A Method for Improving Predictive Modeling by Taking into Account Lag Time: Example of Selenium Bioaccumulation in a Flowing System.” Aquatic Toxicology 176 (July): 172–80.

Brown, C. L.; and Luoma S. N. 1995. Use of the euryhaline bivalve *Potamocorbula amurensis* as a biosentinel species to assess trace metal contamination in San Francisco Bay. Mar Ecol Prog Ser. 124:129-142.

Decho A. L. V.; Luoma S. N. 1991. Time-courses in the retention of food material in the bivalves *Potamocorbula amurensis* and *Macorna balthica*: significance to the absorption of carbon and chromium. Mar Ecol Prog Ser. 8:303-314.

Kleckner, A. E.; Stewart, R. A.; Kent, E.; Luoma, S. N. 2010. Selenium Concentrations and Stable Isotopic Compositions of Carbon and Nitrogen in the Benthic Clam *Corbula amurensis* from Northern San Francisco Bay, California: May 1995 - Februrary 2010. USGS Open File report 2010-1252.

Sun, J.; Davis, J. A.; Stewart, R.; Palace, V. 2019. Selenium in White Sturgeon from North San Francisco Bay: The 2015-2017 Sturgeon Derby Study. SFEI Contribution No. 897. San Francisco Estuary Institute: Richmond, CA.

Yee, D.; Franz, A.; Wong, A.; Ross, J. 2019. 2019 Quality Assurance Program Plan for the Regional Monitoring Program for Water Quality in San Francisco Bay. SFEI Contribution No. 966. San Francisco Estuary Institute: Richmond, CA.

Appendix A.

UC Davis Stable Isotope Facility Resources

Stable isotope sample submission protocols and requirements:
https://stableisotopefacility.ucdavis.edu/samplesubmission.html

Carbon and nitrogen isotopes in solids analytical approach:
https://stableisotopefacility.ucdavis.edu/13cand15n.html

Appendix B.

Quality Control Documents

Brooks Applied Labs quality assurance and quality control sample performance. Provided during the 2019 RMP Selenium Intercomparison Study.
https://docs.google.com/spreadsheets/d/1U0fWPztCMugcrppY_yntE2TLlzmZyfTsD8GqfQLZihA/edit#gid=1275474726&range=B26:B73

Appendix C.

Sample collection field sheet templates

Clam & Water
https://docs.google.com/spreadsheets/d/1A_aHith6WEqktrfpYHR09Eu5XEJ7VTFZfvd5XTZEJd4/edit#gid=1501983697

Sturgeon Muscle Plugs
https://drive.google.com/open?id=1MJH8tQNPF9hMEln7VVXj8Ob_tKxvFgGJ
S:\Programs-Official\CleanWater\Projects\Bay_RMP\6_Special Studies\Selenium WG\Selenium North Bay Special Study

Other field resources

SFEI Navigable Waters Log

https://docs.google.com/spreadsheets/d/1ePFtM07P8QKscu7GxNE8I0n1sTevAfrDW7wgyyIqRlU/edit?usp=sharing

Detailed Sturgeon Muscle Plug Sampling Protocol:
https://docs.google.com/document/d/1j8Mmwy3sWC0cZtiGnHyZf3nFLRox9aPcAfU1Vq7Xyno/edit#