Selenium Workgroup 2021 Special Study Proposal: Selenium in North Bay Clams and Water

Summary: The proposed monitoring would extend and leverage a long-term time series for selenium in clam tissue and associated water sampling. The RMP approved funding in 2017 that to extend a USGS time series through September 2017, and then re-initiated clam and water monitoring in 2019. This proposal would support a third year of monitoring following a monitoring design optimized for cost-effective early detection of changes in selenium trends in clams and water. Clam and water samples would be collected monthly at two locations in one three-month block (Jun-Aug) and one two-month block (Dec-Jan).

Estimated Cost: $71,600

Oversight Group: RMP Selenium Workgroup

Proposed by: Nina Buzby and Jay Davis

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	**Due Date**
Task 1. Collect water and clam samples	June 2021 - January 2022
Task 2. Analyze water and clam samples	May 2022
Task 3. Data Management	July 2022
Task 4. Draft Report	October 2022
Task 5. Final Report	December 2022

Background

In 2016, the USEPA approved a selenium TMDL for North San Francisco Bay (SFBRWQCB 2015). The TMDL established a target concentration of 11.3 µg/g dw in white sturgeon muscle tissue as the basis for evaluating impairment (SFBRWQCB 2015). In June 2016 the USEPA published proposed aquatic life and aquatic-dependent wildlife criteria for

selenium in the Bay and Delta (USEPA 2016). The proposal includes criteria for fish tissue (muscle and whole body), clam tissue, and water (dissolved and particulate).

After establishing the North Bay TMDL, the San Francisco Water Board asked the Selenium Workgroup to develop a robust monitoring design for the North Bay. The goal is to track leading indicators of change to allow prompt management response to signs of increasing impairment. The Workgroup convened a technical workshop on this topic on July 27, 2016. At this workshop, participants reached a consensus that monitoring of sturgeon, clams, and water are all needed to answer management questions. Recommendations for long- term monitoring of these three matrices were presented in a North Bay Monitoring Design document (Grieb et al. 2018).

USGS conducted monthly clam monitoring at multiple locations in the North Bay for over 20 years, but USGS funding for this work ended in 2016. In 2016, the RMP approved the use of Undesignated Funds to support the continuation of the USGS monitoring, which covered monitoring through September 2017. Monitoring was not conducted between October 2017 and June 2019, creating the first gap in this long-term time series. In 2019, the RMP resumed clam and water monitoring following a modified monitoring design optimized for early detection of changes in selenium trends in clams. Following the recommendations in the North Bay Monitoring Design document (Grieb et al. 2018), this monitoring is continuing on an annual basis through 2020.

This work addresses an important gap in systematic selenium monitoring in the North Bay. Previously, studies of selenium speciation across the estuarine salinity gradient were conducted only periodically from 1999-2000, 2010, and 2012. Currently, only dissolved selenium is collected at randomly selected sites in the North Bay once every two years through the RMP Status and Trends program. The RMP also recently retired its biennial Status and Trends Bivalve monitoring, which previously measured selenium in mussel tissue. Recommendations in Grieb et al. (2018) for future water monitoring included monthly water sampling at the two clam stations in the North Bay. The clam and water studies funded by the RMP in 2019 and 2020 included water sampling concurrent with clam sampling at the two primary USGS long-term monitoring stations (4.1 and 8.1, Figure 1) in two three-month blocks (Jun-Aug and Nov-Jan).

Study Objectives and Applicable RMP Management Questions

The goal of this project is to continue long-term monitoring of *Potamocorbula amurensis* and water in the North Bay, to track long-term interannual trends and provide an indication of changes in sources or environmental processes influencing food web selenium exposures in North Bay. This study addresses key questions identified by the Selenium Strategy and the RMP (Table 1).

Table 1. Study objectives and questions relevant to RMP management questions.

RMP Management Question	Priority Management Question for Selenium	Priority Management Question for Selenium in North Bay	Study Objective	Example Information Application
1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely?	2. Are the beneficial uses of north San Francisco Bay impaired by selenium?	1. Are the beneficial uses of north San Francisco Bay impaired by selenium?	Compare measured concentrations to the North Bay TMDL target for water and USEPA selenium criteria for water and clams.	Do the data indicate a need for management actions? What factors are influencing the observed selenium concentrations?
2) What are the concentrations and masses of contaminants in the Estuary and its segments?	3. What is the spatial pattern of selenium impairment?		Compare measured concentrations across two sites in North Bay.	Are there distinct differences in selenium concentrations and patterns across sites? What do these differences indicate about selenium sources and bioaccumulation in different regions of North Bay?
4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased?	2. Are changes occurring in selenium concentrations that warrant changes in management actions?	2. Are changes occurring in selenium concentrations that warrant changes in management actions?	Compare measured concentrations to clam and water concentrations measured during past studies. Evaluate trends using change point and normal range analyses.	Are selenium concentrations increasing or decreasing? What factors may be influencing these trends?

Approach

Field Sample Collection

Potamocorbula amurensis and water samples will be collected near two long-term USGS monitoring locations in northern San Francisco Bay: (1) near station 8.1 at the mouth of the Carquinez Strait in Suisun Bay, and (2) near station 4.1 at the confluence of the

Sacramento and San Joaquin Rivers (Figure 1). Clam samples will be collected and processed by Applied Marine Sciences. Clam sampling will occur aboard a vessel from Dixon Marine Services. Similar to the sampling design from 2019 and 2020 monitoring, clam sampling will take place in two key blocks of monthly sampling preceding fall muscle plug monitoring (June-August) and the spring pre-spawning period (December-January).

Each month, approximately 100 clams will be collected near USGS stations 8.1 and 4.1 using a clam dredge and depurated for 48 hours prior to being measured and divided into 3 composite size classes representing the range in collected clam lengths. Groups of composite clam samples will be shipped to Brooks Applied Labs (BAL) for further sample processing and analysis.

Water sampling will take place aboard the RV Sentinel (CA DWR), during their monthly benthic cruises. Both selenium and ancillary parameters (Chl-A, SSC, TOC) will be collected by DWR field staff via their in-line intake systems at sites D6-R and D4-L (Figure 1). Selenium samples will be collected for both the dissolved and particulate phase. Dissolved phase samples will be collected through a 0.45-µm Voss capsule in-line filter cartridge. Particulate phase samples will be created by SFEI staff after field collection, by vacuum filtering approximately 300 mL of water, depending on sample turbidity, through 0.45 µm polycarbonate filters.

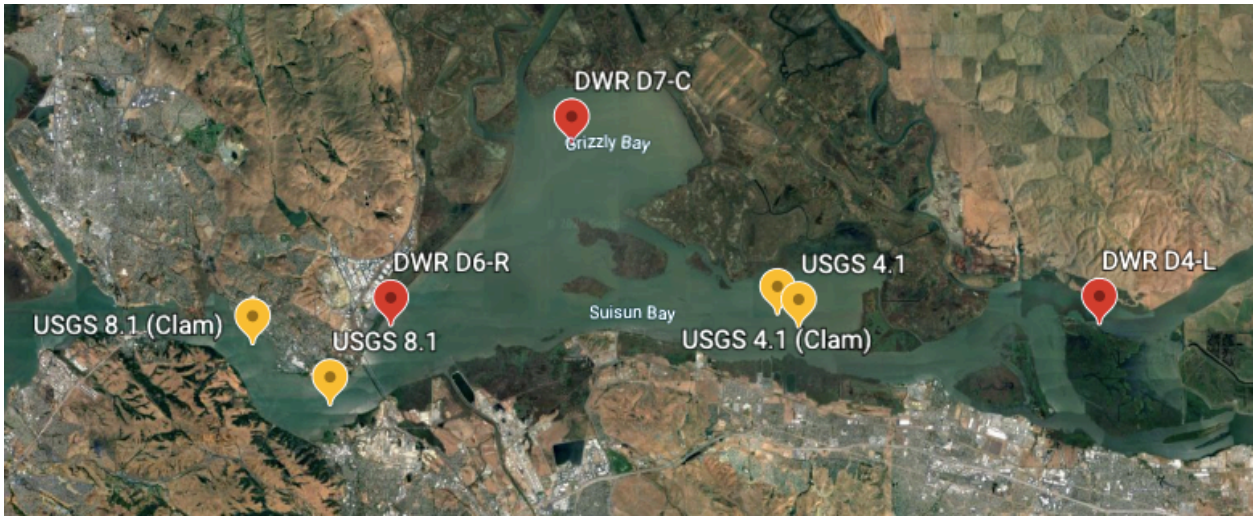

Figure 1. *USGS (clam and water) and DWR (benthic) North Bay stations.*

Laboratory Analyses

Clams will be dissected and homogenized into three composite samples by BAL. A wet weight will be recorded before the samples are freeze dried, after which a dry weight will be recorded and samples will be analyzed for Se concentrations. Samples will also be prepared for analysis of carbon and nitrogen stable isotopes by the UC Davis Stable Isotope Facility.

Clams will be analyzed by BAL monthly, after each sampling event. QA/QC samples will be analyzed at a rate of one laboratory blank, one laboratory duplicate, one matrix spike, one matrix spike duplicate, and one certified reference material for every 20 samples. BAL will also analyze dissolved and particulate water samples, by EPA Method 1640 (Modified with Column Separation and Analysis with ICP-QQQ-MS) and EPA Method 1638 (Modified with EPA 3050B digestion), respectively. Method and reporting details are outlined in Table 2.

Ancillary parameters, including total suspended material, total organic carbon, and chlorophyll-a, will also be collected at each selenium water sampling location and analyzed by Caltest Analytical Laboratory. Method and reporting details are outlined in Table 2.

Table 2a. *Analytical methods and detection limits*

Matrix	**Surface Water**	
Analyte Name	**Average MDL**	**Lab - Method**
Selenium (dissolved)	0.04 ug/L	BR-EPA 1640
Selenium (particulate)	0.04 ug/L	EPA 6020
Chl-a	1 mg/m^3	SM 10200 H
SSC	0.5 mg/mL	ASTM D3977-B
TOC	0.3 mg/mL	SM 5310B
Matrix	**Bivalves**	
Analyte Name	**Average MDL**	**Lab - Method**
Selenium	0.04 ug/g dw	EPA 1638M

Table 2b. *Isotope Analysis Performance and Detection Limits*

Isotope	**Detection Range (ug)**	**Standard Deviation**
15N	20-15	+/- 0.2
13C	200-2000	+/- 0.3

Budget

As noted in the Multi-Year Plan, data management and reporting is planned for the following year of monitoring beginning in 2022.

Table 3 . *Proposed Budget*

Expense	Estimated Hours	Estimated Cost
Labor		
Project Staff	65	$5,900
Senior Mgmt Review	16	$2,850
Project/Contract Mgmt *		$0
Data Technical Services	45	$5,000
		$13,750
Subcontracts		
Applied Marine Sciences **	258	$25,600
Brooks Applied Labs **		$10,800
CalTest Laboratories		$4,500
UC Davis Stable Isotope Lab		$1,850
		$42,750
Direct Costs		
Vessel		$14,600
Equipment		*included in BAL costs*
Shipping		$500
		$15,100
Grand Total		***$71,600***

** Not needed because core RMP funding provides this service.*
*** Also includes equipment/travel costs*

Budget Justification

Field and Direct Costs

This special study proposal has an overall budget of *$71,600*, which includes *$13,750* devoted to labor. These funds would cover field efforts for five cruises, coordination with subcontractors (analytical labs, vessels, and field partner AMS), and preliminary data review. Efforts will be made to minimize direct costs through leveraging vessel partnerships and utilizing sampling equipment from monitoring efforts in previous years.

Laboratory Costs

After an intercomparison study completed in 2018, BAL was chosen as the analytical partner to conduct selenium analyses. The selection was based on comparison to past USGS monitoring results as well as lab accuracy and precision metrics (e.g. CRM performance, replicate agreement). BAL provides analyses for Total Se in the dissolved and particulate phase as $110 and $90/sample, respectively. Clam analysis costs are $185/sample with homogenization and subsampling at $25/sample. 14 water and 60 clam samples will be analyzed, including water field duplicates and blanks. Other BAL costs include sampling equipment (e.g., filter cartridges) and MS/MSDs.

Ancillary water parameter analyses (chlorophyll-a, suspended sediment concentration, and total organic carbon) will be conducted by CalTest laboratories at $158, $86, and $77/sample, respectively. Additional costs for CEDEN formatting and sample pickup are also included in CalTest analytical costs. Stable isotope analysis will be completed by the UC Davis Stable Isotope Laboratory at $27/sample with additional $5/sample solid weight analysis.

Data Management Costs

Data services will include generating EDD templates and analytical laboratory communications. To reduce study costs, previous years conducted data management biennially. Since the 2020 monitoring budget included data services costs, the full set of data management tasks (QA/QC review, CEDEN upload, data report) for 2021 would similarly be deferred until 2022.

Data Management and Reporting

Preliminary data review will be conducted by RMP staff during the collection year, including preparation of data tables that can be available for internal RMP and Workgroup review. Complete RMP data management and reporting will be conducted as part of 2022 monitoring efforts.

References

Grieb, T.; Roy, S.; Rath, J.; Stewart, R.; Sun, J.; Davis, J. A. 2018. North Bay Selenium Monitoring Design. SFEI Contribution No. 921. San Francisco Estuary Institute: Richmond, CA. https://www.sfei.org/documents/north-bay-selenium-monitoring-design-0

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USEPA. 2016. Proposed aquatic life and aquatic-dependent wildlife criteria for selenium in California's San Francisco Bay and Delta. EPA 820-F-16-006. US Environmental Protection Agency.

Selenium Workgroup 2021 Special Study Proposal: Selenium in White Sturgeon Muscle Plugs

Summary: In March 2016, the USEPA approved a Selenium TMDL for North San Francisco Bay, which established a white sturgeon muscle tissue target of 11.3 ug/g dry weight as a basis for evaluating impairment. From 2014-2017, the RMP conducted annual monitoring of selenium in sturgeon muscle plug tissue, through a collaboration with the California Department of Fish and Wildlife (CDFW) and other partners. Preliminary power analyses suggest that long-term monitoring of 60 samples per year at a minimum biennial frequency is needed to detect potential long-term trends driven by changes in environmental selenium sources. This study proposes to continue the biennial sampling started in 2019 as part of the long-term North Bay monitoring work, that aims to track North Bay condition relative to the TMDL target and evaluate long-term trends.

Estimated Cost: $21,825

Oversight Group: RMP Selenium Workgroup

Proposed by: Nina Buzby and Jay Davis

PROPOSED DELIVERABLES AND TIMELINE

Deliverable	Due Date
Task 1. Collect 2021 muscle plugs (field sampling)	August-October 2021
Task 2. Analyze 2021 muscle plugs	January 2022
Task 3. Data Management	March 2022
Task 4. Prepare draft data report	October 2022
Task 5. Prepare final data report	December 2022

Background

In 2016, the USEPA 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). In order to support implementation of the TMDL, the Selenium Workgroup has developed a monitoring method that will allow for the routine collection of large numbers of white sturgeon muscle tissue samples.

Muscle plug sampling provides a non-lethal method for monitoring contaminants that has been successfully used to monitor mercury and selenium concentrations in fish, including threatened fish species. During 2009 and 2014 RMP Status and Trends sport fish sampling, and the 2016 and 2017 RMP Sturgeon Derby special study, paired muscle plug and fillet samples were analyzed for selenium as part of an effort to establish a non-lethal and efficient method of collecting sturgeon muscle tissue using plugs. Results from these studies show that muscle plug and muscle fillet selenium are strongly correlated, indicating that muscle plugs can be used as proxies for muscle fillets to monitor selenium in sturgeon muscle tissue (Sun et al. 2018).

Muscle plug sampling from live sturgeon in the field was also successfully piloted in the 2014-2017 RMP Sturgeon Muscle Plug studies (Sun et al. 2018). This monitoring is made possible through a valuable collaboration with the California Department of Fish and Wildlife (CDFW), which has collected samples for the RMP *pro-bono* during its annual sturgeon population tagging study (DuBois and Danos 2017). Over the past four years, samples have been collected in Suisun and San Pablo Bays between August and October of each year. 30, 38, and 58 muscle plug samples were successfully collected and analyzed for selenium in 2015, 2016, and 2017, with an additional 28 samples collected and archived in 2015. Sufficient sample mass was collected for most samples to also enable analysis of C, N, and S isotopes, to provide information about dietary selenium sources (foraging location and trophic position). Overall, this work has established fall muscle plug monitoring as a valuable tool to continue tracking long-term trends.

A preliminary power analysis conducted using all historically available data on selenium in sturgeon muscle tissue indicated that a sample collection frequency of once every two years should allow for detection of long-term trends of 2-3% per year over a 20 year period (power > 0.75; Grieb et. al., 2018). This supported a decision by the RMP to initiate a biennial sampling design beginning in 2019.

Sampling was attempted in 2019, but the sample masses obtained for most of the samples were too small to support reliable selenium analysis. The 2019 effort was postponed to 2020 because of this, with measures taken to ensure this problem does not occur again. Sample collection is primarily performed pro bono by CDFW, so the budgetary impact of this problem was small.

This proposal outlines a scope and budget for sturgeon muscle plug monitoring in 2021, with analysis of the plugs for selenium and C, N, and S stable isotopes.

Study Objectives and Applicable RMP Management Questions

The ultimate objective of this monitoring element is to obtain a relatively large number of sturgeon muscle samples to assess attainment of the North Bay selenium TMDL target and other regulatory thresholds. These data will also allow continued tracking of long-term interannual trends. This study addresses key questions identified by the Selenium Strategy and the RMP (Table 1).

Table 1. *Study objectives and questions relevant to RMP management questions.*

RMP Management Question	**Priority Management Question for Selenium**	**Study Objective**	**Example Information Application**
1) Are chemical concentrations in the Estuary at levels of potential concern and are associated impacts likely? 1B. What potential for impacts on humans and aquatic life exists due to contaminants in the Estuary ecosystem?	1. Are the beneficial uses of north San Francisco Bay impaired by selenium?	Compare measured concentrations to regulatory thresholds (North Bay Selenium TMDL).	Do the data indicate a need for management actions? What factors are influencing the observed selenium concentrations? How should the TMDL muscle tissue target be assessed?
4) Have the concentrations, masses, and associated impacts of contaminants in the Estuary increased or decreased? 4.B. What are the effects of management actions on the potential for adverse impacts on humans and aquatic life due to Bay contamination?	2. Are changes occurring in selenium concentrations that warrant changes in management actions?	Compare measured concentrations to plug and fillet concentrations measured during past studies, including past iterations of this study. Evaluate trends using linear regression and change point method analyses	Are selenium concentrations increasing or decreasing? What factors may be influencing these trends?

Approach

Muscle plugs from approximately sixty white sturgeon will be collected by California Department of Fish and Wildlife (CDFW) staff between August and October 2021, during the CDFW sturgeon tagging effort in North Bay. SFEI staff will plan and coordinate the study and CDFW staff will collect the samples. SFEI staff will instruct and train CDFW field staff on

muscle plug collection techniques at the beginning of the collection season to ensure that the plugs contain sufficient tissue for analysis (Buzby et. al., 2020). SFEI staff will retrieve samples from CDFW staff periodically throughout the duration of the field season in order to keep samples chilled at a colder and more stable temperature until sample analysis. Masses of the collected plugs will be checked frequently to ensure that they are sufficient.

At the conclusion of the field season, SFEI staff will conduct initial processing of muscle plug samples for shipment to Brooks Applied Laboratories (BAL). BAL will complete processing of the plug samples and perform selenium analyses, and subsequently prepare and ship samples to UC Davis to perform C, N, and S stable isotope analyses.

Table 2a. *Selenium Analytical Methods and Detection Limits*

Matrix	**Sport Fish (ug/g ww)**	
Analyte Name	**Average MDL**	**Lab - Method**
Selenium	0.15	MPSL-DFG 200.8

Table 2b. *Isotope Analysis Performance and Detection Limits*

Isotope	**Detection Range (ug)**	**Standard Deviation (permil)**
15N	20-15	+/- 0.2
13C	200-2000	+/- 0.3

Two laboratory method blanks and one standard reference material will be analyzed with the lab batch; duplicates, matrix spikes, and matrix spike duplicates will be analyzed at a frequency of 1 per 20 samples. Costs for these QA/QC samples will be included in the sample cost; no additional QA/QC samples will be requested.

Budget

As noted in the Multi-Year Plan, data management and reporting is planned for the following year of monitoring beginning in 2022.

Table 3. *Proposed Budget*

Task	**Estimated Cost**
Labor	
Project Planning & Coordination	$4,000
Field Work	$3,000
Data Management	$3,000
Subtotal	***$10,000***
Subcontracts	
BAL – 60 selenium & total solids analyses @ $100/sample**	$6,900
BAL – 60 samples processed & subsampled @ $25/sample	$1,500
UCD – 60 C, N, S analyses @ $32/sample	$2,175
Subtotal	***$10,575***
Direct Costs	
Equipment - biopsy plugs, sample containers, dry ice, etc.	$1,000
Shipping	$250
Subtotal	***$1,250***
Grand Total	***$21,825***

***Includes cost of QA samples*

Budget Justification

Field and Direct Costs

This special study proposal has an overall budget of $21,825, which includes $10,000 devoted to labor. These funds would cover initial field training, coordination with CDWF and analytical subcontractors, and preliminary data review. Direct costs are minimal due to the leveraged collaboration with CDFW as well as the ability to utilize sampling equipment from monitoring efforts in previous years.

Laboratory Costs

After an intercomparison study completed in 2018, BAL was chosen as the analytical partner to conduct selenium analyses. The selection was based on comparison to past RMP monitoring results as well as lab accuracy and precision metrics (e.g. CRM performance, replicate agreement). BAL provides analyses for Total Se in sport fish tissue at $100/sample, with subsampling for isotope analysis at $25/sample. Approximately 60 muscle plug samples will be analyzed, including lab duplicates and blanks. Other BAL costs include MS/MSDs.

Stable isotope analysis will be completed by the UC Davis Stable Isotope Laboratory at $8.50/sample for ^{13}C and ^{15}N analyses and $18.75/sample for ^{34}S analysis. An additional $4.50/sample will go towards solid weight analysis.

Data Management Costs

Due to the staggered data management approach of this study, the full set of data management tasks (QA/QC review, CEDEN upload, data report) will not occur until 2022 data are available. The proposed data management costs in 2021 refer to efforts in generating EDD templates, transcribing field data sheets, and general laboratory communications.

Data Management and Reporting

Data management and reporting will be performed in 2022. Initial data review will be conducted by RMP staff and likely presented to the Selenium Workgroup at the 2023 meeting.

References

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DuBois, J and Danos, A. 2017. 2017 Field Season Summary for the Sturgeon Population Study. California Department of Fish and Wildlife – Bay Delta Region, Stockton, CA.

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