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### 1. Introduction

The San Francisco Bay Regional Water Board developed a Total Maximum Daily Load (TMDL) and implementation plan for selenium in North San Francisco Bay (NSFB) in 2015.<sup>1</sup> The TMDL is based on attainment of water column and fish tissue target concentrations protective of human health, aquatic life, and wildlife, and was approved by the US Environmental Protection Agency in August, 2016.

Analyses in support of the TMDL synthesized the results of different monitoring efforts to characterize selenium concentrations in water and biota in the Estuary. For water quality evaluation in the TMDL, the sources of observational data included studies of selenium speciation across the estuarine salinity gradient, performed in 1999-2000 and again in 2010 and 2012 (Cutter and Cutter 2004, Doblin et al. 2006, Tetra Tech, 2012), as well as samples collected by the San Francisco Bay Regional Monitoring Program (RMP). Changes in wastewater treatment from the five major refineries in NSFB were implemented in the late 1990s, leading to significant reductions in selenium loads. Data at Estuary center-line locations showed small changes for dissolved selenium in the mid-salinity range and no trends in particulate selenium (Baginska, 2015). As part of the TMDL, water quality modeling analyses were performed to characterize NSFB selenium concentrations under a range of hydrologic conditions and changing point-source loads (Baginska, 2015).

Water column selenium concentration data in the NSFB and Delta continue to be collected at selected locations, although these data have not been systematically evaluated following the analyses presented in the TMDL reports. In the near term, possible changes that may cause selenium concentrations to change in the NSFB and Delta include concentration changes in the inflow from the San Joaquin River basin, changes in refinery inputs, changes in stormwater and tributary loads from the Bay margin, and changes in overall Central Valley hydrological conditions, such as the extreme wet and dry periods that occurred between 2012 and 2017. Other drivers, such as nutrient concentrations and algal levels, may also play a role, especially on the concentrations of selenium on particulates. Over the longer term,

<sup>&</sup>lt;sup>1</sup> http://www.waterboards.ca.gov/sanfranciscobay/water\_issues/programs/TMDLs/seleniumtmdl.shtml

selenium changes may occur due to modification of Delta flows and the mix of riverine sources because of the implementation of the WaterFix project<sup>2</sup> by the state of California.

For the above reasons, a sustained monitoring effort in the NSFB and Delta is needed to support the longer term implementation goals of the TMDL. This memorandum is prepared to evaluate the most recent changes in selenium in the NSFB and Delta (post 2012), through analysis of observed data and modeling, and to support future monitoring efforts.

Four key elements of this memorandum include analysis of water selenium data in the Delta and riverine inflows, collected over the past decade; model evaluation of changes in the Bay as a result of changing inflows; model evaluation of the relative mix of riverine sources of selenium that reach the Bay; and updates to the riverine selenium loads delivered to the Bay.

Selenium monitoring in the NSFB is uneven at present. Concentrations at source boundaries in the Sacramento and San Joaquin Rivers are monitored by the USGS via grab samples collected approximately twice per month. Additional data have been reported in the Delta and the confluence of the Sacramento and San Joaquin Rivers near the Bay, with samples collected relatively infrequently in recent years. These data are evaluated to infer recent changes.

Hydrological conditions can affect residence times and selenium concentrations and potentially, bioaccumulation in the Bay. To test the hypothesis of flow impacts on the selenium concentrations, a previously calibrated selenium biogeochemistry model, the ECoS model (Harris and Gorley, 1998; Harris and Gorley, 2003), was used. The ECoS model was previously applied to NSFB using data for the period of 1994-2010 (Chen et al. 2012), and by Meseck (2002) for 1998-1999. The model was later updated with selenium data collected in NSFB during the period of 2010- 2012 (Tetra Tech, 2014a). This updated model was used to evaluate the selenium impacts of decreased freshwater inflows to the Bay, generally representing conditions that occurred during the 2012-2015 California drought.

A different model was used to represent the riverine sources flowing through the Delta into the bay: the Delta Simulation Model (DSM2). The DSM2 model was previously used to estimate contribution from source boundaries and selenium concentrations in the Bay (Tetra Tech, 2014b). The version of the DSM2 used in this study is the latest version (v8.1.2), released in 2013 by Department of Water Resources (DWR), with flow inputs to February 2016. Simulations with the DSM2 model allow exploration of the relative contribution of different freshwater sources to Delta, notably the contribution of the San Joaquin River, which has historically had higher selenium concentrations than other freshwater inflows. The DSM2 model was run to estimate the volumetric contribution from the San Joaquin River to the Delta under different hydrological conditions (above normal, wet, below normal, dry, and critical year classifications). The data and modeling framework were also used to update the loads from the Sacramento River and the San Joaquin River to NSFB.

### 2. Observed Selenium at the Riverine Boundaries

Selenium concentrations in the Sacramento River at Freeport and San Joaquin River at Vernalis are monitored by the US Geological Survey (USGS) as part of routine monitoring and the data are publicly available on the National Water Information System (NWIS) database<sup>3</sup>: the Freeport station is

<sup>&</sup>lt;sup>2</sup> https://www.californiawaterfix.com/

<sup>&</sup>lt;sup>3</sup> https://nwis.waterdata.usgs.gov/usa/nwis/qwdata

referenced as 11447650, and the Vernalis station as 11303500. Prior to 2007, samples collected were analyzed using a hydride generation method, with a high detection limit of 1  $\mu$ g/L. After 2007, samples were measured using the inductively coupled plasma mass spectrometry (ICP-MS) method, which has a detection limit in the range of 0.03-0.06  $\mu$ g/L. Prior to 2007, the analytical method resulted in many samples being reported below the detection limit, particularly for the Sacramento River. Therefore, only data collected after 2007 were evaluated. Along with selenium, chloride concentrations in the both rivers were evaluated. Chloride is a conservative constituent and serves as an indicator of hydrological conditions and irrigation water consumption within the watershed: higher chloride levels correspond to periods with greater evapotranspiration within the watershed. Ratios of selenium to chloride over time were also evaluated for noticeable trends in other factors that may affect selenium concentrations in the rivers.

For the Sacramento River at Freeport, dissolved selenium concentrations in recent years (2008-2017) have varied within a narrow band from  $0.05 \ \mu g/l$  to  $0.2 \ \mu g/l$ . Selenium concentrations appear to exhibit a seasonal variability within this narrow band: higher selenium concentrations are associated with higher chloride concentrations (Figure 1), indicative of water evaporation/loss processes in the watershed as opposed to any change in the magnitude of upstream sources. Thus, selenium as a ratio to chloride has varied within a narrow range and does not show a temporal pattern.

Selenium concentrations in the San Joaquin River at Vernalis, on the other hand, have showed decreases after 2011 (Figure 2). Selenium concentrations as a ratio to chloride concentrations also showed decreasing trends in recent years after 2011, and cannot be explained by changes in water evaporation/loss in the watershed, as for the Sacramento River. The decreases may be due to implementation of the Grassland Bypass Project, which has lowered selenium loads to the river upstream in the watershed from Vernalis. Another contributing factor could be the decreased flow at Vernalis in recent years (2011 – 2016). Trends in selenium as a ratio to chloride correlate with the San Joaquin River flow at Vernalis (Figure 2), suggesting that flow may be a factor affecting selenium levels in the San Joaquin River, at least over the range of flows in 2011-2016. In part this is related to the distributed source of selenium across San Joaquin River.

A statistical trend evaluation of the above data (Figure 3) confirms the presence of a significant negative slope at Vernalis for selenium and the selenium:chloride ratio, and no statistically significant changes at Freeport.

Selenium concentration data for a longer time period (beginning in the mid-1990s) were also available at Vernalis from the California Environmental Data Exchange Network (CEDEN) database, albeit with concentrations reported as total selenium, as opposed to dissolved selenium reported more recently by the USGS. However, when co-located sampling of dissolved and particulate selenium has been performed at Vernalis (e.g., Tetra Tech, 2012), dissolved selenium is >95% of the total selenium. Thus, the two quantities can be compared, although a small difference may exist between total and dissolved values. The combined long-term record (1995-2016) suggests lower concentrations in recent years (2011- 2016) (Figure 4). The selenium concentration trends in Vernalis are likely a consequence of load control efforts as part of the Grassland Bypass Project, with the goal of a 90% load reduction of selenium (Baginska, 2015).



Figure 1. Selenium concentrations in the Sacramento River at Freeport in relation to chloride (data source: USGS, obtained from NWIS at https://nwis.waterdata.usgs.gov/usa/nwis/qwdata for station 11447650).







*Figure 2. Selenium concentrations in the San Joaquin River at Vernalis in relation to chloride (data source: USGS, obtained from NWIS at https://nwis.waterdata.usgs.gov/usa/nwis/qwdata for station 11303500).* 



Figure 3. Trend evaluation of chloride, Se:chloride ratio, and Se concentrations at Freeport and Vernalis using the Mann Kendall (MK) test. The median slope (Sen slope) and significance of the slope is also shown.



Figure 4. Long-term selenium concentrations in the San Joaquin River at Vernalis (data source: CEDEN, http://www.ceden.org/).

### 3. Selenium Concentrations in the Delta

As selenium concentrations in the San Joaquin River at Vernalis have exhibited decreases in recent years, decreases in selenium in the Delta and the Bay may also be expected (Figure 5). A relatively small amount of selenium data in the Delta were also available from the CEDEN database. Two stations in the Delta that have the longest selenium records are BG20 (Sacramento River) and BG30 (San Joaquin River), both measured by the San Francisco Bay Regional Monitoring Program. Although lower concentrations were observed at these two locations in recent years (after 2005), there are not enough data for detection of a trend.

Selenium data for the interior Delta are generally lacking. Although several stations were monitored for selenium concentrations (Figure 6), the sampling periods were very limited, and insufficient to evaluate whether or not trends exist (Figure 7).



Figure 5. Total selenium concentrations in the Delta at station BG20 (Sacramento River) and BG30 (San Joaquin River) (data source: CEDEN, http://www.ceden.org/).



Figure 6. Locations of CEDEN stations in the Delta with observed selenium data (data source: CEDEN).



Figure 7. Total selenium concentrations observed at Delta locations (data source: CEDEN).

# 4. Impact of Reductions in Delta Outflow on Bay Selenium Concentrations

During recent dry periods, relatively high concentrations of selenium in the Bay have been reported (data not shown). One hypothesis for elevated selenium observed in the Bay during dry years (such as 2014 and 2015) are the longer residence times, allowing for greater accumulation of point and non-point loads delivered to the Bay. This hypothesis was tested using the updated ECoS 3 model, calibrated to the estuarine selenium transect data (Tetra Tech, 2014a). To test the impacts of the decreased inflow to the Bay, a scenario of decreasing inflow to the Bay was run by decreasing Sacramento River flow inputs by 80%, with the other point source loads and flows remaining the same. The results at Carquinez Strait suggest that with a substantial decrease in Sacramento River flow, similar to what occurred during the recent drought, selenium concentrations at Bay locations could increase by up to 0.05  $\mu$ g/l (Figure 8). The model results suggest that low flow to the Bay resulting in elevated selenium concentrations is a valid hypothesis.



Figure 8. ECoS simulated dissolved selenium concentrations in Carquinez Strait as a result of decreased flow from the Sacramento River.

### 5. San Joaquin River Contribution (DSM2 Modeling)

The relative contribution of the San Joaquin River was tested for different hydrologic conditions with an extensively used Delta hydrodynamic and water quality model, the Delta Simulation Model, DSM2. DSM2 is a one-dimensional hydrodynamic model for simulating the Sacramento–San Joaquin River Delta hydrodynamics, water quality, and particle tracking (Liu and Sandhu, 2012). The DSM2 model calculates stages, flows, velocities, transport of individual particles, and mass transport processes for conservative and non-conservative constituents, including salts, water temperature, dissolved oxygen, and dissolved organic carbon. The DSM2 model can be applied using a 'fingerprinting' mode to predict sources of water at a given location in the Delta. The version of the DSM2 used in this study is the latest version (v8.1.2), released in 2013 by Department of Water Resources (DWR).

For computing the contribution of the San Joaquin River to the NSFB, the model was run using the 'fingerprinting' mode to estimate water composition for the period of 10/1992-03/2016 at three output locations:

- Sacramento River at Rio Vista;
- San Joaquin River at Antioch; and
- Mallard Island.

These locations characterize the Central Valley loads as well as concentrations in the eastern portion of San Francisco Bay (at Mallard Island). The DSM2 simulation considered contributions from five inputs including:

- Sacramento River at Freeport,
- San Joaquin River at Vernalis,
- Martinez, representing tidal inputs from the Bay to the Delta,
- East side tributaries (Cosumnes, Calaveras, and Mokelumne Rivers), and
- Agricultural return flows from islands in the Delta.

The simulated composition of water at the Sacramento River at Rio Vista, the San Joaquin River at Antioch and Mallard Island is shown in Figure 9. For the Sacramento River at Rio Vista, the dominant source of inflow is the Sacramento River. For the San Joaquin River at Antioch, the major source of flow is also the Sacramento River. However, contributions from the San Joaquin River, Martinez and east side tributaries at Antioch are considerably larger than those at Rio Vista. Contributions from the San Joaquin River and east side tributaries are more significant during the wet years. For Mallard Island, the dominant source of water is the Sacramento River at Freeport. Contribution from the San Joaquin River to Mallard Island is generally low with some exceptions during the wet years. During wet years, contribution from the San Joaquin River to Mallard Island can be as high as 40% for limited periods.

The volumetric contribution of San Joaquin River to these locations as a function of months and water year classification clearly showed higher contribution during the wet years and above normal years than the drier years (Figure 10). In particular, the San Joaquin River contribution to Antioch and Mallard Island is the highest during wet months of wet years.



Figure 9. Simulated volumetric contribution from source boundaries to San Joaquin River at Rio Vista, Antioch and Mallard Island. Five sources are considered: Agricultural return flows (Ag), East side tributaries (East), Martinez (MTZ), San Joaquin River at Vernalis (SJR), and Sacramento River at Freeport (Sac).





Figure 10. DSM2 simulated volumetric contribution by calendar month (from 1 through 12) from San Joaquin River to Rio Vista, Antioch, and Mallard Island for different water year types as classified by DWR (http://cdec.water.ca.gov/cgi-progs/iodir/WSIHIST): Wet (W), Above normal (AN), Below normal (BN), Dry (D), and Critical (C).

### 7. Calculated Selenium Loads from the Delta to North San Francisco Bay

In the NSFB selenium TMDL, loads from the Delta are the single largest source under current conditions (Baginska, 2015) and also a matter of interest given the proposed construction of the WaterFix project which may alter the relative mix of Sacramento and San Joaquin River flows to the Bay. This analysis provides an update to the load analysis performed for the NSFB selenium TMDL with the most recent data available. Since the time the analyses for the NSFB TMDL were performed, California experienced an unusual hydrologic period, with a severe drought followed by a very wet year. In addition, as presented in Section 2, there have been significant reductions in selenium concentrations in San Joaquin River flows to the Delta. Both of these factors have affected loads to the Bay.

Simulated volumetric contributions from source waters in conjunction with selenium concentrations in the source water were used to calculate concentrations at given locations within the Delta. We consider six distinct sources in the load calculation (agricultural return flows, east side tributaries, ocean influence through Martinez, the San Joaquin River at Vernalis, the Sacramento River at Freeport, and Yolo Bypass). Of these sources, dissolved selenium concentrations are reported for the Sacramento River at Freeport and the San Joaquin River at Vernalis (available for 2007-2016, as shown in Figure 1 and Figure 2). Of these two riverine sources, the Sacramento River values range from 0.05  $\mu$ g/l to 0.2  $\mu$ g/l, and the San Joaquin River values range from 0.05  $\mu$ g/l to 1.4  $\mu$ g/l. Although San Joaquin River concentrations have decreased in recent years, they are still 2 to 3 times greater than other sources. Dissolved selenium concentrations for Martinez, east side tributaries and agricultural return flows used in the calculation were assumed to be 0.09  $\mu$ g/L, 0.1  $\mu$ g/L and 0.11  $\mu$ g/L and were assumed constant. These are relatively minor flows, and the concentrations are similar to those used in other modeling studies, such as those performed for the WaterFix Environmental Impact Report (https://www.californiawaterfix.com/resources/planning-process/eir-eis/).

For the San Joaquin River at Antioch, calculated dissolved selenium concentrations compared to the observed data from CEDEN are shown in Figure 11. Estimated dissolved selenium concentrations are generally at ~0.1  $\mu$ g/l with some peak values greater than 0.3  $\mu$ g/l. Calculated selenium concentrations at Empire Tract of Delta are also compared to the observed data from CEDEN (Figure 11). These data, although temporally limited, exhibit much greater concentrations due to the greater contribution of San Joaquin River values.

Calculated selenium loads at the Sacramento River at Rio Vista are shown for dry and wet seasons of each water year (Figure 12). The wet season was defined as Oct 1st to Apr. 30th and the dry season was defined as May 1st to Sep. 30th, similar to the previous approach in Tetra Tech (2008). Estimated dissolved selenium loads averaged 2,285 kg/yr for the entire period of 1993-2016.

Calculated selenium loads at Antioch are shown for dry and wet seasons (Figure 13). Estimated dissolved selenium loads from Antioch ranged from 8 kg/yr to 3,907 kg/yr. Selenium inputs at this location reflect the variable mixture of inputs from the Sacramento River, the San Joaquin River, the east side tributaries and agricultural return flow.

Estimated total dissolved selenium loads from the Delta to the Bay are shown in Figure 14. The estimated loads compared to previous estimates for the same time period by Tetra Tech (2008) are slightly higher, particularly during the wet years. This is possibly due to the DSM2 model computing a

higher contribution from the San Joaquin River during the wet years, plus higher selenium concentrations from the San Joaquin River, resulting in higher overall loads during wet years. A summary of dissolved selenium loads by year and season is presented in Table 1.

Tidally-averaged daily flows and concentrations from DSM2 can be used to compare loads at different locations in the Bay-Delta. For example, one approach is to compare the loads from Rio Vista and Antioch to loads downstream at Mallard Island (Figure 15). Another approach is to subtract selenium loads exported through the aqueducts from the loads *to* the Delta (i.e., sum of Freeport, Yolo, Vernalis and east-side tributary loads). The results from this mass balance approach are compared to the estimated loads at Rio Vista plus Antioch and the estimated loads at Mallard Island (Figure 16). Although the loads from the different approaches are comparable, the values from the mass balance approach are slightly higher; this is associated with the flow volumes associated with the individual inputs, and a result of losses of water volume in the Delta, likely through consumptive use on the Delta islands.

In summary, we have been able to use the most recent information on flows and concentrations to update the loads at certain Delta locations, and loads from the Delta to NSFB at Mallard Island. Given the dry years that have occurred in the recent past, the non-point sources are low, and minimal during the dry seasons. The San Joaquin River, in particular, exhibits a somewhat binary response, with extremely low load contributions in dry years, and a loading of similar magnitude to the Sacramento River in wet years. These results are consistent with the observations of high concentrations in the Bay in very wet years, which cannot be explained by the presence of point sources in the Bay. Similarly, these results also suggest that in dry months of dry years, the riverine contributions are small, and Bay concentrations are dominated by local point sources. The underlying flow data in the calculations reflect the operations and management of the Delta under variable hydrologic conditions. Continued evaluation of these load calculations in future years will provide a greater understanding of the potential selenium exposure to biota in the Bay, and can be coupled with other monitoring programs tracking concentrations in clams and fish.





Figure 11. Simulated Se concentrations in the Delta compared to observed data from CEDEN.



Figure 12. Estimated dissolved selenium loads in the Sacramento River at Rio Vista by water year and season.



Figure 13. Estimated dissolved selenium loads in the San Joaquin River at Antioch by water year and season. The water year type classification is based on DWR's water year hydrologic classification for the San Joaquin Valley (cdec.water.ca.gov/cgi-progs/iodir/WSIHIST). W: Wet, AN: Above normal, BN: Below normal, D: Dry, C: Critical year.



Figure 14. Estimated total dissolved selenium loads to the Bay by water years. The water year type classification is based on DWR's water year hydrologic classification for the San Joaquin Valley (cdec.water.ca.gov/cgi-progs/iodir/WSIHIST). W: Wet, AN: Above normal, BN: Below normal, D: Dry, C: Critical year.

Water Year (October 1 to September 30)	Туре	Dry season (kg/season)	Wet season (kg/season)	Total (kg/yr)
1993	W	485	1340	1825
1994	С	173	399	572
1995	W	1810	3561	5371
1996	W	639	2348	2987
1997	W	303	4985	5288
1998	W	2787	6984	9771
1999	AN	468	2125	2593
2000	AN	397	1933	2331
2001	D	217	493	710
2002	D	216	656	873
2003	BN	460	910	1370
2004	D	227	1204	1432
2005	W	804	877	1681
2006	W	1584	3670	5254
2007	С	210	438	648
2008	С	230	876	1106
2009	BN	252	492	744
2010	AN	457	1212	1669
2011	W	770	2158	2928
2012	D	299	536	835
2013	С	258	916	1174
2014	С	148	399	547
2015	С	130	713	843

Table 1. Summary of calculated alsoon ca scieman rouas to the bay	Table 1. Summary	y of calculated	l dissolved	selenium	loads to	the Bay.
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Figure 15. Comparison of estimated dissolved selenium loads as sum of loads from Sacramento River at Rio Vista and San Joaquin River at Antioch and estimated loads at Mallard Island.



Figure 16. Comparison of estimated dissolved selenium loads as sum of loads from Sacramento River at Rio Vista and San Joaquin River at Antioch, and estimated loads as mass balance of Freeport + Vernalis + Yolo + east – export loads.

### 8. Findings and Consequences for Future Water Quality Monitoring

The major findings of this analysis and relevance to planned monitoring efforts are as follows.

- Selenium concentrations at the San Joaquin River boundary (at Vernalis) have shown decreases in recent years. This change indicates the benefits of water quality controls implemented in the Grassland Bypass Project, and continued monitoring at Vernalis and Freeport is strongly recommended to evaluate whether the trends continue. Reductions in Vernalis loads have an important effect on loads to the NSFB, and are also relevant to long-term outcomes from the implementation of the WaterFix project.
- Selenium concentrations remain low in recent drought years in the Delta at a few locations that were monitored, although long-term data are lacking. A systematic sampling effort for selenium in the Delta in coordination with the Delta Regional Monitoring Program will greatly benefit the understanding of selenium movement in the Estuary. A sustained monitoring effort at Mallard Island is recommended, because this location is a good representation of the relative contribution of Sacramento and San Joaquin Rivers.
- DSM2 modeling of the Delta suggests that San Joaquin River volumetric contribution to the
  Delta locations is higher during wet years. ECoS modeling of the Bay suggest higher selenium
  concentrations when overall freshwater flows are low. Different mechanisms therefore apply in
  different seasons and water year types: high concentrations during high flows may be
  associated with a greater San Joaquin contribution, and high concentrations during low flows
  may be a consequence of longer residence times of selenium sources in the Bay. Continued
  monitoring in the Bay, across all water year types will provide additional support for these
  proposed mechanisms, and provide insight into selenium exposures under different hydrologic
  conditions and seasons. This information enhances interpretation of changes that are observed
  in biota that are planned to be monitored in the Bay, such as sturgeon and clams. For example,
  the water quality modeling/monitoring effort can help evaluate whether changes in biota are
  the result of the hydrologic variability in the system, or are caused by a change in the system,
  such as loading levels, operational changes, or new infrastructure.
- Riverine loads to the Delta are highly dependent on the freshwater flows; during average and wet periods, riverine loads are the largest source of selenium to the Bay, during severe drought periods, such as in 2014 and 2015, the riverine loads may be of the same magnitude as point source loads as reported in Baginska (2015). During the dry seasons of dry and critical years, point-source loads are dominant compared to riverine loads. Continued evaluation of these load calculations in future years will provide a greater understanding of the potential selenium exposure to biota in the Bay, and can be coupled with other monitoring programs tracking concentrations in clams and fish. They will also provide insight into the types of loading changes that may occur with potential implementation of the WaterFix project or potential changes to Delta through the operations of the Central Valley Project and State Water Project.

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