Update on Mercury Studies Laura Valoppi

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Summary

The results of the 2013 study found that Tern egg mercury concentrations decreased by 59% between 2011 and 2013 at Restored Ponds, compared to a decline of 23% between years at Reference Ponds. The end result of this 3-year comparison was that Tern egg mercury concentrations decreased between 2010 and 2013 by 31% at both Restored Ponds and Reference Ponds. Despite the dramatic increase observed right after Pond A8 was opened in 2011 and correspondingly large decrease (2011 to 2013) in Tern egg mercury concentrations at the Restored Ponds, Tern egg mercury concentrations in the Restored Ponds are currently at levels that are similar to what would have been expected without the restoration actions having occurred. Results from the collection of slough fish in 2013 for mercury analysis did not appear to show major increases in sentinel slough fish Hg in relation to the opening of the Pond A8 notch to triple its previous volume (2011=1 gate (5 feet), 2013=3 gates (15 feet)). Bathymetric survey data from 2010 to November 2013 showed continued erosion and deposition occurring, with a net scour of about 16 cm throughout slough. Hg remobilization occurring mostly near A6 breaches, but also some Hg is being remobilized near A8. Researchers are estimating between 2010 and November 2013, that between about 21 to 24 kg of Total Mercury have been remobilized in Alviso Slough with up to 3 gates open, compared to a previously predicted amount of 66 kg Total Mercury released with 4 gates open (20 feet). The project is working with researchers to develop an Alviso Slough scour model to help us understand the main drivers for slough scour and mercury remobilization.

While it is a goal of the South Bay Salt Pond Restoration Project (SBRP) to restore as much as 50% or more of the ponds to tidal marsh, concerns with legacy mercury deposits in the Alviso Complex due to historic mercury mining activities upstream, gave the managers pause in moving forward with a full tidal breach of the Pond A5/A7/A8 system (Pond A8). Pond A8 had some of the highest levels of mercury detected in sediments in the area, as well as high levels of mercury in bird eggs, fish and other organisms. The concerns with opening up Pond A8 to tidal flows were twofold: 1. Opening Pond A8 would increase the erosion of sediments in Alviso Slough, which would likely release mercury that had long been buried in the slough sediments, and 2. Opening Pond A8 might increase the methylation of mercury and result in increased uptake of mercury in birds, fish, and other aquatic life. Methyl mercury is the more toxic form of the compound and of most concern. In response, managers installed a 40' notch consisting of eight 5-foot gates that could be successively opened over time to study the effect of opening of the Pond A8 notch on wildlife within the pond itself as well as in the adjacent Alviso Slough. Starting in 2010, prior to the notch opening in 2011, and continuing every year thereafter, a range of mercury studies have been conducted to assess the effect of opening the Pond A8 notch.

2013 Bird Egg Results

Bird eggs were collected by Josh Ackerman of the U.S. Geological Survey for mercury analysis in 2011, right after the Pond A8 notch was opened. Dr. Ackerman found that mercury concentrations in Tern eggs increased by 69% between 2010 (prior to the notch opening) and 2011 (after the notch opening) at Ponds A5/A7/A8 (Pond A8) after the restoration actions, compared to a slight decline in egg mercury concentrations (by 10%) between years at Reference Ponds. These results were made available to

managers in Spring of 2013. This very dramatic increase in mercury related to the notch opening concerned the managers, and therefore they decided to open the same number of gates (3 of 8) in June of 2013 as was opened in 2012. Lack of funding in 2012 allowed only limited study of scour in Alviso Slough in response to the opening of the Pond A8 notch.

In 2013, due to a grant from the U.S. Environmental Protection Agency, researchers were able to collect samples of bird eggs and slough fish in Pond A8 and Reference Ponds. Results from the 2013 study found Tern egg mercury concentrations decreased by 59% between 2011 and 2013 at Pond A8, compared to a decline of 23% between years at Reference Ponds. The end result of the 3-year comparison between 2010 and 2013 was that Tern egg mercury concentrations decreased between by 31% at both Pond A8 and Reference Ponds. In addition to these changes between years, Tern egg mercury concentrations in Pond A8 were 6% higher than levels in Reference Ponds in 2013, and similar to 2010 baseline conditions. Tern egg mercury concentrations in Pond A8 are currently at levels that are similar to what would have been expected without the opening of the notch having occurred. Despite this good news, the majority of Tern egg mercury concentrations in Pond A8 in 2013 (70%) still remained above those associated with reproductive impairment (>0.90 μ g/g fww). In particular, Ponds A7 and A8 are still a mercury "hotspot" for bird eggs compared to other ponds in 2013.

2013 Slough Fish Results

Darell Slotton of University of California, Davis collected three-spined stickleback and Mississippi silverside fish from 2 locations in Alviso Slough, at the notch (ALSL2) and mid-way down the slough (ALSL3). Fish were also collected from Reference locations in Artesian Slough (aka Mallard Slough) to the east of Alviso Slough and also on the Guadalupe Slough (GUASL) to the west of Alviso Slough, and near the Sunnyvale Wastewater Treatment Plant (SUNNY) on a channel that leads into the Guadalupe Slough.

In 2011, with opening of one gate of eight gates at the Pond A8 notch, fish collected in Alviso Slough showed an initial increase in mercury which persisted for some 1-3 months in comparison to data collected in Alviso Slough prior to the opening, as well as at the Reference site on Mallard Slough. Mercury in Alviso Slough fish returned to near baseline soon by the Fall of 2011.

With the 3-gate opening in 2013, stickleback fish collected in Alviso Slough near the notch showed unusually elevated levels in April and May, though the notch was sealed throughout that time and before (notch was closed in December of 2012, per NMFS permit restrictions). Silversides, with much lower variability, showed no similar early season elevation. Both species in 2013 had Hg at levels similar to baseline collections from 2010, with moderate increases following the 3 gate notch opening between July and August, though within the ranges seen in 2010. Interestingly, there was a very similar trend at the new reference locations GUASL and SUNNY, which are remote from the A8 notch activities, suggesting that the seasonal trend may be have been more regional in nature.

At the mid-Alviso Slough location (ALSL3), between the Pond A8 operation and potential impacts from Pond A6, stickleback Hg was higher in April and May 2013. Again, April and May preceded the A8 notch opening. Stickleback mercury levels from July, August and October sampling events saw no trend. So, in conjunction with a lack of trend closer to the notch, these observed mercury levels may be unrelated to A8 notch activities. Silverside data across 2013 at this mid-Alviso Slough site were very steady and generally equal to or lower than corresponding readings from 2010 and 2011.

In 2013, Mallard Slough shifted from control site to another test case site, with the opening of Pond A16 (a managed pond) outflows to Mallard Slough on March 15, 2013. A sharp increase in stickleback mercury levels was noted in April and July, though not in May, and levels were back to baseline by August. Silversides were somewhat elevated in July, August, and October in 2013 (relative to 2010-11) though remaining at a similar range as seen in April. These results suggest that there was perhaps a temporary increase in fish mercury levels in Mallard Slough as a result of the opening of Pond A16 outflows.

New Reference locations on Guadalupe Slough (GUASL) and SUNNY (Sunnyvale WWTP discharge) were similar to each other, particularly in silversides. Silverside Hg was highest in Aug and October at both sites, similar to trends noted in Alviso Slough. Stickleback Hg was more variable, but often similar to trends seen in Alviso Slough. Guadalupe Slough may provide a new Reference location to compare to Alviso Slough fish data. The Sunnyvale WWTP channel site will be discontinued, due to its very close correspondence with the Guadalupe site.

In summary, the 2013 slough fish data do not appear to show major increases in sentinel slough fish Hg in relation to the opening of the Pond A8 notch to triple its previous volume (2011 1-gate, 2013 3-gates).

2013 Bathymetry and Mercury Remobilization Results

Bathymetric studies (mapping of the seafloor) of Alviso Slough were conducted from late 2010 to November 2013 by Bruce Jaffe of the U.S. Geological Survey. Data collected through the end of 2012 found that most of the scour and erosion of sediments on the bottom of Alviso Slough occurred near the Pond A6 breaches, which was restored to full tidal flows in December of 2010. Upstream of the Pond A6 breaches, but downstream of the Pond A8 notch, Alviso Slough was eroding slightly. Deep cores of the sediment, with interval sampling of mercury with depth were previously collected by Mark Marvin Di-Pasquale of the U.S. Geological Survey. The mercury core data were used in conjunction with the bathymetric mapping to estimate the amount of mercury that was released from the slough sediments eroding. It was estimated that 10.8 to 12.9 kg of Total Mercury have been remobilized in Alviso Slough by the end of 2012 - with over half of the THg remobilized being from the segment around Pond A6. This is much less than an early estimate based on the amount of scour to achieve channel equilibrium that predicted 66 kg Total Mercury released with 4 of the 8 gates open, and 125 kg of Total Mercury released if all 8 gates were opened. This estimate did not consider the breaching of Pond A6, but only the construction and operation of the adjustable notch structure in Pond A8.

Continued bathymetric studies in April and November 2013 found that most of the erosion was continuing to occur near the Pond A6 breach locations, but that upstream more of the sediments in Alviso Slough were beginning to erode. Additional deep sediment cores for mercury were taken in 2012 to better characterize the amount of mercury being released in the eroded sediments. All the mercury core data, along with the latest bathymetric data, estimated that about 24 kg of Total Mercury have been released from 2010 to 2013, with most of the remobilized mercury associated with the erosion from the breaching of Pond A6.

2013 Sediment Flux Study Results

In order to characterize the amount of sediment moving in Alviso Slough, a sediment flux (turbidity and velocity) and water quality (temperature, salinity, and dissolved oxygen) station was installed about midway between the Pond A8 notch and the mouth of Alviso Slough. Dave Schoellhamer and Greg Shellenbarger of U.S. Geological Survey have studied the sediment movement at this location since WY2011. This station tracks the amount of suspended sediment and temperature, salinity, and dissolved oxygen in the slough water that is moving past the station every 15 minutes as the tides ebb and flood daily. They have found that net sediment movement in the water is generally landward, or upstream, except during rainfall events. Interestingly, peak suspended sediment levels are associated with the movement of the salt wedge past the station during flood tides, which can cause concentration of particulates through flow convergence, resuspension of benthic particles from increased shear, and formation of flocs from chemical changes in the water due to the presence of salts. The data indicate that during Spring Tides, peak suspended sediment levels occur on the flood tide cycle, while during Neap Tides, peak suspended sediment levels (neap concentration peaks are about three times lower than flood peaks) occur on the ebb tide cycle. Preliminary water quality data also indicates that opening of the gates stabilizes and slightly increases the salinity levels in Alviso Slough water.

2013 Mercury Diel Study Results

Understanding the movement of sediment in Alviso Slough allows for a better understanding of the movement of mercury in the slough since much of the mercury is attached to the suspended sediment particles (though some is also dissolved in the water). To better understand the relationship between the sediment and the mercury attached to the sediment, a Mercury Diel Study was conducted by Mark Marvin-DiPasquale of the U.S. Geological Survey in 2012/2013, in conjunction with the sediment flux study noted above. Four times a year, Spring, Summer, Fall, Winter, along with a first-of-the-season storm event ('first flush"), a station was set up at the sediment flux station and over a 24 hour period, to capture the full tidal cycle, samples for mercury speciation and additional water quality parameters were collected every 60 minutes.

Results from this intensive study indicate that suspended particulate Total Mercury concentrations responded strongly to tidal cycles, generally increasing during ebb tide and decreasing during flood tide. Peak Total Mercury on particles in the water corresponded to the lower of the two low tides during each sampling event. The December 'first flush' event exhibited the least amount of concentration variability. More detailed analysis found that the portioning of Total Mercury between the particulate and dissolved phases changed throughout the tidal cycle, with the strongest portioning of Total Mercury onto suspended particles during the low tide phases. To the degree that dissolved Hg is more bioavailable (for uptake into aquatic life) than is particle bound Hg, this suggests an enhanced degree of Hg bioavailability during the flood tide phase. Both the magnitude and direction of net daily sediment and associated mercury flux changed seasonally, with the highest flux being net landward during the spring & summer periods carrying approximately 15-17 g THg per day. During the fall/winter and 1st flush periods the THg flux was net bayward with an approximate range of 0.5-6.3 g THg per day.

Pond A6 Sediment Mercury Accumulation Results

All of the above studies have been done in Pond A8, the adjacent slough and the associated Reference locations. Researchers have also initiated a study to begin to understand the mercury accumulation in sediments of a pond newly restored to full tidal flows. Pond A6 was restored to full tidal flows in December of 2010 by breaching the levee at four locations – two on the east side into Alviso Slough, and

two on the west side into Guadalupe Slough. John Callaway of University of San Francisco was periodically collecting information on sediment accumulation rates within Pond A6 bottom after tidal restoration. Mark Marvin-DiPasquale of U.S. Geological Survey arranged for Dr. Callaway to also collect surface sediment samples for mercury analysis, resulting in a time series of mercury concentrations as sediment accumulated in a newly restored pond (from December 2010 (pre-breach) through March 2013)). Analysis of the mercury sediment samples evaluated pre vs. post breach and seasonal differences in mercury sediment concentrations.

Results indicate that there was no difference in Total Mercury or Methyl Mercury or % of Methyl Mercury levels in the time series of sediments before versus after the breach opening. During the post-breach period exclusively, there were significant seasonal differences in the pools of both sediment "Reactive Mercury" and Methylmercury. The former is operationally defined (tin-reducible Hg(II)) and represents the pool of inorganic mercury in the sediment that is most readily available for bacteria for Hg(II) methylation. During summer, Reactive Mercury concentrations were low, while Methylmercury concentrations were high. This contrasted with samples collected during the winter, when reactive mercury concentrations were high, while Methylmercury concentrations were low.

Marvin-DiPasquale also estimated that approximately 132 kg of Total Mercury was deposited into Pond A6 during the first 2 years post-breach, with only about 10 kg of that attributable to scour in slough around A6 breaches. The vast majority of the mercury in Pond A6 is likely not available for methylation. It is not known if the mercury accumulating in Pond A6 is coming from the sediments derived from the larger South Bay area, , or if it is coming from upstream sources within Alviso Slough (an/or its watershed), or a combination of sources. Also unknown is the amount of the mercury that is accumulating in wildlife that inhabit Pond A6.

Conclusion

It was not completely unexpected that mercury levels inside Pond A8 would increase after opening the notch to muted tidal flows. Other wetlands systems and reservoirs have observed a spike in birds, fish and other aquatic life initially after restoration or construction, called "the reservoir effect". Often the mercury levels in fish and wildlife return to baseline levels, in a timeframe ranging from a few years to several decades. So while it is very encouraging that 2 years after the opening of the notch at Pond A8 that levels in bird eggs have decreased, it is too soon to say if this trend will continue as more gates are opened and there is increased tidal flows through Pond A8 and potential continued sediment erosion in the upper end of Alviso Slough, near the A8 notch. Outside the Pond, in Alviso Slough, biosentinel fish mercury returned to pre-notch baseline levels after brief increases in the several months immediately following the initial 1-gate opening in 2011. It was particularly encouraging that 2013 samples were also at baseline levels following the increase in connectivity and flow from opening 1 gate to opening 3 gates.

In consultation with National Marine Fisheries Service, in late 2013 we initiated a steelhead smolt study which enabled managers to open Pond A8 notch early, in March of 2014. Mercury researchers and managers believed this might improve water quality conditions in Pond A8 to minimize mercury methylation, and to stabilize water levels to benefit nesting birds. Based on the results from 2013, the group decided the available information supported keeping 3 gates open from March through the end of the planned 2014 Hg sampling period (Fall of 2014), and then open 2 more gates for a total of 5 out of 8 gates (25 feet open out of a 40 foot notch). In addition, managers will not be closing the gates from

December 1 to June 1 as was done in prior years, in hopes of further reducing mercury accumulation in wildlife.

Researchers have continued to collect fish and bird egg samples in 2014, and plans are in place for continued collections in 2015. Researchers are also developing a sediment scour model of Alviso Slough to better understand the effect of opening additional gates at the Pond A8 notch will have on erosion and remobilization of mercury in Alviso Slough, and where the sediments might be depositing. These studies will enable managers to determine the best management of the Pond A8 system to minimize mercury accumulation in wildlife and prevent unacceptably high rates of erosion and mercury remobilization in Alviso Slough.

Publications/presentations

The final Hg biosentinel report for 2010 through 2011 is available at: http://www.southbayrestoration.org/documents/technical/Mercury OFR Report May28 2013 Final.pdf.

The final 2014 Open File Report for the Waterbird Eggs is available at:

Ackerman, J.T., Herzog, M.P., Hartman, C.A., Watts, T., and Barr, J., 2014, Waterbird egg mercury concentrations in response to wetland restoration in south San Francisco Bay, California: U.S. Geological Survey Open-File Report 2014-1189, 22 p., http://dx.doi.org/10.3133/ofr20141189
http://www.southbayrestoration.org/documents/technical/Ackerman_etal_2014_Bird%20Egg_Mercury_ofr2014-1189.pdf

Dr. Marvin-DiPasquale prepared and presented a poster at State of the Estuary conference (Oakland CA; October. 29-30), which highlighted results from the Alviso Slough Hg flux study, including the Methylmercury results paid for under this EPA grant.

Marvin-DiPasquale, M., Schoellhamer, D., Downing-Kunz, M., and Shellenbarger, G., 2013, *Mercury In Motion - Quantifying Mercury Flux in Alviso Slough*, State of the Estuary, 11th Biennial Meeting, October 29-30, 2013: Oakland, California, Poster Presentation. On-line:

http://www.southbayrestoration.org/science/SOE2013posters/SotE 202013 Poster – Alviso Hg flux 2.pdf

Dr. Bruce Jaffe also prepared and presented posters at the State of the Estuary conference which described the bathymetryic studies conducted in conjunction with the Hg core work, to estimate amount of scour in Alviso Slough and the amount of Hg remobilized in Alviso Slough. http://www.southbayrestoration.org/science/SOE2013posters/Fregoso Hg Bathy SOE 2013.pdf http://www.southbayrestoration.org/science/SOE2013posters/SOE 2013 Foxgrover etal(1).pdf

The final Open File Report for the bathymetric data results collected through October 2012 is available, http://pubs.usgs.gov/of/2011/1315/.

Dr. Gregg Shellenbarger is presenting this work at an international conference: Shellenbarger, G.G., M.A. Downing-Kunz, and D.H. Schoellhamer. 2014. Suspended-sediment dynamics in the tidal reach of a San Francisco Bay tributary. Proceedings of the 17th Physics of Estuaries and Coastal Seas Conference, 19-24 October 2014, Porto de Galinhas, Brazil. 5 p.

Findings from the December 9, 2013 Researcher/Managers meeting are available at: http://www.southbayrestoration.org/science/Summary Notes from 2013_PI PMT meeting Final.pdf