# **CACHE CREEK OFF-CHANNEL AGGREGATE MINING PONDS –**

# **2018-2019**

# **BOTTOM SEDIMENTS**

**FINAL Data Report** July 2020

*Monitoring and Report by*

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## **SUMMARY BULLET POINTS**

- **•** Bottom sediment testing was done in September 2018 through July 2019, to provide the County's OCMP Mercury Monitoring Program with supplemental information about the ponds identified as elevated in fish mercury (Teichert Esparto – Reiff, Syar – B1, Cemex – Phase 3-4), plus the low mercury control pond (Cemex – Phase 1) and a representative deep pond (Syar – West).
- These initial tests were of basic sediment measures (total mercury, solids percentage, organics percentage), looking to see if any notable, large differences existed that might explain conditions.
- Sediment mercury levels in the ponds were found to average between 0.27 ppm and 0.52 ppm, a fairly narrow range similar to the 0.39 ppm average found by USGS in the downstream Cache Creek Settling Basin. Pond mercury was higher than at 'clean/background' sites, as is to be expected for this watershed with historic mercury mining zones upstream. The ponds had much lower sediment mercury levels than sites near the mines in the upper watershed.
- **•** In general among the ponds, higher sediment mercury corresponded to higher fish mercury. But the two lowest sediment mercury sites, Cemex – Phase 1 and Teichert Esparto – Reiff, included both the lowest and the highest fish mercury conditions. This suggests that sediment mercury in these ponds is not the main factor linked to fish mercury levels.
- **•** This is helpful new information that will help guide potential remediation directions. The related water column profiling work seeks to identify other factors that are more directly linked to fish mercury – and might be altered through remediation.

#### **INTRODUCTION**

The sediment testing reported here was a one-time addition to the general mercury monitoring program for the off-channel aggregate mining ponds along lower Cache Creek. Several of the ponds have been identified as having significantly elevated fish mercury levels, relative to baseline fish mercury levels in nearby Cache Creek. These ponds are Cemex – Phase 3-4, Teichert Esparto – Reiff, and Syar – B1. Basic information about the ponds in the overall mercury monitoring program is given in Table A, and locations are shown in Figure A (taken from Slotton and Ayers 2018).

As per the recently updated guidelines of the County Ordinance for mercury in the aggregatemining ponds (Yolo County 2019), the first phase of potential remediation at identified ponds is to obtain physical and chemical information to better understand what may be leading to the elevated fish mercury levels and to help develop and guide possible mitigation strategies. These tests include seasonal water column profiling, five times per year, for a wide range of potentially relevant parameters (presented in an accompanying annual report). They also include the subject one-time, basic characterization of surficial sediments at the bottom of each of the identified ponds. For both the water column profiling and the sediment testing, an identified low-mercury pond (Cemex – Phase 1) was also included, as a relative control, to help with data interpretation. We also included a fifth pond in the supplemental testing, Syar – West. Fish mercury in this pond was just below 'significantly elevated' status, but the pond is much deeper than the others and represents an important endpoint condition for off-channel aggregate mining throughout the region. Because of the depth, we also suspected that this pond may be the best candidate at this time for a straightforward, known mitigation approach (summer mixing/aeration of the bottom water if it becomes anoxic).

Ultimate fish mercury bioaccumulation depends on a large combination of factors that affect the production of methylmercury and its movement into and up the food chain. These initial sediment tests were of basic measures (total mercury, solids percentage, organics percentage), looking to see if any notable, large differences existed that might begin to explain conditions.

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A description of the field and laboratory techniques used is given in the Methods section below. Following the methods, we present the sediment data results for each tested pond. In the Discussion/Conclusions section, the ponds sediment data are compared among the tested ponds and in relation to global averages, known sediment mercury trends in the Cache Creek watershed, and in relation to remediation considerations.

#### **Table A. Wet Pits Subject to Annual Mercury Monitoring**

*(modified from Yolo County Exhibit C and annual mercury monitoring reports)*

**Red text**: sediment sampling conducted – identified elevated-mercury ponds **Blue text**: sediment sampling conducted – low-mercury control pond



**\*** *Syar West Pond was slightly below 'elevated-mercury' status at this time; sampled for reasons described in text.*



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#### **METHODS**

The ponds were accessed with our field boat. General bottom configurations were known from the water profiling project and were supplemented with additional sounding work, using a sensitive depth finder. Six sampling sub-sites were distributed across each of the tested ponds, to obtain a representative collection of the overall bottom sediments.

At each sub-site, GPS location and bottom depth were recorded. An Ekman Grab sampler was carefully lowered, on a line, to just above the bottom and then dropped into the bottom. This type of sampler (shown in the cover photos) is basically a heavy, open-bottomed metal box, designed to cut down several inches, cleanly, into the bottom sediments. Two thin 'doors' are spring-loaded to the sides before each descent. When ready, a weighted 'messenger' is attached to the line and dropped down the line from the boat to trip a release latch at the top of the grab sampler. This releases the spring-loaded doors, which slice through the mud below the sampler, snapping shut to form a bottom for the box. The sampler is then carefully pulled out of the surrounding mud and slowly hauled up through the water column to the surface. The top of the box is protected by a pair of free-swinging, thin doors which flap up and out of the way when the sampler is moving down through the water and into the bottom, but which flap down across the top when the sampler is moved in an upward direction. This keeps the sediment contents undisturbed.

At the pond surface, any water overlying the sediment sample was slowly decanted. The sample was collected using acid-cleaned utensils, into pre-cleaned and labeled jars. Samples were all taken from the top 2 cm, as is standard and represents the zone most relevant to mercury chemistry in the overlying water. Samples were stored on ice in the field and then in a laboratory refrigerator at  $4^{\circ}$ C.

In the laboratory, wet samples were stir-homogenized, weighed, and then dried to constant weight in a drying oven for 4 days at 55 °C. Dry sample weight was recorded, to determine percentage solids and the wet:dry weight concentration conversion value. The dry, brick-like sample was then powdered with a laboratory mortar and pestle.

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#### *The cover photos show the sediment collection and processing steps to this point.*

One subsample of the resulting powdered sample was used for organics percentage determination, another for mercury analysis, and the remainder archived in case it was needed for re-analyses. For organics percentage, Loss-On-Ignition was conducted. This analysis uses a 550 °C laboratory muffle furnace to burn away any combustible organic matter in the sample. Samples are weighed into pre-weighed, inert porcelain cups which are then placed into the muffle furnace. After four hours, the samples are removed to return to room temperature in a desiccator and then re-weighed to find the amount lost through organics combustion.

An identical sample of the powdered sediment was used for analysis of mercury, using the same procedures as the routine fish mercury monitoring. Sediment samples were weighed into 20 ml digestion tubes and digested at 90 °C in a mixture of concentrated nitric and sulfuric acids with potassium permanganate, in a two stage process. Digested samples were then analyzed for total mercury by standard cold vapor atomic absorption (CVAA) spectrophotometry, using a dedicated Perkin Elmer Flow Injection Mercury System (FIMS) with an AS-90 autosampler. The method is a variant of EPA Method 245.6, with modifications developed by our laboratory (Slotton et al. 2015). Extensive Quality Assurance / Quality Control (QAQC) samples were included in the analytical runs and tracked with control charts. Results were all well within control limits.

### **PRESENTATION OF THE 2018-2019 SEDIMENT DATA**

#### **1. Cemex – Phase 1 (West) Pond**

The Cemex – Phase 1 Pond data are presented below in Table 1 and Figure 1.

This is a relatively shallow pond, with bottom depths ranging from 1.8-5.8 m (6-19 feet) at the subsites sampled in September 2018. As can be seen in the figure, this is a pond that receives slurry effluent from the Cemex gravel processing plant. The slurry, composed of water and the fine silt and clay fractions of mined soil, discharges into the west side of the pond, near sub-sites 1 and 2.

The samples were all similar in composition, all fine-grained and of a similar tan color. Samples from the eastern 2/3 of the system (sub-sites 3-6) were very similar in solids percentage (33.4- 34.8%), with the sites near the slurry inflows denser, at 36.5% and 44.8%. Organics percentage at those near-inflow sites, at 6.64-7.15%, was lower than at the other sites (7.85-9.23%). Mercury concentrations were very similar in 5 of the 6 samples (0.263-0.301 ppm, dry weight) and lower in one of the near-inflow samples (0.184 ppm). The mean concentration was 0.266 ppm, lowest of the ponds sampled.

## **Table 1. Cemex – Phase 1 (West) Pond: Bottom Sediments Data**

*Collected 9/24/18 by Ekman grab; composites of top 2 cm (m = meters; LOI = Loss On Ignition; ppm = parts per million; dry wt = dry weight)*





**Figure 1. Cemex – Phase 1 Pond: Sediment sampling locations**

### **2. Cemex – Phase 3-4 (East) Pond**

The Cemex – Phase 3-4 Pond data are presented below in Table 2 and Figure 2.

This is a large, two-part pond of intermediate depth. Depths in September 2018 ranged between 5.2 m and 8.8 m (17-29 ft). Sub-sites 1-3 sampled the western basin, and sub-sites 4-6 sampled the eastern. All of the samples were fine-grained, 'pudding-like' material, as in the other ponds and as normal for depositional sediment at the bottom of lakes and ponds. Color of the top 2 cm varied between tan (indicating oxygenated/aerobic) and gray-black (indicating some anoxia in the deeper samples). Portions of aquatic vegetation were present in two of the samples; these were removed. Live amphipods (2-4 mm little crustaceans similar to beach 'sand fleas') were present in 3 of the samples; these were also removed. Organics percentage ranged from 8.7-11.8%.

Sediment mercury ranged between 0.240 ppm and 0.657 ppm, with a mean level of 0.444 ppm. Interestingly, the concentrations showed a distinct gradient, with the highest levels (0.605-0.657 ppm) at the westernmost sites, declining steadily to the east.

## **Table 2. Cemex – Phase 3-4 (East) Pond: Bottom Sediments Data**



standard errors:  $\pm 2.1\%$ 

*Collected 9/24/18 by Ekman grab; composites of top 2 cm (m = meters; LOI = Loss On Ignition; ppm = parts per million; dry wt = dry weight)*



**Figure 2. Cemex – Phase 3-4 Pond: Sediment sampling locations**

## **3. Teichert Esparto – Reiff Pond**

The Teichert Esparto – Reiff Pond data are presented below in Table 3 and Figure 3.

This pond was relatively shallow, with the deepest location in September 2018 being 5.2 m (17 ft, sub-site 5). The other 5 sites ranged from 1.8-4.3 m (6-14 ft). Like the Cemex – Phase 1 Pond, the Teichert Esparto – Reiff Pond has received plant slurry discharge over the years, at the northwest part of the basin. Most of the samples were composed of fine-grained sediment, ranging in color from beige to dark gray. One was notably coarser (sandy, sub-site 4). Solids percentage ranged between 21.6% and 44.4% in the 5 fine-grained samples, higher at 61.5% in the coarser-grained sample. Organics percentage ranged between 5.28% and 9.81%, with lower levels in the samples with higher solids percentage and higher organic levels in samples with lower solids percentage.

Mercury ranged fairly narrowly between 0.215 ppm and 0.320 ppm, with a mean level of 0.279 ppm. Concentrations generally trended with organics percentage and in the inverse of solids percentage.

# **Table 3. Teichert Esparto – Reiff Pond: Bottom Sediments Data**







**Figure 3. Teichert Esparto – Reiff Pond: Sediment sampling locations**

### **4. Syar – B1 Pond**

The Syar – B1 Pond data are presented below in Table 4 and Figure 4.

This was a pond of intermediate depth, with sampling depths ranging between 5.8 m and 7.6 m (19- 25 ft) in September 2018. The six samples were all very similar in composition: dark gray and finegrained. Solids percentages were 23.8-34.6%. Organic contents were 8.46-10.97%.

Mercury in the samples was found at 0.385-0.632 ppm, with a mean concentration of 0.518 ppm. Higher concentrations generally corresponded with the higher organics percentages, and vice-versa. Overall mercury levels were highest of the ponds tested, though the overall range between lowest and highest was only two-fold.

## **Table 4. Syar – B1 Pond: Bottom Sediments Data**

*Collected 9/27/18 by Ekman grab; composites of top 2 cm (m = meters; LOI = Loss On Ignition; ppm = parts per million; dry wt = dry weight)*





**Figure 4. Syar – B1 Pond: Sediment sampling locations**

### **5. Syar – West Pond**

The Syar – West Pond data are presented below in Table 5 and Figure 5.

This is a notably deep pond, as compared to the others, with a large central region with depths over 50 feet (15 m). Because of this, it represents an important potential mining endpoint condition across the region, and one that may be uniquely suited for potential mercury remediation strategies. However, the fish in this pond, while quite high in mercury, have not quite been statistically elevated above baseline bass from Cache Creek. The pond was therefore not flagged for the first phases of remediation, including water column profiling and initial sediment testing. However, because of the potential insights we might gain from this different pond configuration, and the potential for meaningful remediation trials, we added the Syar – West Pond to the water and sediment testing program, at no additional cost. Bottom sediments were sampled in July 2019.

The collection sub-sites ranged in depth between 13.4 m and 17.4 m (44-57 ft). Sediment samples were all similarly fine-grained and in a range of gray tone colors. Solids percentages were 22.0-33.4% and organics percentages between 8.18% and 11.33%. Mercury was in a similar range throughout, at 0.385-0.512 ppm, with an average of 0.448 ppm.

# **Table 5. Syar – West Pond: Bottom Sediments Data**

*Collected 7/30/19 by Ekman grab; composites of top 2 cm (m = meters; LOI = Loss On Ignition; ppm = parts per million; dry wt = dry weight)*





**Figure 5. Syar – West Pond: Sediment sampling locations** 

#### **DISCUSSION AND CONCLUSIONS**

This initial round of sediment characterization was done to provide the County's OCMP Mercury Monitoring Program with basic new information about the ponds identified as elevated in fish mercury (plus the low mercury control pond and the representative deep pond). The bottom sediments are by far the main ultimate source of mercury in the ponds. Sediment mercury is mainly in inorganic (not methylmercury), mineral forms. It is relatively elevated in the Cache Creek watershed and depositional flood zone due to long-time erosion from upstream historic mercury mining sites in Yolo, Colusa, and Lake Counties. Table 6 shows the current ponds data (in blue), together with comparison sediment mercury data from throughout the Cache Creek watershed.



**Table 6. Aggregate-Ponds Sediment Mercury vs. Comparison Cache Watershed Data**

*All data from fine-grained, silt-clay fractions, except as noted with \* (Avg = average; ppm = parts per million; dry wt = dry weight)*

\* *un-sieved, raw samples; some contained larger grain sizes of fine sand to gravel (generally lowering mercury results)*

The watershed upstream of the Yolo County aggregate-mining zone contains a wide range of sediment mercury concentrations, from very low mercury zones away from mercury-mining (Cache Creek above Harley Gulch, 0.06 ppm) to extensive elevated areas with concentrations over 1.00 ppm, and with near-mine sediments into the hundreds of parts per million. Downstream, at the base of Cache Creek in the Settling Basin, long-term, extensive work by USGS found an average sediment mercury concentration of 0.39 ppm, with an overall range to over 16.00 ppm.

Mercury is an element that has been concentrated to sometimes problem levels mainly through human activities. Background global averages for mercury in lake/pond sediments with no human-industry enrichment generally fall below 0.100 ppm (Wentz et al. 2014). The current ponds bottom sediment data are shown together in Figure 6 below, ranging between mean levels of 0.266 and 0.518 ppm. These levels are similar to the 0.390 ppm average from the USGS Settling Basin studies. The ponds are elevated above 'clean/background' levels, as is to be expected for this watershed, with a relatively small, approximate two-fold range between lowest and highest concentrations.



**Figure 6. Mean sediment mercury at all of the tested ponds** (ppm dry wt with standard error)

In Figure 7, pond *fish* mercury levels from 2018 are plotted against pond sediment mercury concentrations. Four of the five comparisons follow a general trend of increasing sediment mercury corresponding to increased fish mercury. The lowest fish mercury pond, Cemex – Phase 1, had the lowest sediment mercury levels, and the pond with the highest sediment mercury, Syar – B1, was one of the higher fish mercury locations. However, the very highest fish mercury site in recent years, Teichert Esparto – Reiff, had sediment mercury nearly as low as the 'low mercury control' Cemex – Phase 1 pond. This highlights the complicated nature of mercury cycling.



**Figure 7. Mean 2018 Bass Mercury** *(fillet muscle, wet wt ppm ± std errors)* **vs. 2018-2019 Sediment Mercury** *(dry wt ppm ± std errors)* **at all of the tested ponds**

It is now established that sediment inorganic mercury levels alone, except very broadly, do not directly predict mercury concentrations in fish and other biota in the overlying water (Marvin-DiPasquale et al. 2018). This is because bioaccumulation in animals is nearly entirely of *methylmercury*. Only a tiny fraction of the sediment inorganic mercury is converted to methylmercury – in a biological process mediated by common, essential microbes (sulfur-reducing and iron-reducing bacteria). This process

of mercury methylation, and transfer into the food web, depends on a number of different factors, including:

- general concentration of inorganic mercury in the bottom sediments
- fraction of that inorganic mercury that is readily available for microbial uptake (i.e. molecules weakly bound to the surface of sediment particles, vs. incorporated within the mineral matrix)
- location of the oxic/anoxic transition zone, where microbial mercury methylation mainly occurs: deep in the sediments, vs. at the sediment surface and/or up in the water column
- ability of methylmercury, if produced, to make it through the sediments, past other alternate 'sticky' particles in the water, and into the biological food web.

In general, higher sediment mercury in the ponds corresponded to higher fish mercury. But the two lowest sediment mercury sites, Cemex – Phase 1 and Teichert Esparto – Reiff, included both the lowest and the highest fish mercury conditions. Clearly, the ranges of sediment mercury levels present in these ponds are all more than enough to potentially lead to elevated fish mercury levels. The low fish mercury at the Cemex – Phase 1 pond and very high fish mercury at Teichert Esparto – Reiff, with nearly identical sediment mercury at both, strongly suggests that other conditions of the ponds are more important. This is an advance that will help guide potential remediation directions. These initial sediment characterization tests were looking for potentially dramatic sediment mercury trends that were much higher than baseline and/or vastly different between ponds. That has been ruled out. This points remediation ideas more toward modification of other pond conditions that may lead to differences in methylmercury production and transfer, and to the large differences seen in fish mercury levels. The accompanying water column profiling work seeks to identify some of these possible factors.

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