CACHE CREEK OFF-CHANNEL AGGREGATE MINING PONDS –

2018

WATER COLUMN PROFILING

Final Report May 2020

Monitoring and Report by

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SUMMARY BULLET POINTS

- Water testing was initiated in 2018 at 4 Yolo County off-channel, aggregate-mining ponds. These were a subset of the 7 ponds currently being monitored for mercury, per County Ordinance. Three ponds were identified as significantly elevated in fish mercury in 2 or more years, relative to Cache Creek comparison samples. These were Syar-B1, Teichert-Reiff, and Cemex-Phase 3-4. A fourth pond, Cemex-Phase 1, was also chosen for water testing, as a relatively low-mercury comparison site. Water testing began at these 4 ponds in 2018, to provide supplemental information to better understand why fish mercury is high at some sites and low at others, and to help devise potential mercury remediation strategies.
- **•** A suite of chemical and physical parameters were measured at each pond, from surface to near bottom, on 5 different dates spanning the warm season between early May and late October. These included bottom depth, water clarity, temperature, dissolved oxygen, conductivity, pH, and other metrics.
- **•** Several of the monitoring parameters fell within similar ranges at all of the tested ponds. These included pH (basic/non-acidic to very basic), salinity, conductivity, dissolved solids, and redox levels.
- **•** Two of the tested ponds were relatively shallow, with depths averaging app. 6 m (20 ft): Cemex-Phase 1 and Teichert-Reiff. The other two were deeper: Syar B1, averaging 8.4 m (28 ft); and Cemex-Phase 3-4, averaging 10.6 m (35 ft). None of these depths or pond configurations were enough to completely isolate the pond bottom waters during the warm season in a common process known as thermal stratification. Instead, the bottom waters of all of the tested ponds showed evidence of periodic mix-in of warmer, oxygen-containing water from above.
- **•** Despite periodic mixing from above, two of the tested ponds Teichert-Reiff and Syar-B1 maintained enough bottom water separation, together with oxygen consumption, to promote the depletion of dissolved oxygen in the bottom waters. This condition is known to accelerate the production of toxic methylmercury and its movement into fish. These two ponds have also been found to contain the highest fish mercury levels of the 7 ponds monitored in the overall mercury program. In contrast, the lowest fish-mercury pond, Cemex-Phase 1, showed no oxygen depletion. Seasonal bottom water anoxia (oxygen depletion) was identified as a likely key factor contributing to elevated fish mercury in some of the ponds – and a target for remediation.
- **•** However, another relatively elevated fish-mercury pond, Cemex-Phase 3-4, had no oxygen depletion, indicating that additional factors must be at play. Methylmercury production and subsequent movement into fish can be affected by many processes. Differences in water clarity were identified as likely important. Several key constituents of 'water clarity' could not be measured in 2018, due to disappointing performance of new monitoring equipment. That has been fixed for 2019 and beyond with improved, replacement equipment. Additional information should help with the development of potential remediation strategies.

INTRODUCTION

The Water Column Profiling work and this data report are in support of the ongoing Mercury Monitoring program for the Yolo County off-channel aggregate-mining ponds. The primary (fishbased) report for monitoring year 2018 can be found at (Slotton and Ayers, 2020). This supplemental data report presents new information on water quality parameters from a subset of the ponds being monitored for mercury. The full set of aggregate ponds being monitored for mercury is shown in Table A and Figure A.

The County Ordinance (Yolo County Code, 1996) specifies the investigation of a suite of water quality parameters that may provide evidence of factors influencing the methylmercury cycle in subject ponds, as follows:

(c) Lake condition profiling during the period of June through September, including measurements of pH; eH (or redox potential); temperature; dissolved oxygen; and total dissolved carbon.

'Profiling' refers to taking a set of measurements throughout the water column, from surface to bottom. The intention of the June-September timing was to capture the warm season of primary biological activity. Based on much work since the time the Ordinance was written, we expanded that focus period to the 6 months between May and October, to be characterized with 5 sampling events each year. We also expanded the parameter list to include the potentially important components of algal density and turbidity. This work was conducted in compliance with the original (1996) version of the code section in effect at the time. In December 2019 the County adopted a comprehensive update to the CCAP which included a revision of this code section. Future monitoring and reporting will comply with the updated ordinance requirements.

In 2018, water column profiling was initiated at 3 ponds identified as having fish mercury significantly elevated over Cache Creek baseline comparisons in 2 or more years. These ponds are Syar-B1, Teichert-Reiff, and Cemex-Phase 3-4. In addition, water testing is being conducted at a fourth pond, Cemex-Phase 1, which was identified as a relatively low-mercury control. The objective of the water column profiling work is to provide supplemental information to better

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understand why fish mercury may be elevated in some ponds and not in others, and to help in the development of potential mercury remediation strategies.

The chemical and physical constituents measured in the water columns of the ponds are detailed below in Methods.

For each of the profiled ponds and each survey date (5 total between May and October), a table of the survey data is presented, together with a figure depicting the water column with several key, foundational parameters including temperature, dissolved oxygen, maximum depth, and Secchi water clarity. Then, for each pond, water column profiles are shown of individual parameters across all 5 surveys in May-October plots.

Table A. Wet Pits Subject to Annual Mercury Monitoring

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

Blue text: water profiling conducted – low-mercury control pond **Red text**: water profiling conducted – identified elevated-mercury ponds

METHODS

Water column profiling was conducted from our sampling boat, at the deepest part of each pond. Pond bottom contours and the location of the deepest region were determined by slowly crisscrossing the pond area with a high-resolution depth meter mounted to the boat just below the water surface. General water clarity was measured with a limnological Secchi disk: a 25 cm (10") weighted disk lowered into the water, noting the depth of visual disappearance. Specific water quality constituents were measured by lowering a suite of sensors from the surface to near bottom, pausing for several minutes at each meter of depth for equilibration and collection of the various readings. A new, custom-designed, multi-parameter unit was purchased for this work (AquaRead AP-7000). The meter included sensors for measuring:

Temperature Dissolved Oxygen: mg/L / % Saturation Conductivity / Salinity / Total Dissolved Solids (TDS) pH / Oxidation-Reduction Potential (ORP) Turbidity Algal Density (Chlorophyll) Dissolved Organic Matter (DOC)

The sensors were carefully calibrated in the laboratory before each survey. Most performed well in the field. However, the optical sensors for turbidity, algal density, and DOC repeatedly delivered unusable results; the normal concentrations present in the ponds fell below the apparent levels of detection. We spent hours in consultation with engineers from the company and recalibrated carefully and daily, hoping to lower the detection levels to useful ranges. We assumed the problem was our short experience with the new equipment. By the end of the sampling season it became clear that the problem was the technology, not our operations. We have since (for 2019) replaced the apparatus with a new multi-parameter limnological unit from a different company, the best model available (YSI–EXO2). We can report (in 2020) that it is performing well, at levels of detection that allow accurate measurement of all the desired parameters. However, for this 2018 reporting, we are omitting the compromised readings for turbidity, algae, and DOC.

PRESENTATION OF THE 2018 DATA

1. CEMEX–PHASE 1 (West) POND

1. Cemex–Phase 1 Pond

The Phase 1 Pond data are presented in Tables $1(a) - 1(e)$ and Figures $1(a) - 1(i)$, and summarized below.

Water Depth (Tables and Figs. $1(a)-1(e)$): ranged narrowly between 6.1 and 6.7 m (20-22 ft) across the 2018 May-Oct profiling. This pond routinely received plant discharge slurry/water, replacing evaporation losses.

Secchi Water Clarity (Tables and Figs. $1(a)-1(e)$): was uniformly low/turbid, at 1.1-1.9 m (3.6-6.2) ft). A function of plant slurry inflows clouding the water.

Temperature (Tables and Figs. 1(a)-1(e), Fig. 1(f)): Overall range 17-28 °C (63-82 °F) between May and October. A slight thermal stratification developed between May and October, with surface waters warming to 2-4 $^{\circ}$ C (~3-7 $^{\circ}$ F) warmer than bottom water. However, the large increases in bottom water temperatures during this time (to temperatures near surface levels) indicates ongoing, periodic mixing of the water column, presumably due to wind mixing of this shallow pond, together with the mixing influence of slurry inflows. Without such periodic mixing from above, bottom temperatures would remain essentially unchanged and cool through the summer. The water column became well mixed (low gradient between surface and bottom temperatures) as overall temperatures dropped in September and October.

Dissolved Oxygen (Tables and Figs. 1(a)-1(e), Fig. $1(g)$: remained at or near saturation levels throughout the season, between 8.7 and 10.5 mg/L (ppm). This corresponded to between 93% and 120% of saturation levels. Oxygen above saturation (or super-saturated) is a typical phenomenon in waters containing moderate or greater densities of algae; oxygen is produced during photosynthesis. 'Saturation' levels refer to the amount of oxygen that will stay dissolved in water with no ongoing sources or sinks. It is temperature-dependent – cooler water can hold more dissolved oxygen than warm water. A slight 'D.O. sag' was apparent in May bottom waters when the pond was most thermally stratified. This ended when the pond mixed in succeeding months, as shown by the temperature profiles. Under typical warm season conditions and particularly in deeper systems, a strong thermal stratification often develops in lakes and ponds, with sun-warmed surface waters floating above the winter-cooled bottom water. Because water masses of different temperature are very resistant to mixing (similar to oil and water), this seasonal stratification has the effect of isolating the bottom water from the upper water layers and the air above. If there is a moderate or greater amount of biological activity in the isolated bottom waters during this time, normal metabolism of microbes and other organisms will gradually deplete the dissolved oxygen, which cannot be replaced in the bottom waters until the pond mixes, bringing in new oxygen from above. We are particularly interested in potential seasonal oxygen depletion in this monitoring program, as that is a condition that can greatly accelerate the production and bioavailability of methylmercury. The temperature and oxygen data indicate that this pattern did not develop in the shallow Phase 1 Pond, presumably due to wind mixing and ongoing slurry inflows from the aggregate processing plant. It is notable that this pond was the lowest in fish mercury of the 7 being monitored in the mercury program.

Conductivity (Tables 1(a)-1(e), Fig. 1(h)): ranged between 770 and 918 μ S/cm overall. Levels were somewhat lower at the surface, higher at depth. Conductivity was very similar between May and September (839-918 µS/cm) and lower in October, when the water was coolest (770-825 μ S/cm).

Salinity (Tables 1(a)-1(e)): was fairly uniform, at 0.35-0.39 ppt (parts per thousand, g/L) between May and September, and somewhat lower in October (0.32-0.35 ppt). Typical freshwaters range below 0.50 ppt; seawater averages 35 ppt.

Total Dissolved Solids (TDS) (Tables 1(a)-1(e)): ranged narrowly within the range of 533-596 mg/L (ppm) between May and September, and was somewhat lower in October, at 500-536 mg/L.

pH (Tables 1(a)-1(e), Fig. 1(i)): was notably very basic (non-acidic; $pH > 7.00$) in all of the monitored ponds. This is a function of their mining history and the basic nature of local sediments. Water pH in the Phase 1 Pond fell between 8.09 and 8.70 across all depths and dates.

Oxidation/Reduction Potential (ORP) (Tables 1(a)-1(e)): stayed within the range of 96-151 mV (millivolts) across all depths and dates.

In summary, the Cemex–Phase 1 Pond, the relative 'control / low fish mercury' pond, was found to be shallow, turbid (cloudy water) from processing plant slurry discharges, and well-mixed with no bottom anoxia.

Table 1(a). Cemex – Phase 1 (West) Pond: 2018 Water Column Profiling Data

MAY 5: max. depth 6.5 m (21 ft); Secchi disk water clarity: 1.3 m (4.3 ft)

Figure 1(a). MAY 5, 2018 – Phase 1 Pond framework parameters

Table 1(b). Cemex – Phase 1 (West) Pond: 2018 Water Column Profiling Data

JUN 18: max. depth 6.1 m (20 ft); Secchi disk water clarity: 1.3 m (4.3 ft)

Figure 1(b). JUN 18, 2018 – Phase 1 Pond framework parameters

Table 1(c). Cemex – Phase 1 (West) Pond: 2018 Water Column Profiling Data

AUG 2: max. depth 6.4 m (21 ft); Secchi disk water clarity: 1.1m (3.6 ft)

Figure 1(c). AUG 2, 2018 – Phase 1 Pond framework parameters

Table 1(d). Cemex – Phase 1 (West) Pond: 2018 Water Column Profiling Data

SEP 17: max. depth 6.4 m (21 ft); Secchi disk water clarity: 1.2 m (3.9 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 1(d). SEP 17, 2018 – Phase 1 Pond framework parameters

Table 1(e). Cemex – Phase 1 (West) Pond: 2018 Water Column Profiling Data

OCT 27: max. depth 6.7 m (22 ft); Secchi disk water clarity: 1.9 m (6.2 ft)

Figure 1(e). OCT 27, 2018 – Phase 1 Pond framework parameters

Figure 1(f). Cemex – Phase 1 (West) Pond: 2018 May-Oct TEMPERATURE

Figure 1(g). Cemex – Phase 1 (West) Pond: 2018 May-Oct OXYGEN

Figure 1(h). Cemex – Phase 1 (West) Pond: 2018 May-Oct CONDUCTIVITY

Figure 1(i). Cemex – Phase 1 (West) Pond: 2018 May-Oct pH

2. CEMEX–PHASE 3-4 (East) POND

2. Cemex–Phase 3-4 Pond

The Phase 3-4 Pond data are presented in Tables 2(a)-2(e) and Figures 2(a)-2(i), and summarized below.

Water Depth (Tables and Figs. $2(a)-2(e)$): ranged between 9.8 and 11.2 m (32-37 ft) maximum depth across the 2018 May-Oct profiling.

Secchi Water Clarity (Tables and Figs. 2(a)-2(e)): was relatively clear to very clear, at 2.9 to >11.0 m (10 - >33 ft). On the clearest date, the Secchi disk was still visible at the 11 m bottom.

Temperature (Tables and Figs. 2(a)-2(e), Fig. 2(f)): Overall range 18-28 °C (64-82 °F) between May and October. Despite the greater depth of this pond, as compared to the Phase 1 Pond, the temperature data show a very similar trend. A thermal stratification began to develop in May, with surface waters warming to 4.2 $\rm{^{\circ}C}$ (7.6 $\rm{^{\circ}F}$) higher than the bottom water. But this degraded on all the subsequent dates, with the bottom water temperature increasing to levels close to those at the surface. This indicated frequent mixing of the water column, though with the surface waters always 1-2 °C warmer than bottom waters.

Dissolved Oxygen (Tables and Figs. $2(a)-2(e)$, Fig. $2(g)$): remained well above saturation levels throughout the season and at all depths, between 10.0 and 13.3 mg/L (ppm) and between 115 and 143% of saturation. All of these levels were super-saturated due to algal photosynthesis in the clear water. Oxygen depletion in the bottom waters never developed, as the water column remained thermally mixed and not stratifying significantly during the warm season. Additionally, the clear water allowed oxygen-generating photosynthesis at all or most depths. The different appearance of the May oxygen profile, as compared to the uniform profiles in other months, was apparently a function of temperature (a near mirror image) and photosynthesis, with the cooler water holding greater amounts of dissolved oxygen.

Conductivity (Tables 2(a)-2(e), Fig. 2(h)): ranged between 951 and 1074 μ S/cm overall. Levels were somewhat lower at the surface, higher at depth. Conductivity was very similar between May and September (~1030-1075 μ S/cm at most depths) and lower in October (951-998 μ S/cm).

Salinity (Tables 2(a)-2(e)): was very uniform at 0.48-0.51 ppt (parts per thousand, g/L) at all depths below the surface between May and September, and somewhat lower in October (0.40-0.42 ppt) following rain inputs and wind mixing. Typical freshwaters range below 0.50 ppt; seawater averages 35 ppt.

Total Dissolved Solids (TDS) (Tables 2(a)-2(e)): ranged within the range of $\sim 650-700$ mg/L (ppm) between May and September, and was somewhat lower in October, at 618-649 mg/L.

 pH (Tables 2(a)-2(e), Fig. 2(i)): as at the other monitored ponds, was notably very basic (nonacidic; $pH > 7.00$). This is a function of their mining history and the basic nature of local sediments. Water pH in the Phase 3-4 Pond fell between 8.35 and 8.86 across all depths and dates. The water became slightly more basic on each sampling date from early May to late October

Oxidation/Reduction Potential (ORP) (Tables $2(a)-2(e)$): stayed within the range of 99-143 mV (millivolts) across all depths and dates.

In summary, the Cemex–Phase 3-4 Pond, an identified 'elevated fish mercury' pond, was found to be of moderate depth, very clear, well-mixed, and showing no bottom anoxia. This particular pond may be challenging for remediation.

Table 2(a). Cemex – Phase 3-4 (East) Pond: 2018 Water Column Profiling Data

MAY 5: max. depth 11.2 m (37 ft); Secchi disk water clarity: 4.6 m (15 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 2(a). MAY 5, 2018 – Phase 3-4 Pond framework parameters

Table 2(b). Cemex – Phase 3-4 (East) Pond: 2018 Water Column Profiling Data

JUN 18: max. depth 10.1 m (33 ft); Secchi disk water clarity: 6.2 m (20 ft)

Figure 2(b). JUN 18, 2018 – Phase 3-4 Pond framework parameters

Table 2(c). Cemex – Phase 3-4 (East) Pond: 2018 Water Column Profiling Data

AUG 2: max. depth 9.8 m (32 ft); Secchi disk water clarity: 2.9 m (10 ft)

Figure 2(c). AUG 2, 2018 – Phase 3-4 Pond framework parameters

Table 2(d). Cemex – Phase 3-4 (East) Pond: 2018 Water Column Profiling Data

SEP 19: max. depth 10.7 m (35 ft); Secchi disk water clarity: 9.5 m (31 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 2(d). SEP 19, 2018 – Phase 3-4 Pond framework parameters

Table 2(e). Cemex – Phase 3-4 (East) Pond: 2018 Water Column Profiling Data

OCT 27: max. depth 11.0 m (36 ft); Secchi disk water clarity: >11.0 m (>36 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 2(e). OCT 27, 2018 – Phase 3-4 Pond framework parameters

Figure 2(f). Cemex – Phase 3-4 (East) Pond: 2018 May-Oct TEMPERATURE

Figure 2(g). Cemex – Phase 3-4 (East) Pond: 2018 May-Oct OXYGEN

Figure 2(h). Cemex – Phase 3-4 (East) Pond: 2018 May-Oct CONDUCTIVITY

Figure 2(i). Cemex – Phase 3-4 (East) Pond: 2018 May-Oct pH

3. TEICHERT–REIFF POND

3. Teichert–Reiff Pond

The Reiff Pond data are presented in Tables $3(a)$ -3(e) and Figures $3(a)$ -3(i), and summarized below.

Water Depth (Tables and Figs. 3(a)-3(e)): in this shallow pond dropped from 7.0 m (23 ft) in May to 4.9 m (16 ft) in August and September. Some rainfall runoff raised this slightly in October to 5.2 m (17 ft).

Secchi Water Clarity (Tables and Figs. 3(a)-3(e)): was uniformly very low/turbid, at 0.6-1.5 m (2.0-4.9 ft). A function of plant slurry inflows and wind turbulence / sediment resuspension clouding the water.

Temperature (Tables and Figs. 3(a)-3(e), Fig. 3(f)): Overall range 16-28 °C (61-82 °F) between early May and late October. A thermal stratification was apparent in May, with surface waters 7° C $(-13 \degree F)$ warmer than bottom water. The bottom water subsequently warmed from 16 $\degree C$ in May to 22 °C in June and 25 °C in August, indicating some periodic mixing with the warmer surface waters (without such mixing from above, bottom temperatures would remain almost unchanged through the season). However, a thermal gradient of 3-5 $\rm{^{\circ}C}$ (5-9 $\rm{^{\circ}F}$) persisted through this time. This would have isolated the lower water for periods of time. Later, in the fall, the water column became well mixed (low gradient between surface and bottom temperatures) as overall temperatures dropped in September and October.

Dissolved Oxygen (Tables and Figs. 3(a)-3(e), Fig. 3(g)): in the top 3 m of depth, remained at or above saturation levels throughout the season, between 8.8 and 11.2 mg/L (ppm) and 102-129% of saturation. However, even with the incomplete thermal stratification present between May and August, oxygen levels in the bottom water plummeted to under 1 mg/L and under 10% of saturation. These are levels that fish cannot survive in and, most relevant to this mercury-monitoring program, they are levels that can promote methylmercury production and its movement into the water from the bottom sediments, as well as mercury methylation directly in the bottom waters. These processes can significantly increase the uptake of methylmercury by fish and other aquatic organisms (and predators and fishermen that consume them). The Reiff Pond has had among the highest fish mercury levels of the monitored ponds. Another contributing factor is the high turbidity of the

water, which blocks photosynthesis and oxygen re-charge at depth here, and also blocks UV light from degrading methylmercury.

Conductivity (Tables 3(a)-3(e), Fig. 3(h)): ranged between 767 and 943 µS/cm overall. Levels were somewhat lower at the surface, higher at depth. In the May survey, conductivity was between 767 and $850 \mu S/cm$. Subsequently, levels were somewhat higher and similar between June and October (877-943 µS/cm).

Salinity (Tables 3(a)-3(e)): was fairly uniform, at 0.32-0.40 ppt (parts per thousand, g/L) across all depths and dates. Typical freshwaters range below 0.50 ppt; seawater averages 35 ppt.

Total Dissolved Solids (TDS) (Tables 3(a)-3(e)): ranged between 498 and 612 mg/L (ppm) across all dates and depths.

pH (Tables 3(a)-3(e), Fig. 3(i)): was notably very basic (non-acidic; $pH > 7.00$) in all of the monitored ponds. This is a function of their mining history and the basic nature of local sediments. Water pH in the Reiff Pond was very uniform on each date within the well-mixed surface 3 m, gradually increasing across the season from app. 8.6 to 9.0. However, in the semi-isolated deeper water that experienced oxygen depletion between May and August, pH dropped as low as 7.66, still basic but considerably less so. This was a function of reduced oxygen, which typically shifts systems in a more acidic (less basic) direction.

Oxidation/Reduction Potential (ORP) (Tables 3(a)-3(e)): generally ranged between app. 100 and 185 mV (millivolts) across all depths and dates. The exceptions were at the bottom in October (35 mV) and, particularly, in August in conjunction with anoxia (-238 mV).

In summary, the Teichert–Reiff Pond, one of two identified as highly elevated in fish mercury, was found to be shallow and turbid (cloudy water) from processing plant slurry discharges. Despite this, bottom waters became anoxic, particularly between June and August, almost certainly increasing methylmercury levels. This presents a remediation avenue, through disruption of summer anoxia.

Table 3(a). Teichert – Reiff Pond: 2018 Water Column Profiling Data

MAY 4: max. depth 7.0 m (23 ft); Secchi disk water clarity: 0.6 m (2.0 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Figure 3(a). MAY 4, 2018 – Reiff Pond framework parameters

Table 3(b). Teichert – Reiff Pond: 2018 Water Column Profiling Data

JUN 21: max. depth 6.1 m (20 ft); Secchi disk water clarity: 1.4 m (4.6 ft)

Figure 3(b). JUN 21, 2018 – Reiff Pond framework parameters

Table 3(c). Teichert – Reiff Pond: 2018 Water Column Profiling Data

AUG 3: max. depth 4.9 m (16 ft); Secchi disk water clarity: 1.0 m (3.3 ft)

Figure 3(c). AUG 3, 2018 – Reiff Pond framework parameters

Table 3(d). Teichert – Reiff Pond: 2018 Water Column Profiling Data

SEP 17: max. depth 4.9 m (16 ft); Secchi disk water clarity: 0.8 m (2.6 ft)

Figure 3(d). SEP 17, 2018 – Reiff Pond framework parameters

Table 3(e). Teichert – Reiff Pond: 2018 Water Column Profiling Data

OCT 29: max. depth 5.2 m (17 ft); Secchi disk water clarity: 1.5 m (4.9 ft)

Figure 3(e). OCT 29, 2018 – Reiff Pond framework parameters

Figure 3(f). Teichert – Reiff Pond: 2018 May-Oct TEMPERATURE

Figure 3(g). Teichert – Reiff Pond: 2018 May-Oct OXYGEN

Figure 3(h). Teichert – Reiff Pond: 2018 May-Oct CONDUCTIVITY

Figure 3(i). Teichert – Reiff Pond: 2018 May-Oct pH

6. SYAR–B1 POND

4. Syar–B1 Pond

The B1 Pond data are presented in Tables $4(a)-4(e)$ and Figures $4(a)-4(i)$, and summarized below.

Water Depth (Tables and Figs. $4(a)-4(e)$): ranged between 7.6 and 10.1 m (25-33 ft) across the 2018 May-Oct profiling. Evaporation losses lowered the standing water level between May and September, with app. 1 foot of rise from rain runoff between the September and October surveys.

Secchi Water Clarity (Tables and Figs. $4(a)$ - $4(e)$): was fairly clear, ranging from 2.9-6.5 m (10-21) ft). This pond, like Cemex Phase 3-4, is dominated by macro aquatic plants, as compared to the murkier systems dominated by microscopic algae.

Temperature (Tables and Figs. 4(a)-4(e), Fig. 4(f)): Overall range between 18 and 29 °C (63-84 °F) between May and October. A slight thermal stratification developed throughout the May-October warm season, with surface waters 1-4 $^{\circ}C$ (\sim 2-7 $^{\circ}F$) warmer than bottom water. However, as at the other ponds, the overall change in bottom water temperatures during this time (to temperatures nearer surface levels) indicates periodic mixing of the water column, presumably due to wind mixing. The surface exposure and area relative to depth in this system was apparently enough to transmit wind energy to the bottom periodically. The water column became fairly well mixed (low gradient between surface and bottom temperatures) as surface temperatures dropped in September and October, though temperatures on each date were always lowest at the bottom and warmer toward the surface, maintaining some separation.

Dissolved Oxygen (Tables and Figs. $4(a) - 4(e)$, Fig. $4(g)$): in the top 6 m remained at or above saturation levels throughout the season, between 8.7 and 11.0 mg/L (ppm) and between 101 and 126% of saturation. This can be attributed to photosynthesis in the clear water. Cooler water can hold more dissolved oxygen than warm water. However, the coolest water, below 6 m depth on all dates, was consistently *lowest* in oxygen, indicating some depletion, particularly on the dates with the most thermal stratification (figs. $4(f-g)$). In May, this amounted to a 33% absolute decrease from a surface average of 10.8 mg/L and 120% of saturation to 7.2 mg/L and 77% near bottom. In June, bottom oxygen dropped to under 5 mg/L and 59% of saturation level, 50% below concentrations in the surface 6 m. We did not lower our sensitive probes to closer than app. 1 m

above the bottom, to avoid damage, but it is very likely that oxygen depletion was more pronounced near the sediment surface. It is notable that, like Reiff Pond, the BI Pond has been one of the two with the most elevated bass mercury levels.

Conductivity (Tables 4(a)-4(e), Fig. 4(h)): ranged between 815 and 936 μ S/cm overall. As in the other ponds, levels were somewhat lower at the surface, higher at depth. Conductivity was highest in June (884-936 μ S/cm) and lowest in October (815-852 μ S/cm).

Salinity (Tables $4(a) - 4(e)$): was fairly uniform, at 0.34-0.39 ppt (parts per thousand, g/L) across all dates and water depths. Typical freshwaters range below 0.50 ppt; seawater averages 35 ppt.

Total Dissolved Solids (TDS) (Tables 4(a)-4(e)): fell within the range of 529-608 mg/L (ppm) across all dates and water depths.

pH (Tables 4(a)-4(e), Fig. 4(i)): was notably very basic (non-acidic; $pH > 7.00$) in all of the monitored ponds. This is a function of their mining history and the basic nature of local sediments. Water pH in the B1 Pond fell between 8.30 and 9.02 across all depths and dates. Most readings were more constrained in the 8.62-9.02 range. Levels below pH 8.6 were only present in deep waters with some oxygen depletion.

Oxidation/Reduction Potential (ORP) (Tables 4(a)-4(e)): ranged between 46 and 180 mV (millivolts) across all depths and dates.

In summary, the Syar–B1 Pond, second of the two identified as highly elevated in fish mercury, was found to be of medium depth, inactive (re mining), and clear. Bottom waters, though not going fully anoxic, became significantly reduced in oxygen during the warm season, possibly enhancing methylmercury exposure levels. This system may also get remediation benefits from disruption of summer anoxia.

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Table 4(a). Syar – B1 Pond: 2018 Water Column Profiling Data

MAY 4: max. depth 10.1 m (33 ft); Secchi disk water clarity: 6.5 m (21 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 4(a). MAY 4, 2018 – B1 Pond framework parameters

Table 4(b). Syar – B1 Pond: 2018 Water Column Profiling Data

JUN 21: max. depth 8.5 m (28 ft); Secchi disk water clarity: 5.7 m (19 ft)

Figure 4(b). JUN 21, 2018 – B1 Pond framework parameters

Table 4(c). Syar – B1 Pond: 2018 Water Column Profiling Data

AUG 3: max. depth 7.9 m (26 ft); Secchi disk water clarity: 2.9 m (10 ft)

Figure 4(c). AUG 3, 2018 – B1 Pond framework parameters

Table 4(d). Syar – B1 Pond: 2018 Water Column Profiling Data

SEP 19: max. depth 7.6 m (25 ft); Secchi disk water clarity: 4.0 m (13 ft)

(% Sat. = % of saturation; µS = micro Siemens; ppt = parts per thousand; ORP = oxidation/reduction potential); mV = millivolts)

Dissolved Oxygen (mg/L) / Water Temperature (°C)

Figure 4(d). SEP 19, 2018 – B1 Pond framework parameters

Table 4(e). Syar – B1 Pond: 2018 Water Column Profiling Data

OCT 29: max. depth 7.9 m (26 ft); Secchi disk water clarity: 5.4 m (18 ft)

Figure 4(e). OCT 29, 2018 – B1 Pond framework parameters

Figure 4(f). Syar – B1 Pond: 2018 May-Oct TEMPERATURE

Figure 4(g). Syar – B1 Pond: 2018 May-Oct OXYGEN

Figure 4(h). Syar – B1 Pond: 2018 May-Oct CONDUCTIVITY

Figure 4(i). Syar – B1 Pond: 2018 May-Oct pH

CONCLUSIONS

This first season of water column profiling provides an initial look at some of the water quality features of the monitored ponds. Table C summarizes the 2018 water profiling data from all of the tested ponds. Most of the parameters fell within similar ranges, including conductivity, salinity, dissolved solids, pH, and oxidation/reduction potential. Among the three identified elevated fish mercury ponds, Syar-B1, Teichert-Reiff, and Cemex-Phase 3-4, there was not an obvious, consistent trend. However, the data provide some important clues. In particular, there were key differences in bottom water anoxia and general water clarity.

Table C. Summary Comparisons of Profiling Data From All Four Tested Ponds

Seasonal bottom water anoxia was anticipated to be a potentially important driver of increased methylmercury production and movement into fish. That is because of the way methylmercury is produced. Methylmercury is almost entirely generated *biologically* – as a peripheral byproduct of the normal metabolism of important, naturally occurring microbes, primarily sulfur-reducers and iron-reducers. These microbes congregate just below the transition zone between oxygenated (oxic, aerobic) and anoxic conditions, where they obtain their energy by converting the oxidized forms of sulfur or iron (sulfate, ferric iron) to the reduced forms (hydrogen sulfide, ferrous iron). They do not purposely consume mercury or use it in any way. But mercury, if present, can move through their metabolic pathways – and be converted into toxic methylmercury, the form that bioaccumulates in organisms.

Ordinarily, the oxic/anoxic transition zone and its associated microbes is located within the bottom sediments, at some depth below the pond water and below the sediment surface. Sediments below the transition level are typically black and have a 'rotten egg' (hydrogen sulfide) smell. When the oxic/anoxic transition zone is deep in the sediments, any methylmercury that is produced there has a layer of oxic sediments between it and the pond water. Those sediments contain a tremendous number of potential binding sites that slow down or stop the transfer of the methylmercury into the overlying water. However, if the bottom waters of the pond become anoxic, the oxic/anoxic transition zone moves up into the water itself – together with the mercury-methylating microbes. Under those conditions, any methylmercury that is produced can move directly into the aquatic food web.

For a water body to become seasonally anoxic in its bottom water, the bottom water must first become isolated from aerated surface layers. This normally occurs during the warm season, mainly in systems deeper than these ponds, when the surface app. 6 m (20 ft) is warmed by the sun to temperatures well above that of the cool lower water. The water of different temperatures has different densities, that are strongly resistant to mixing. This results in a warm season 'mixed surface layer' (by wind) and an isolated, cool hypolimnion (bottom waters). If there is a net consumption (vs. replenishment) of dissolved oxygen in the hypolimnion during the time it is isolated, the bottom water will eventually become anoxic. This can persist until the surface waters cool in the fall to temperatures matching the bottom waters, and winds can re-mix and aerate the

entire water column. This annual phenomenon is known as 'fall turnover'. Warm season separation of the water column into non-mixing layers is called 'thermal stratification'. These aggregate-mining ponds currently have depths and basin configurations that mostly do not allow for the development of full thermal stratification across the warm season. If they did, the temperature profiles would show a nearly un-changing cool temperature in the bottom water throughout the summer. Instead, the bottom temperatures rose closer to surface levels, showing that there was at least occasional mixing from above. Despite this, the relatively small temperature gradients that persisted were apparently enough to allow the depletion of dissolved oxygen at two of the ponds – the same two that have the very highest fish mercury levels.

Seasonal bottom water anoxia was clearly found at the Reiff Pond, in conjunction with the highest 2018 bass mercury levels among all 7 monitored ponds. Oxygen depletion in the bottom waters was also present, to a lesser degree, at the B1 Pond, also among the highest in fish mercury since 2015. And in contrast, at the low fish mercury Cemex-Phase 1 Pond, there was no seasonal anoxia. These three cases were all consistent with the factor of deep anoxia correlating with elevated fish mercury, and vice-versa. However, the Phase 3-4 Pond was also a fairly elevated fish mercury site, but it showed no sign of bottom anoxia. This illustrates the complex, potentially multi-factor nature of mercury cycling in aquatic systems. All of these ponds occupy former depositional zones impacted by historic mercury mining upstream in the watershed; all likely contain sediment inorganic mercury at concentrations and bioavailabilities sufficient to lead to problem levels of methylmercury production and movement into fish – under certain conditions. Seasonal bottom water anoxia appears to be one important factor.

Additionally, the observed differences in general water clarity (Secchi disk visibility) were almost certainly linked to corresponding differences in fish bioaccumulation of methylmercury. However, there are multiple factors, some of which can influence the cycle in opposite directions. Low clarity / highly turbid water, which by definition contains a lot of suspended particles, also contains a lot of alternate binding sites for methylmercury, potentially making it less available for uptake into the food web. However, low clarity / high turbidity also acts to block sunlight from reaching below the surface water layers, shutting down algal photosynthesis and the production of dissolved oxygen. This can accelerate the development of bottom water anoxia and methylmercury

production. In contrast, high clarity / low turbidity water, which contains fewer suspended particles, has fewer alternate binding sites for methylmercury to be deflected to, resulting in a higher proportion of what methylmercury there is accumulating in the food web. In a competing effect, though, high water clarity also promotes photosynthesis and oxygen production to much greater depths, potentially all the way to the bottom of some of these relatively shallow ponds, keeping bottom water oxygenated and driving methylmercury production into the sediments. Additionally, methylmercury can be broken down or 'de-methylated' by ultraviolet light, the component of sunlight that gives us sunburns and degrades items left out in the sun. With high water clarity, this can become an important removal process, a 'natural remediation'. It is likely that these and additional related effects played a role in the differences seen in ultimate mercury accumulations in fish of the different ponds.

The first year water profiling results are not entirely straightforward. The lowest fish-mercury pond (Cemex-Phase 1) and the highest (Teichert-Reiff) were very similar in both being shallow, turbid, and with plant slurry inflows. One became anoxic (Reiff), the other did not (Cemex-Phase 1). The Cemex-Phase 3-4 Pond, fairly elevated in fish mercury, showed no trace of oxygen depletion.

In future monitoring, with new equipment and the ability to assess the additional, clarity-related parameters of turbidity, algal density, and dissolved organic carbon, new insights may become apparent, helping us refine potential remediation strategies. At this point, though, it is encouraging that three of the four ponds being tested indicate potential remediation benefits from approaches that provide summer mixing and the disruption of bottom water anoxia.

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