Summary Report for Permit Number CO-0048837

(12-12-13)

Goal

The goal of this study was to improve the linkages between total phosphorus (TP), chlorophyll-a (Chl-a), alkalinity (Alk), Secchi Depth (SD), and pH in Barr Lake (Barr). Since concentrations of TP have never been below 200 µg/L during the summer season (July – September), it is unclear how Chl-a, Alk, SD, and pH will respond to decreased TP.

According to Phase 1 of the Barr/Milton pH TMDL that was based on empirical models, the pH standard should be met if the summer TP maximum is 100 µg/L, which equates to a TP summer season average of 40-60 µg/L for Barr, 46-69 µg/L for Milton, Chl-a of 25 µg/L or less, and Alk below 100 mg$CaCO_3$/L (CDPHE, 2013). To reduce pH, in-reservoir testing was conducted to lower TP and Alk (independent variables) and to then observe the response variables, Chl-a, pH, and SD. The data from this study will be used to help improve the reservoir water quality models.

General Approach

Four limnocorrals (corrals) were used to isolate columns of water from the reservoir surface to the bottom sediment between 05/14/13 and 09/09/13. Two of the corrals were treated with liquid aluminum sulfate (alum) to precipitate phosphorus from the water in an effort to maintain TP concentrations below 100 µg/L and to also lower Alk. The other two corrals were treated with buffered alum (sodium aluminate) to lower TP but to not change Alk. The purpose to not change Alk in two of the corrals was to see how pH responds when only one independant variable TP) is changed. Then changes in pH would be directly linked to changes in Chl-a and TP. No control corral was used in this study because previous studies show that the corrals themselves do not impact the response variables.

This field test was based on previously conducted small bench top tests and provided an opportunity to see actual reservoir results without having to experiment on the entire reservoir. The use of alum required an NPDES permit. The permit was issued by the Colorado Discharge Permit System from the Colorado Water Quality Control Division (Division) of the Colorado Department of Public Health and Environment (CDPHE). The permit number is CO-0048837 and was issued on 01/23/12. This summary report is part of the permit requirements.

Materials and Methods

Limnocorrals and Study Area

The corrals were made out of woven, polyethylene fibers. The corrals had an open bottom exposure to the lake bottom sediments with a weighted skirt to seal off the bottom from the hypolimnion water. Half inch plastic piping was used to form hoops that shaped the corral into a 3-m diameter circle. At the surface, an eight inch foam buoyed a square metal frame.

The corrals were constructed by Curry Industries (Winnipeg, Manitoba). Each corral was approximately 3-m in diameter and 10-m in length. The volume of water in each corral at full pool was approximately 70.7 m^3 (18,660 gallons). All seams were double stitched and welded to assure water tightness.

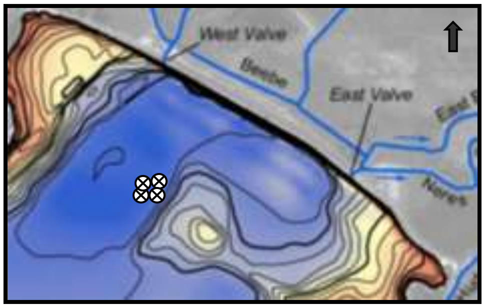


Figure 1. Limnocorral location at Barr Lake.

The corrals were assembled on shore and deployed from a pontoon boat. Corrals were secured together to make a single square unit. Each corner was securely fastened to heavy anchors to avoid drifting. The corrals were anchored in the deepest section of Barr (Figure 1).

At the time of deployment, Barr was 10-m deep. The water elevation gradually declined through the summer and was 6.5-m by 08/13/13 marking the end of the study. The elevation continued to decline in August and reached 3.5-m by 09/11/13 when the corrals were removed from the reservoir.

The study period ended 08/13/13 because of shallow water and because of a manufacturing error with the corrals. The impervious fabric did not extent more than an inch above the water line so surface water was allowed to enter the corrals at all of the corners. Throughout the study, surface water entered each of the corrals; therefore, the waters in the corrals were not isolated.

Alum

Alum was applied because it is effective at removing phosphorus from the water column and has been used for this purpose for over 40 years.

Alum ($Al_2(SO_4)_3$) quickly dissassociates in water and forms an aluminum hydroxide precipitate ($Al(OH)_3$). The flocculation process then does two things: first the hydroxide floc binds with phosphorus by adsorbtion, and secondly it physically entraps particulate material within the precipitant as it settles through the water column. The sweeping floc then settles on the lake bottom where it remains even during anoxic periods.

The aluminum phosphate precipitate ($AlPO_4$) is stable and remains bound regardless of sediment redox potential. Alum lowers the pH because of the initial formation of sulfuric acid, but small doses and the high Alk in Barr resulted in a pH of 6.5 or higher throughout the entire study. All water quality sampling occurred weekly after the addition of alum.

Sodium aluminate ($NaAl(OH)_4$) also quickly dissassociates in water and forms aluminum hydroxide. Unlike aluminum sulfate, the sodium aluminate does not form sulfuric acid. Therefore, aluminate will not alter the natural Alk or pH of the water in the corrals. The end result was that the aluminum hydroxide floc was formed minus the reduction in Alk and pH but still reduced the phosphorus.

Dosage

Application rate was based on laboratory jar testing conducted on 04/29/13, 04/30/13, and 05/15/13. Well mixed one liter water samples from Barr's epilimnion were tested with various amounts of both alum compounds. Then pH, Alk, and TP were analyzed to determine the best ratio of alum to water to lower TP below 100 µg/L.

The final jar test on 05/15/13 indicated the appropriate alum dosage to be 14 liters per 70,690 liter corral (0.02 % by volume) to maintain pH above 6.5 and to lower TP. This was based on using 200 µl of alum in a 1 liter jar test. The jar test also included testing for potentially dissolved aluminum (Al_{PD}). The 50 mL alloquots were collected from each test jar seven hours after the alum test. The Al_{PD} results were high (Table 1).

Table 1. Alum Jar Testing Results for 05/15/13.

Jar (1 liter)	$pH_{initial}$ @ 9:00	Alum (µL)	pH @ 6hr	pH @ 24hr	Al(pd)[1] (µg/L)	ALK (mg/L)	TP (µg/L)
1	7.80	0	8.17	8.12	10	135	230
2	7.83	150	6.55	7.32	-	43	0
3[2]	7.84	200	6.66	7.34	567	62	0
4	7.85	250	6.34	7.18	1220	33	0
5	7.86	300	5.75	6.51	-	0	20
6	7.85	320	5.33	5.40	-	0	20

1. Visible floc floating at surface, sampled 7 hours after adding alum.
2. 200 µL/1 liter of water ratio used to estimate dosage of 14 liters of alum per corral.

Table 2. Buffered Alum Jar Testing Results for 05/15/13.

Jar (1 liter)	$pH_{initial}$ @ 9:00	2:1 Alum:NaAl (µL)	pH @ 6hr	pH @ 24hr	Al(pd)[1] (µg/L)	ALK (mg/L)	TP (µg/L)
2	7.79	80:40	7.59	7.76	578	117	10
3	7.82	100:50	7.66	7.86	561	116	40
4[2]	7.83	140:60	7.75	7.93	914	110	10
5	7.84	200:100	8.78	8.59	9120	166	20

3. Visible floc floating at surface, sampled 7 hours after adding sodium aluminate.
4. 200 µL/1 liter of water ratio used to estimate dosage of 11 liters of alum per corral.

Based on the jar testing with buffered alum, the dosage ratio was also 200 µL (Table 2). This was based on a ratio of 2:1 for alum: sodium aluminate. A 2:1 ratio is typically recommended for buffered alum treatments (Osgood, 2010). A 140 µL of alum was added along with 60 µL of sodium aluminate to Jar #4 to get similar results. Alk did not change drastically from jar #1 (control), but the TP was below 100 µg/L and pH remained above 6.5. The ratio of 2:1 when the volume of each test corral was 70,690 liters allowed for 8.6 liters of alum and 4.3 liters of sodium aluminate to be added to each of the buffered alum corrals.

Application

Alum was added to corrals 1 and 2 on 05/29/13. Fourteen liters of liquid alum were applied to each of the two test corrals. During the application, the surface water was mixed with paddles. pH was monitored before, during, and after the application.

The buffered 2:1 alum mixture was added to corrals 3 and 4 on the same date. Nine liters of alum and five liters of sodium aluminate were applied to each of the two test corrals. Both chemicals were added with separate containers and mixed inside the corrals with paddles.

Based on phosphorus lab results that were available the next day, it was determined that more alum was needed. In order to keep TP below 100 µg/L, another four liters of alum were added to each of the alum test corrals on 06/04/13, 06/12/13, and 06/27/13. It was clear that phosphorus was not leaving the water column. After a closer inspection of the corrals, it was discovered that the surface water was leaking in from the corners of the corrals. The alum was working but more phosphorus laden water was replenishing the corrals. The corral manufacture sent corner patches to fix the problem so one last alum treatment occurred on 07/23/13. The corner patches did not work, and the corrals leaked again. A total of five applications occurred during the test.

Field and Laboratory Methods

Pre, during, and post water quality monitoring occurred after the initial alum application based on the discharge permit requirements. In addition, weekly monitoring for the study occurred from 06/03/13 to 08/21/13. Field monitoring included collection of water samples from one meter depth and one meter from the bottom, profile data from surface to the bottom at half meter increments, and SD for each of the four corrals and the open water next to the corrals. Monitoring was conducted from a boat and occurred between 0900 and 1500.

For each sampling event, all water samples were tested for TP, SRP, Alk, Chl-a, ammonia, nitrite/nitrate, and Total Kjeldahl Nitrogen (TKN). Profile data included dissolved oxygen (DO), percent DO, temperature, specific conductivity, turbidity, and pH. Composite water samples of the photic zone were collected and analyzed for algae and zoooplankton species and concentrations. Water clarity was measured during each visit using a Secchi disk.

Pre-Monitoring

Before the initial alum application on 05/29/1, the corrals and open water were tested (Table 3). Water samples and profile data were collected. To satisfy the discharge permit pre-monitoring requirements, pH and DO data were collected on 05/28/13, once at 0900 and then again at 1400 (Table 4).

Table 3. Pre-monitoring data collected on 05/28/12 from the epilimnion (0.5 - 2.0 meters).

Location	TP (µg/L)	SRP (µg/L)	Chl-a (µg/L)	SD (meters)	pH	Alk (mg/L)	DO (mg/L)	%DO (%)
Open Water	230	200	0.88	5.7	7.94	138	6.67	87.1
Alum Corral 1	210	170	1.85	5.0	8.17	137	8.64	111.2
Alum Corral 2	200	170	1.60	5.2	8.20	136	8.92	115.8
Buffered Alum Corral 3	190	170	2.50	5.0	8.22	138	9.05	117.2
Buffered Alum Corral 4	190	160	2.35	5.0	8.37	137	10.38	135.6

Table 4. Pre-monitoring data collected on 05/28/13.

Location	Time	Depth	pH[1]	DO[1] (mg/L)
Open Water	900	Top Half	7.94	6.67
		Bottom Half	7.57	1.08
	1400	Top Half	-	-
		Bottom Half	-	-
Alum Corral 1	900	Top Half	8.17	8.64
		Bottom Half	7.62	2.04
	1400	Top Half	8.30	10.00
		Bottom Half	7.68	1.39
Alum Corral 2	900	Top Half	8.20	8.92
		Bottom Half	7.65	2.18
	1400	Top Half	8.39	10.76
		Bottom Half	7.71	2.32
Buffered Alum Corral 3	900	Top Half	8.22	9.05
		Bottom Half	7.66	2.44
	1400	Top Half	8.36	10.50
		Bottom Half	7.70	2.79
Buffered Alum Corral 4	900	Top Half	8.37	10.38
		Bottom Half	7.71	2.89
	1400	Top Half	8.51	12.27
		Bottom Half	7.77	2.73

1. pH and DO averages were calculated from the profile data to get depth integrated values.
2. Depth integrated sample of the epilimnion defined by the permit requirements that was used for jar test

During-Monitoring

Both pH and DO were monitored in-situ before application (05/28/13) and then 30 minutes and three hours after the alum application on 05/29/13 (Table 5). pH and DO data were collected from the surface to the bottom at every half meter. The depth-integrated values were calculated from the profile data by averaging the top half and bottom half readings.

Table 5. pH and DO depth integrated values during alum application on 05/29/13.

Location	Time	Depth	pH[1]	DO[1] (mg/L)
Alum Corral 1	Before	Top Half	8.17	8.64
		Bottom Half	7.62	2.04
	30 minutes after	Top Half	5.93	7.98
		Bottom Half	6.63	2.88
	3 hours after	Top Half	6.58	10.30
		Bottom Half	6.41	3.52
Alum Corral 2	Before	Top Half	8.20	8.92
		Bottom Half	7.65	2.18
	30 minutes after	Top Half	5.75	8.47

		Bottom Half	6.49	2.73
	3 hours after	Top Half	6.09	10.51
		Bottom Half	6.33	3.53
Buffered Alum Corral 3	Before	Top Half	8.22	9.05
		Bottom Half	7.66	2.44
	30 minutes after	Top Half	6.46	8.20
		Bottom Half	7.66	4.82
	3 hours after	Top Half	6.82	10.03
		Bottom Half	7.82	5.66
Buffered Alum Corral 4	Before	Top Half	8.37	10.38
		Bottom Half	7.71	2.89
	30 minutes after	Top Half	7.25	9.07
		Bottom Half	7.41	4.49
	3 hours after	Top Half	7.58	10.87
		Bottom Half	7.43	5.89

1. pH and DO averages were calculated from the profile data to get depth integrated values.

Weekly Monitoring

Weekly monitored was conducted between 05/28/13 and 08/21/13. A total of 13 sampling events occurred during this period.

For the purpose of understanding how pH and Chl-a respond to lower TP levels, summary of the data for the study only includes epilimnion data from 06/03/13 to 08/13/13 (Table 6). The reservoir experienced typical draw down during the study. It is clear by the data summary that the corrals did not work.

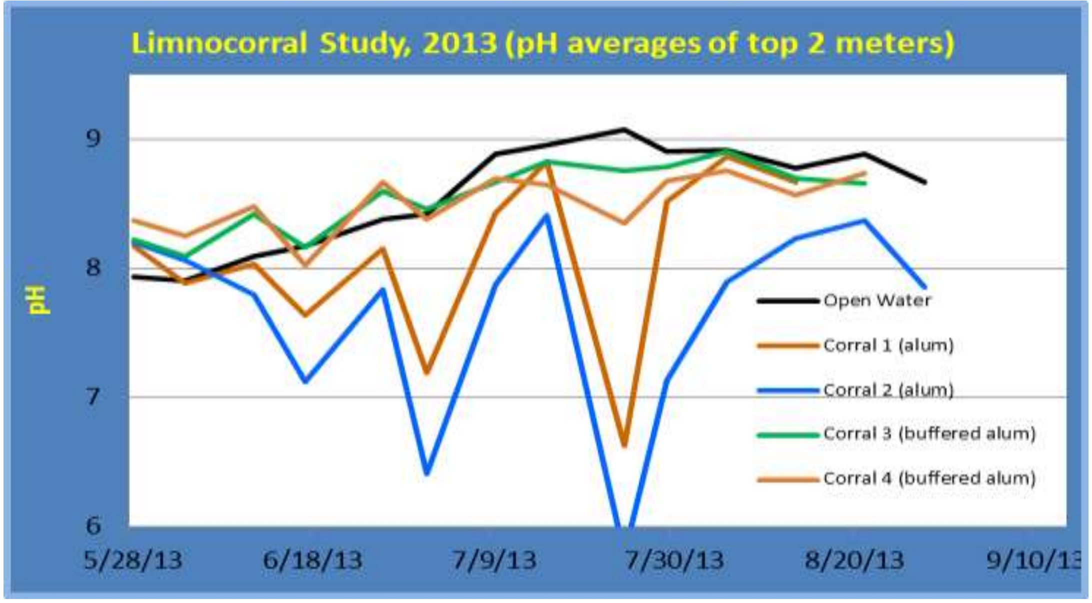
Table 6. Averages of weekly limnocorral data from 06/03/13 to 08/13/13.

Location	TN (mg/L)	TP (µg/L)	SRP (µg/L)	TN:TP	Chl-a (µg/L)	SD (m)	pH[1]	Alk (mg/L)	DO (mg/L)	DO (%)
Open Water	2.79	460	393	7.8	46.6	2.2	8.59	146	8.36	118.1
Alum Corral 1	2.98	357	252	7.9	34.4	2.2	8.08	134	7.49	108.5
Alum Corral 2	3.10	234	177	10.6	33.7	2.6	7.51	110	7.07	99.1
Buffered Alum Corral 3	3.74	391	243	6.5	76.9	2.3	8.58	143	8.65	121.8
Buffered Alum Corral 4	3.32	299	237	8.5	34.2	2.4	8.50	139	8.01	113.3

1. pH is the 85th percentile for all pH values recorded between 06/03/13 and 08/13/13.

Profile data were also collected at all five locations on a weekly basis. All pH values for the four test corrals remained below 9.0 during the study (Figure 2).

Figure 2. Average pH data (0.5 - 2.0 meters) for the study.



Post Monitoring

In order to remove the corrals from Barr, pH, DO, and $Al_{(PD)}$ standards all needed to meet water quality limits inside each corral. The pH standard was met in all four corrals (Figure 2). Similar to the 2012, low DO occurred in the corrals because of shallow, calm water. All of the corrals had DO above 5.0 mg/L at the surface except for Corral 2 which was 2.6 mg/L. The open water DO was 5.5 mg/L. Barr's dissolved oxygen saturation remained above 5.0 mg/L throughout the removal process. The percent volume of water in the four corrals was only 0.7% of the entire reservoir volume at the time of removal.

The $Al_{(PD)}$ samples were collected on 07/09/13. The results showed concentrations below the state standard of 87 µg/L except for Corral 2 which was 95.1 µg/L (Table 7). Again, because of an insignificant volume of water in Corral 2 compared to the entire reservoir at the time of removal (0.2%), the impact of taking out the corrals was not measurable.

Similar to 2012 when DO and $Al_{(PD)}$ were not in compliance inside the corrals, a decision was made to remove the corrals based on the open water concentrations and the relatively small volume of water inside the corrals compared to the rest of the reservoir.

Table 7. Potentially dissolved aluminum data.

Location	$Al_{(PD)}$ (µg/L)
Open Water	9.32
Alum Corral 1	23.5
Alum Corral 2	95.1
Buffer Alum Corral 3	76.8
Buffer Alum Corral 4	34.7

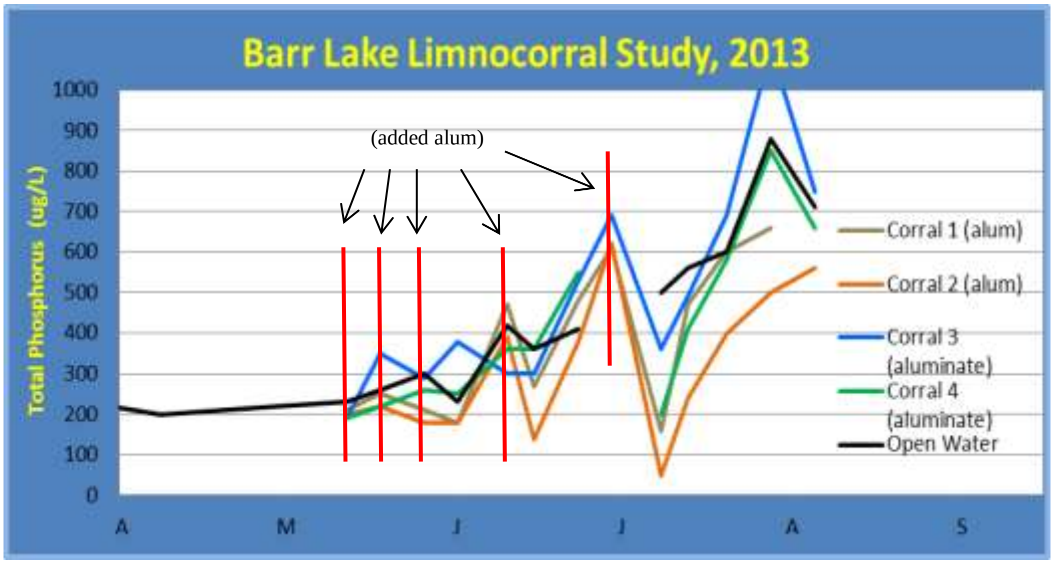
Results

The goal of this study was to improve the linkages between TP and the response variables. This was an opportunity to repeat the limnocorral study from 2012 in a non-drought year and try to minimize variablity with the data. It was also an opportunity to test a buffered alum solution.

Unfortunately, the newly purchased corrals were built incorrectly allowing for surface water to freely flow in and out of each of the corrals. It is clear from the TP data that all four corrals were unable to isolate a column of water during the study.

Despite the design flaw, the data did reveal some slight differences. TP did not get below 100 µg/L, but some of the corral TPconcentrations were clearly less than the open water, mainly immediately following each application (Figure 3). There was also a decline in pH as TP was reduced (Figure 4). Primary productive was less in 2013 than other years so even the open water's pH was below 9.0 for most of the study period.

Figure 3. TP data (1.0 meter depth) for the study.



TP & SRP

TP and SRP average was lowest in Corral 2 and highest in Open Water (Table 6). The goal to have TP below 100 µg/L was not achieved with this study. The ratio of TN to TP was highest in Corral 2 and lowest in the Open Water.

Alk & pH

Alk was slightly reduced in the alum corrals, and the buffered alum corrals were similar to the Open Water. The pH averages were well under 9.0. Corral 2 had the lowest pH average while Open Water had the highest. By having higher Alk in the buffer alum corrals, the average pH for Corral 3 and 4 were both higher than the alum corrals.

Chl-a & Secchi Depth

Chl-a for the test corrals and Open Water all remained over the goal of 25 µg/L. Water clarity is closely linked to Chl-a during the summer season. Corral 2 had the least Chl-a throughout the study; average Chl-a was 33.7 µg/L. The clarity in Corral 2 was also the highest. Corral 3 had the highest Chl-a for the four test corrals; average Chl-a was 76.9 µg/L.

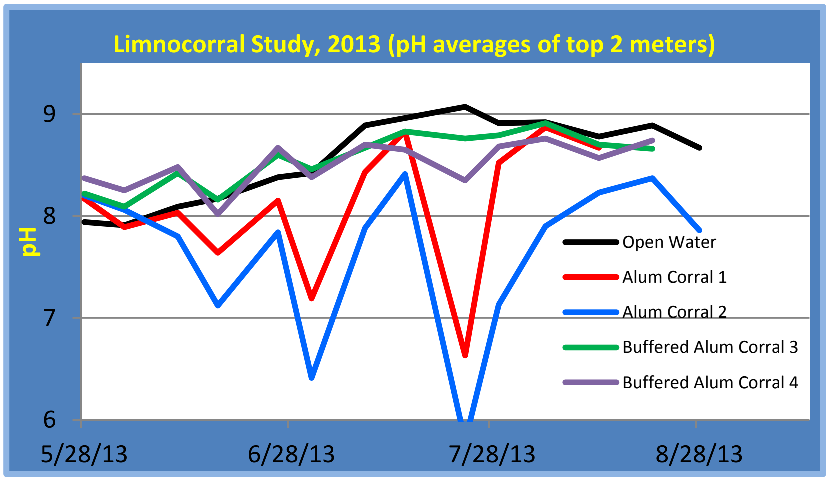
It was obvious from the weekly sampling events that the corrals were not working as planned.

Discussion

The variability issue from 2012 seemed to be less for this study. Both of the two alum corrals seemed to do a better job tracking similar data results as well as the two buffer alum corrals. There was also a clear difference in pH and Alk between the alum and buffered alum corrals (Figure 4). The Alk and pH in the buffered alum corrals resembled the Open Water data.

Buffered alum did not influence Alk or pH directly. If pH changed in the buffered alum corrals, then it was because of productivity not because of the alum.

Figure 4. pH average of top 2 meters for 2013 study



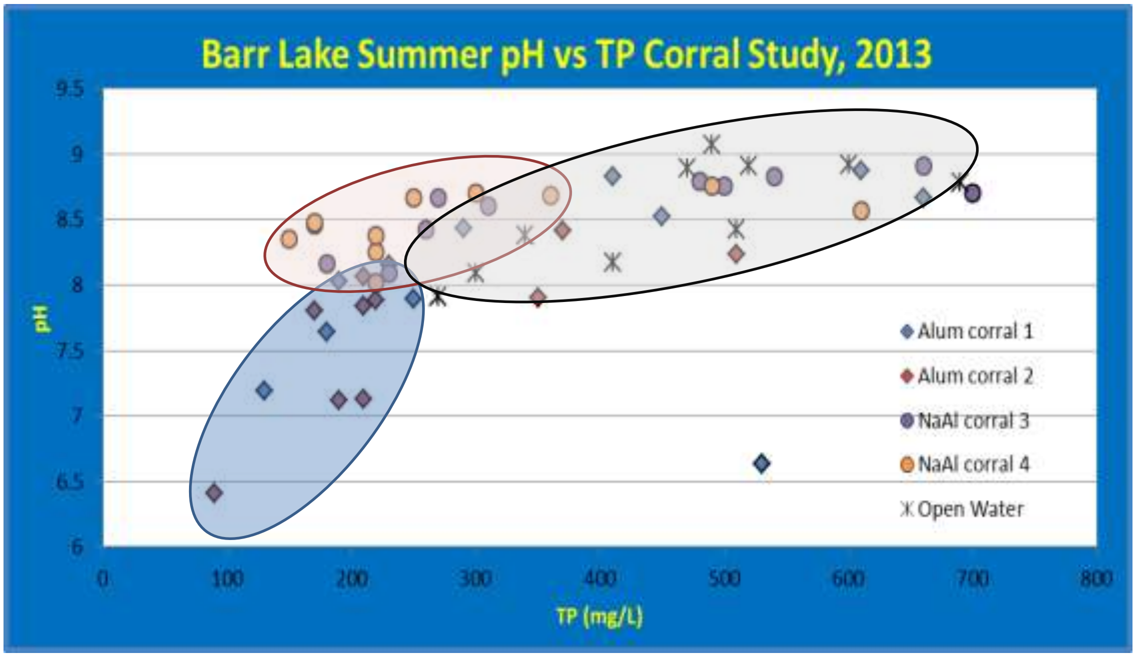
Based on pH equilibrium, if Alk is close to 150 mg/L of $CaCO_3$ then the baseline pH should be 8.1 leaving only 0.9 pH units to be added by primary productivity (Wagner, 2013). The buffered alum corrals had an Alk around 140 mg/L of $CaCO_3$ so the baseline pH should have been around 8.07. The Chl-a for the buffered alum corrals was 8.54. That means productivity (Chl-a average of 55.6 ug/L) raised the pH by 0.47 units. Dividing the two results in 0.008 pH units/unit of Chl-a. Chl-a of 58 µg/L would meet a pH standard of 9.0.

This Chl-a value seems high compared to previous estimates of 25 µg/L as the Chl-a upper limit. For some reason, Barr's pH did not increase above 9.0 when the Chl-a increased as in other years. One reason is that Alk has slightly decreased over the past few years. An approximate average was historically 176 mg/L $CaCO_3$ and now it is closer to 145 mg/L.

The TN:TP ratio and the Alk may have had a role in why Alum Corral 2 performed the best out of the four test corrals (Table 6). The ratio of nitrogen to phosphorus was not >25, but it was still higher than the other three corrals. Alk was the lowest in Corral 2 along with the pH.

Even though the corrals were not water-tight, the data showed signs of clustering (Figure 5). The Open Water data tended to be highest in TP and pH (grey oval). The buffered alum corrals tended to have lower TP than the Open Water and slightly higher pH than the alum corrals (pink oval). The two alum corrals had the lowest TP and pH values (blue oval).

Figure 5. Relationship between TP and pH.



Conclusions

The goal to better understand the linkages between TP, Chl-a, Alk, SD, and pH in Barr was not achieved in this study due to corral design flaws. Some information was gathered about using a buffered alum to help reduce TP while not changing the Alk or baseline pH. Again, the corral with the lowest Alk and the highest TN:TP ratio seemed to have the better overall water quality.

For 2014, new water-tight corrals will be installed in the deepest area of Barr. Both alum and buffered alum will be used to keep TP below 100 µg/L during the summer season (July through September).

References

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