Summary Report for Permit Number CO-0048837

(12-29-14)

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, prior to initiation of this study, had not 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 $mgCaCO_3/L$ (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 06/02/14 and 09/04/14. 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 of not changing Alk in two of the corrals was to see how pH responds when only one independant variable (TP) is changed so that 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 required per the permit.

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.

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).

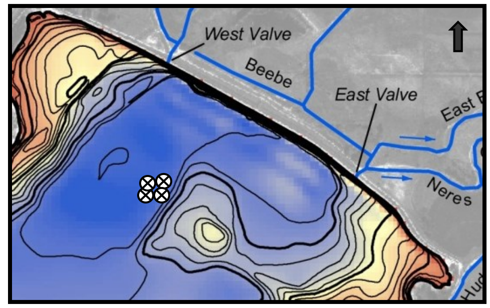


Figure 1. Limnocorral location at Barr Lake.

At the time of deployment, Barr was 10-m deep. The water elevation remained constant through the summer and was 9.6-m by 08/12/14 marking the end of the study. The water depth was 6.9-m by 9/4/14 when the corrals were removed from the reservoir.

The study period ended 08/12/14 because of impacts from waterfowl. This was the first year that waterfowl roosted on the corrals which created a major source of nutrients to the surface water. Starting in late July, cormorants and white pelicans began to sit on the floats. Approximately 30-50 birds were seen on the corrals during each visit. The birds would defecate in the corrals. The nutrient data was definitely impacted by the birds.

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 without the reduction in Alk and pH, but still reduced the phosphorus.

Dosage

Application rate was based on laboratory jar testing conducted on 04/29/14 and 05/13/14. 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 05/13/14 indicated the appropriate alum dosage to be 11 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 160 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 because of floc formation in the small beaker (Table 1).

Table 1. Alum Jar Testing Results for 05/13/14.

Jar (1 liter)	$pH_{initial}$ @ 9:00	Alum (µL)	pH @ 1hr	pH @ 24hr	Al(pd)[1] (µg/L)	ALK (mg/L)	TP (µg/L)
1	7.04	0	6.76	6.76	11.1	129	620
2	7.04	20	6.73	6.76	765	115	70
3	7.04	60	6.63	6.72	2250	86	20
4	7.03	100	6.62	6.72	481	97	30
5[2]	6.96	160	6.52	6.68	562	57	10
6	7.01	300	6.46	6.64	621	36	0

1. Visible floc floating at surface, sampled 7 hours after adding alum.
2. 160 µL/1 liter of water ratio used to estimate dosage of 11 liters of alum per corral.

Table 2. Buffered Alum Jar Testing Results for 05/13/14.

Jar (1 liter)	$pH_{initial}$ @ 9:00	2:1 Alum:NaAl (µL)	pH @ 1hr	pH @ 24hr	Al(pd)[1] (µg/L)	ALK (mg/L)	TP (µg/L)
2	7.15	40:20	6.76	6.74	1350	114	40
3	7.17	60:30	6.8	6.82	1470	110	0
4[2]	7.17	100:50	7.29	6.97	1950	118	20
5	7.16	140:70	7.37	7.18	3200	116	20
6	7.17	200:100	7.22	7.15	505	99	20

1. Visible floc floating at surface, sampled 7 hours after adding sodium aluminate.
2. 100:50 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 close to 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 100 µL of alum was added along with 50 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 7 liters of alum and 3.5 liters of sodium aluminate to be added to each of the buffered alum corrals.

Application

Alum was added to corrals 1 and 2 on 06/04/14. Eleven 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. Seven liters of alum and 3.5 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, it was determined that more alum was needed through the study. In order to keep TP below 100 µg/L, another dose was added to each of the corrals on 06/17/14, 07/08/14, 07/24/14, and 08/04/14. It was clear in June and July that internal loading of phosphorus was substantial. By August, alum addition was not able to keep up with both waterfowl excretion and the internal loading inputs. The alum was working but the dose was not enough. A total of four 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 06/03/14 to 08/27/14. 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 the hours of 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 06/04/14, 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 06/03/14, once at 0900 and then again at 1400 (Table 4).

Table 3. Pre-monitoring data collected on 06/03/14 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	310	290	1.83	6.0	8.00	120	6.16	84.4
Alum Corral 1	400	360	1.51	5.8	7.88	120	5.74	74.4
Alum Corral 2	370	340	1.83	5.1	7.92	118	5.38	72.7
Buffered Alum Corral 3	440	390	1.32	5.7	7.99	119	5.24	71.0
Buffered Alum Corral 4	330	300	2.02	5.5	7.97	120	5.46	74.3

Table 4. Pre-monitoring data collected on 06/03/14.

Location	Time	Depth	pH[1]	DO[1] (mg/L)	Al(pd) (µg/L)
Open Water	900	Top Half	7.91	6.27	5.12
		Bottom Half	7.84	5.27	8.51
	1400	Top Half	-	-	-
		Bottom Half	-	-	-
Alum Corral 1	900	Top Half	7.88	5.74	5.01
		Bottom Half	7.89	1.39	7.91
	1400	Top Half	8.14	5.74	-
		Bottom Half	7.85	0.95	-
Alum Corral 2	900	Top Half	7.92	5.38	6.35
		Bottom Half	7.89	1.12	7.98
	1400	Top Half	7.97	5.58	-
		Bottom Half	7.80	0.97	-
Buffered Alum Corral 3	900	Top Half	7.99	5.24	5.38
		Bottom Half	7.94	1.24	7.29
	1400	Top Half	7.96	5.40	-
		Bottom Half	7.82	0.97	-
Buffered Alum Corral 4	900	Top Half	7.97	5.46	4.70
		Bottom Half	7.98	1.86	6.44
	1400	Top Half	7.97	5.65	-
		Bottom Half	7.86	1.26	-

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 the alum application, then 30 minutes afterwards, and then three hours after the application on 06/04/14 (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 06/04/14.

Location	Time	Depth	pH[1]	DO[1] (mg/L)
Alum Corral 1	Before	Top Half	8.21	5.56
		Bottom Half	8.11	2.38
	30 minutes after	Top Half	7.38	5.54
		Bottom Half	6.89	2.58
	3 hours after	Top Half	7.00	5.21
		Bottom Half	6.70	2.44
Alum Corral 2	Before	Top Half	7.99	4.96
		Bottom Half	7.95	1.73
	30 minutes after	Top Half	6.57	4.63
		Bottom Half	6.28	1.78

	3 hours after	Top Half	6.26	4.57
		Bottom Half	6.12	2.07
Buffered Alum Corral 3	Before	Top Half	7.89	4.43
		Bottom Half	7.88	1.98
	30 minutes after	Top Half	6.62	4.13
		Bottom Half	6.75	2.36
	3 hours after	Top Half	6.40	4.05
		Bottom Half	6.59	2.00
Buffered Alum Corral 4	Before	Top Half	7.88	5.04
		Bottom Half	7.89	1.95
	30 minutes after	Top Half	6.88	4.68
		Bottom Half	6.96	2.25
	3 hours after	Top Half	6.73	4.75
		Bottom Half	6.81	2.47

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

Weekly Monitoring

Weekly monitored was conducted between 06/11/14 and 08/12/14. A total of 10 sampling events occurred during this period.

For the purpose of understanding how pH and Chl-a respond to lower TP levels, a summary of the data only includes epilimnion data from 06/11/14 to 08/12/14 (Table 6). The reservoir experienced no draw down during the study. It is clear by the data summary that the corrals were heavily impacted by internal loading and then later by waterfowl.

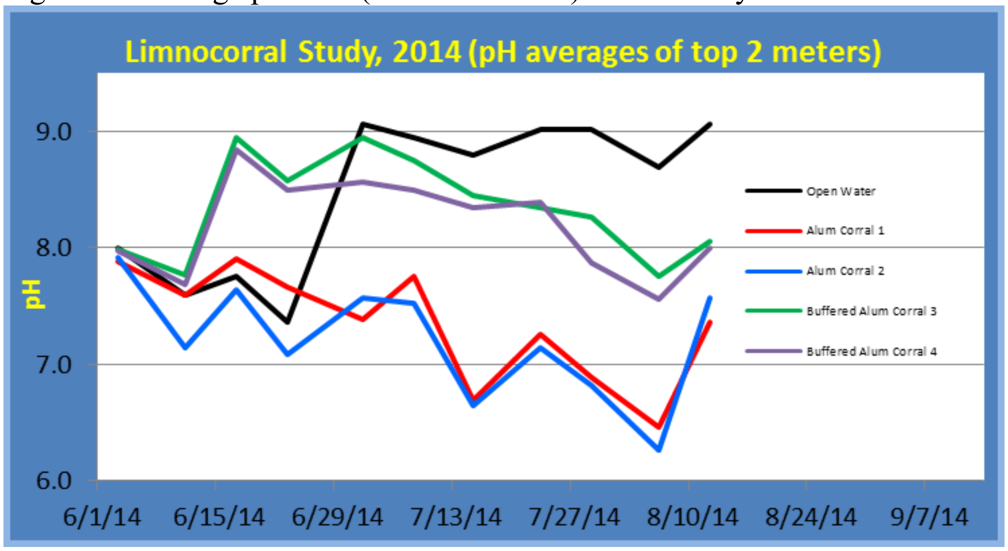
Table 6. Averages of weekly limnocorral data from 06/11/14 to 08/12/14.

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	1.82	295	226	6.1	35.6	2.1	8.87	114	8.83	122.2
Alum Corral 1	5.53	596	518	16.0	18.0	3.2	7.59	76	5.58	75.4
Alum Corral 2	4.71	543	464	13.7	16.7	3.4	7.53	76	5.77	78.5
Buffered Alum Corral 3	5.48	761	643	9.1	30.5	2.8	8.48	115	7.96	108.6
Buffered Alum Corral 4	6.24	827	668	9.5	21.2	2.8	8.37	117	6.95	95.2

1. pH is the 85th percentile for all pH values recorded between 06/11/14 and 08/12/14.

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 and 2013 study periods, low DO occurred in the corrals because of isolation of the water column.

DO was measured in the open water and each coral before removing them, 60 minutes after removing them, and then 3 hours after all of the corrals were removed. The DO in the open water was below 5.0 mg/L and only increased after removing the corrals (Table 7). The low DO water in the corrals did not affect the DO in the lake. The percent volume of water in the four corrals was only 0.001% of the entire reservoir volume at the time of removal.

Table 7. DO and pH before and after corral removal.

Location	pH			DO (mg/L)		
	Before	1hr	3hr	Before	1hr	3hr
Open Water	7.90	7.92	8.03	3.52	3.73	4.18
Alum Corral 1	7.82	7.92	8.03	2.76	3.72	4.14
Alum Corral 2	7.82	7.92	8.02	2.86	3.60	3.97
Buffer Alum Corral 3	7.87	7.91	8.01	2.60	3.40	3.91
Buffer Alum Corral 4	7.85	7.91	8.00	2.24	3.28	3.71

The $Al_{(PD)}$ samples were collected on 07/09/13. The results showed concentrations below the state standard of 87 µg/L for all the corrals (Table 8).

Table 8. Potentially dissolved aluminum data from 8/27/14.

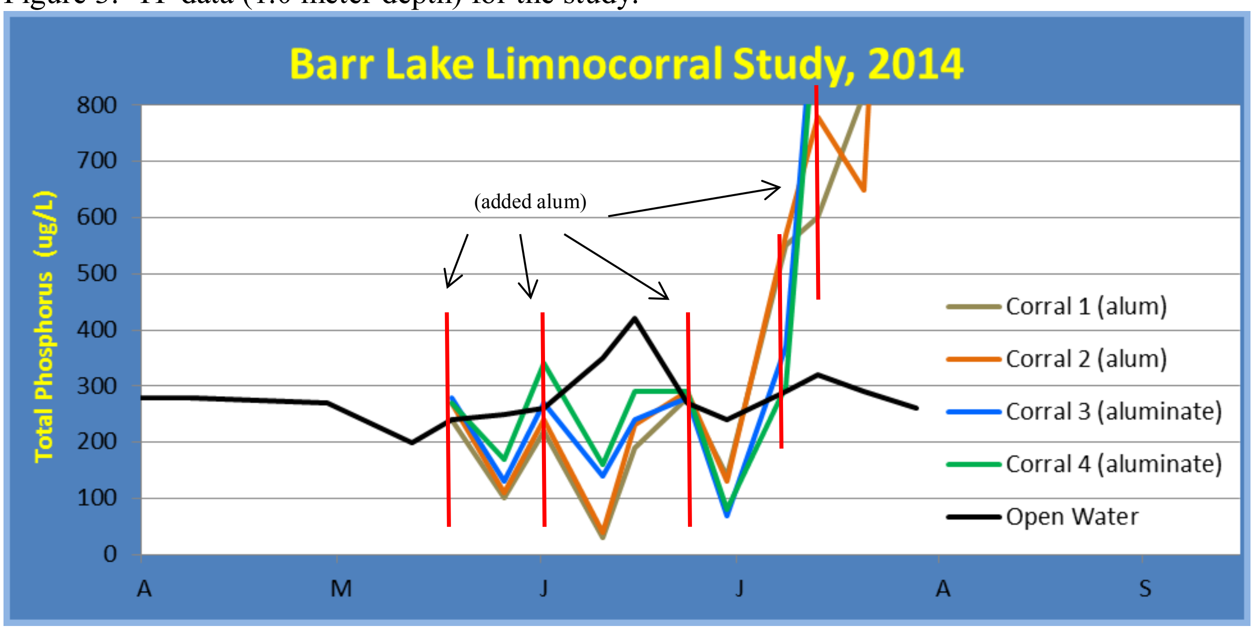
Location	$Al_{(PD)}$ (µg/L)
Alum Corral 1	35.4
Alum Corral 2	44.8
Buffer Alum Corral 3	71.4
Buffer Alum Corral 4	57.0

Results

The goal of this study was to improve the linkages between TP and the response variables. The 2014 study presented an opportunity to repeat the limnocorral study from 2012 and 2013 in a non-drought year to minimize variablity with the data. It was also an opportunity to test use of a buffered alum solution.

Despite the internal loading and waterfowl issues, the data revealed some slight differences. TP declined below 100 µg/L, but for only a short period of time (Figure 3). There was also a decline in pH as TP was reduced with each application (Figure 4). Primary productive and alkalinity was less in 2014 than other years so even the open water's pH was below 9.0 for most of the study period. This difference in open water is most likely the result of the fall 2013 floods that resulting in filling Barr Lake with essentially Bear Creek Reservoir water.

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



TP & SRP
Average TP and SRP concentrations were lowest in the open water due to refilling with Bear Creek Reservoir water after the fall 2013 floods (Table 6). The goal to have TP below 100 µg/L was achieved during brief periods. Internal loading and the added nutrients from waterfowl caused high phosphorus concentrations in July and August. The alum corrals showed the highest ratio of TN to TP which indicates a better balance of nitrogen and phosphorus.

Alk & pH
Alk is typically around 160 mg/L for the open water. In 2014, the average Alk for the open water was 114 mg/L. Alum corrals 1 and 2 had the lowest Alk and pH because of the reaction with the aluminum sulfate. The buffered alum corrals were successful in maintaining similar open water Alk. The buffered corrals did not chemically reduce the pH. The buffered corrals had a 0.39 – 0.50 reduction in pH based only on the change in primary productivity caused by the reduction in TP.

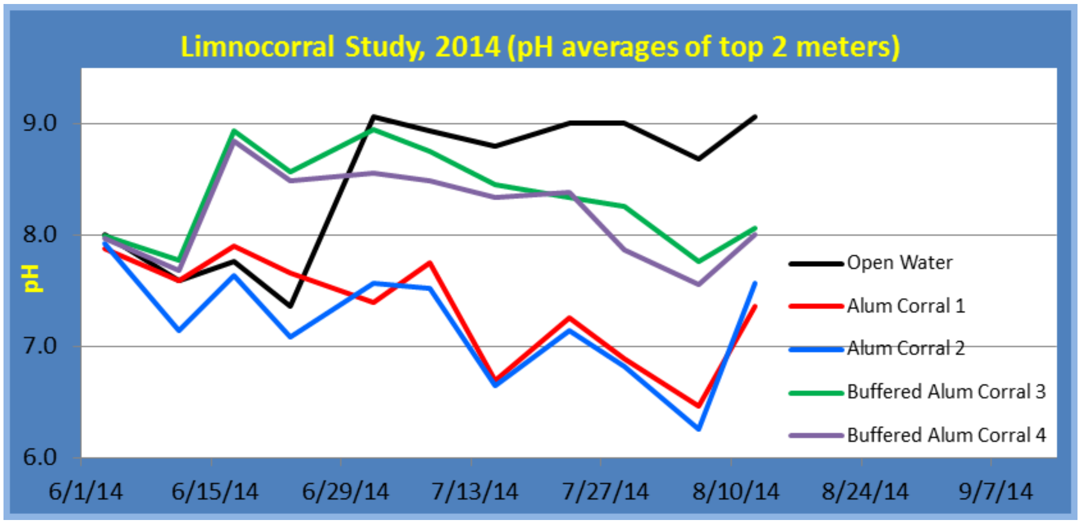
Chl-a & Secchi Depth
Chl-a in the test corrals remained under the goal of 25 µg/L for most of the sampling. There was an initial algal blooms in each of the corrals at the beginning of the study that raised the average. The open water Chl-a also stayed below the goal for 5 of the 11 samples. Water clarity is closely linked to Chl-a during the summer season. The alum corrals had the least Chl-a and the clearest water. Corral 2 had the lowest Chl-a (16.7 µg/L) and the deepest Secchi depth (3.4 m). The two buffered alum corrals had slightly higher Chl-a with slightly shallower water clarity. All four corrals did better than the open water (Table 3).

It was obvious from the weekly sampling events that the corrals were not working as planned after 7/15/14 because of the additional nutrient inputs from waterfowl. Two alum treatments conducted on 7/24/14 and 8/04/14 did not effectively reduce the phosphorus concentrations (Figure 3).

Discussion
The variability issue amongst the two different corrals (alum and buffered alum) from 2012 were less noticeable in the 2014 study. Both of the alum corrals as well as the two buffered alum corrals seemed to track each other more closely with similar data results. 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 2014 study.



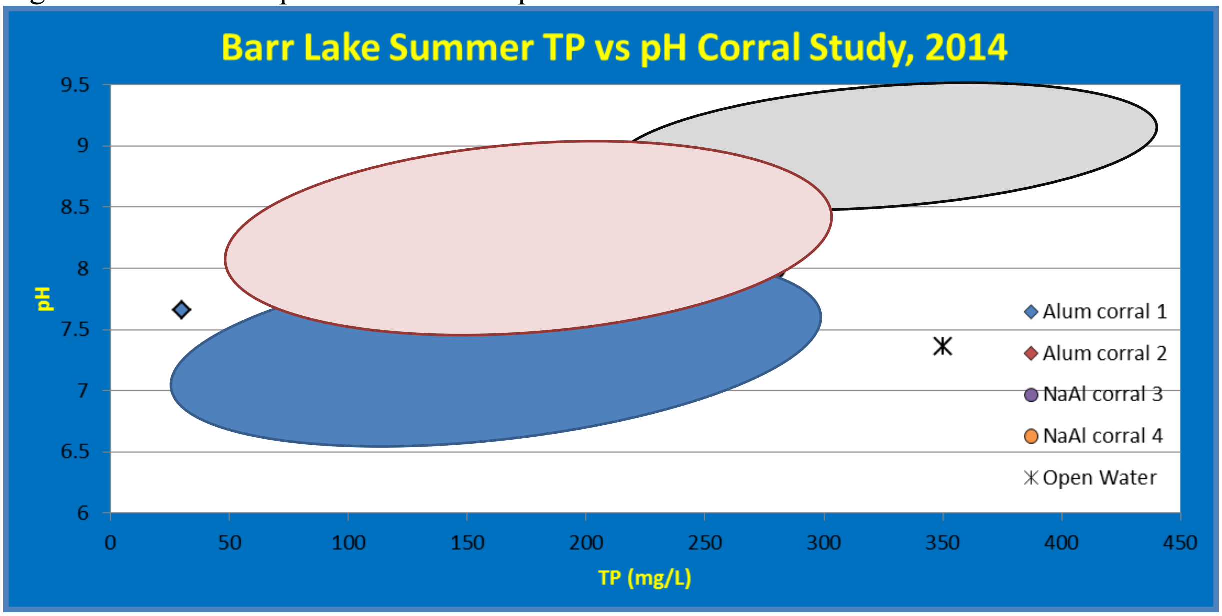
Based on pH equilibrium, if Alk is close to 150 mg/L of $CaCO_3$ then the baseline pH should be 8.1 leaving only 0.9 pH units to be added by primary productivity (Wagner, 2013). The buffered alum corrals had an Alk around 116 mg/L of $CaCO_3$ so the baseline pH should have been around 7.95. The pH for the buffered alum corrals was 8.30. That means productivity (Chl-a average of 25.9 ug/L) raised the pH by 0.48 units (0.47 units in 2013). Dividing the two results in 0.02 pH units/unit of Chl-a, a Chl-a of 52.5 µg/L would meet a pH standard of 9.0 (2013 study showed 58 µg/L of chl-a would meet the standard).

This Chl-a value seems high compared to previous estimates of 25 µg/L as the Chl-a upper limit. This is the second year in a row that Barr's pH did not violate the standard. One reason for these results is that Alk has continued to decrease in the past few years allowing for a lower baseline pH. An approximate average was historically 176 mg/L $CaCO_3$ and in 2014 it was 115 mg/L.

The TN:TP ratio is also an important factor for these corral studies. The average TN:TP ratio for the alum corrals was 15. As this ratio gets larger, the reservoir will become phosphorus limited.

Even though the corrals were influenced heavily by internal loading and waterfowl (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 achieved in this study along with being able to duplicate previous corrals studies from 2012 and 2013. For 2014, internal loading and waterfowl inputs clearly impacted the phosphorus loading to the corrals. Further data analysis will include calculating internal flux loads and possibly waterfowl excrement inputs. Clearly, using a buffered alum allowed for a better correlation between phosphorus reduction and primary productive and what they mean to pH values. Alum did seem to do a better job overall in controlling algae and keeping pH lower. Again, the corral with the lowest Alk and the highest TN:TP ratio seemed to have the best overall water quality.

References

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