Summary Report for Permit Number CO-0048837

(12-27-12)

Goal

The goal of this study was to determine 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 ug/L during the growing season (July – September), it is unclear how Chl-a, Alk, SD, and pH will respond.

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 with an average TP between 40-60 µg/L and a Chl-a of 25 µg/L or less. To reduce the uncertainty around pH, in-reservoir testing was conducted to lower TP 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 were used to isolate columns of water from the reservoir surface to the bottom sediment between 05/15/12 and 10/08/12. Three of the mesocosms were treated with liquid aluminum sulfate (alum) to precipitate the TP from the water in an effort to maintain TP concentrations below 100 µg/L.

This in-situ 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 was 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 limnocorrals were made out of woven polyethylene fibers and were laminated on both sides. The limnocorrals had an open bottom exposure to the lake bottom sediments with a weighted skirt to seal off the bottom from the hypolimnetic water. Half inch plastic piping was used to form hoops that shaped the corral into a 3-m diameter circle every 2-3 meters along its length. At the surface, an eight inch foam buoy frame kept waves from spilling into the corral.

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 was approximately 53.2 m^3 (15,000 gallons). The corral 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 unit. Each corner of the corral unit was securely fastened to heavy anchors. The limnocorrals were anchored near the deepest section of Barr (Figure 1).

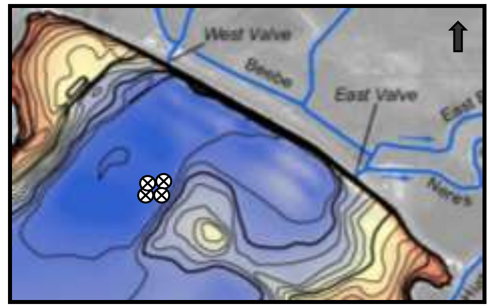


Figure 1. Limnocorral location at Barr Lake.

At the time of deployment, Barr was 8-m deep. The water elevation gradually declined through June and was 6.3-m by 06/27/12. Due to drought conditions and the typical irrigation demands, the reservoir dropped to 4.5-m by 07/23/12. The elevation continued to decline in August and reached 2.1-m by 09/21/12. By the end of the growing season, Barr's depth was 1.3-m. The rapid decline in reservoir depth and volume posed unforeseen challenges to this study and became an additional test variable. Because of the effects caused by the low water conditions, the study ended on 09/07/12.

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 ($Al(OH)_3$). This flocculation process then does two things: first the hydroxide floc binds with phosphorus by adsorbtion and then 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.

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.

Dosage

Application rate was based on laboratory jar testing conducted on 04/18/12, 05/09/12, and 05/16/12. Well mixed one liter water samples from Barr's epilimnion were tested with various amounts of alum. Then pH, Alk, TP, and soluble reactive phosphorus (SRP) were analyzed to determine the best ratio of alum to water to lower TP below 100 µg/L.

The final jar test on 05/16/12 indicated the appropriate alum dosage to be 11 liters per 53,200 liter corral (0.02 % by volume) to maintain pH above 6.5 and to lower TP. 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. Jar Testing Results for 05/16/12.

Jar (1 liter)	$pH_{initial}$ @ 8:30	Alum (ul)	pH @ 9:00	pH @ 10:30	pH @ 13:30	Al(pd)[1] (ug/L)	ALK (mg/L)	TP (ug/L)	SRP (ug/L)
1	7.95	0	7.26	7.30	7.29	29	159	1040	1030
2	8.00	20	7.24	6.92	7.23	324	145	140	0
3	7.99	80	7.16	6.78	7.22	485	128	60	0
4	8.01	140	6.97	6.95	7.19	484	114	50	0
5[2]	8.02	200	6.81	6.97	7.01	491	97	40	0
6	8.01	260	6.66	6.69	6.85	870	76	30	0
7	8.00	500	5.83	6.04	6.11	2310	27	60	0

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 11 liters of alum per corral.

Based on the jar testing, the dosage ratio of 200 µL of alum to one liter of water was used to calculate the alum dosage. Alk was below 100 mg/L, TP was below 100 µg/L, and the pH remained above 6.5. The ratio of 200:1 when the volume of each test corral was 53,200 liters allowed for 11 liters of alum to be added to each of the three test corrals. The final aluminum application rate was 12 mg of Al/L.

Application

Alum was added to corrals 2, 3, and 4 on 05/30/12. Corral 1 was the control so no alum was applied during the study. Eleven liters of liquid alum were applied to each of the three test corrals. During the application, the surface water was mixed with a paddle. pH was monitored before, during, and after the application.

Based on phosphorus lab results that were available two weeks after the first application of alum, it was determined that more alum was needed. In order to keep TP below 100 µg/L, another eight liters of alum were added to all three test corrals on 06/20/12. After another two weeks of monitoring, TP levels began to increase due to internal loading so anther eight liters of alum were added on 07/05/12. Again on 07/24/12, eight liters of alum were added to each test corral based on TP results. 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 05/30/12 to 09/26/12. 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 900 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 05/30/12, the corrals and open water were tested (Table 2). Water samples and profile data were collected. To satisfy the discharge permit pre-monitoring requirements, pH and DO data were collected on 05/23/12, once at 900 and then again at 1400, and $Al_{(PD)}$ data were also analyzed (Table 3).

Table 2. Pre-monitoring data collected on 05/30/12 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	410	360	3.0	3.3	7.94	162	6.06	77.7
Control Corral 1	400	360	2.0	3.4	8.19	157	8.96	113.9
Test Corral 2	390	340	3.4	3.4	8.11	159	8.19	104.5
Test Corral 3	400	360	2.9	3.3	8.24	156	9.55	117.9
Test Corral 4	360	320	5.2	3.6	8.21	155	9.09	112.3

Table 3. Pre-monitoring data collected on 05/23/12.

Location	Time	Depth	pH[1]	DO[1] (mg/L)	$Al_{(PD)}$[2] (µg/L)
Open Water	900	Top Half	8.05	5.60	
		Bottom Half	7.90	3.65	
	1400	Top Half	8.87	9.09	
		Bottom Half	8.84	8.03	
Control Corral 1	900	Top Half	8.18	7.13	5.81
		Bottom Half	8.08	5.70	
	1400	Top Half	8.10	7.66	
		Bottom Half	7.92	4.94	
Test Corral 2	900	Top Half	8.13	6.83	20.3
		Bottom Half	7.89	4.98	
	1400	Top Half	8.04	7.69	
		Bottom Half	7.93	5.53	
Test Corral 3	900	Top Half	8.13	6.55	5.31
		Bottom Half	7.99	4.52	
	1400	Top Half	7.99	7.41	
		Bottom Half	7.90	5.38	
Test Corral 4	900	Top Half	8.16	7.05	12.7
		Bottom Half	8.04	4.79	
	1400	Top Half	8.03	7.77	
		Bottom Half	7.94	5.48	

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

During-Monitoring

Both pH and DO were monitored in-situ immediately before application and then 30 minutes and three hours after the alum application (Table 4). 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 4. pH and DO depth integrated values during alum application on 05/30/12.

Location	Time	Depth	pH[1]	DO[1] (mg/L)
Test Corral 2	Before	Top Half	8.11	8.12
		Bottom Half	7.94	6.30
	30 minutes after	Top Half	6.33	9.07
		Bottom Half	6.60	6.86
	3 hours after	Top Half	6.54	10.53
		Bottom Half	6.53	7.56
Test Corral 3	Before	Top Half	8.22	9.38
		Bottom Half	8.06	7.63
	30 minutes after	Top Half	6.26	10.69
		Bottom Half	6.50	8.18
	3 hours after	Top Half	6.54	10.53
		Bottom Half	6.53	7.56
Test Corral 4	Before	Top Half	8.20	8.85
		Bottom Half	7.97	6.57
	30 minutes after	Top Half	6.77	9.98
		Bottom Half	6.51	7.67
	3 hours after	Top Half	6.78	12.78
		Bottom Half	6.47	7.79

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

Weekly Monitoring

Weekly monitored was conducted between 05/30/12 and 09/26/12. A total of 18 sampling events occurred during this period.

For the purpose of understanding how pH and Chl-a response to lower TP levels, summary of the data for the study only includes data from 06/05/12 to 08/07/12 (Table 5). The shallow, isolated water in the corrals was quickly depleted of oxygen in August and September which resulted in an increase in internal TP loading. The study period ended 08/07/12 due to the low reservoir volume, only the first 11 of the 18 sampling events were used in the data analysis.

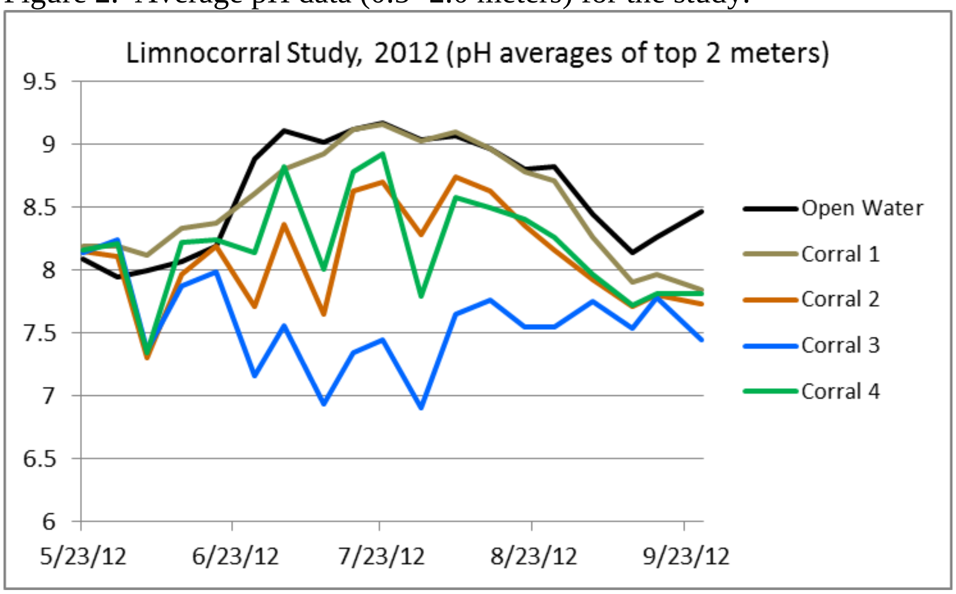
Table 5. Averages of weekly limnocorral data from 06/05/12 to 08/07/12.

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	3.24	447	339	6.3	50	1.4	9.08	164	8.15	115.1
Control Corral 1	3.61	392	308	6.8	25.2	1.9	9.06	156	8.09	113.1
Test Corral 2	3.50	276	209	9.7	11.6	2.6	8.63	139	6.77	94.4
Test Corral 3	5.25	137	80	32.4	2.8	3.8	7.77	95	7.45	103.8
Test Corral 4	3.75	290	169	10.5	62.5	1.7	8.69	138	8.62	120.7

1. pH is the 85th percentile for all pH values recorded between 06/05/12 and 08/07/12.

Profile data were also collected at all five locations on a weekly basis. All pH values for the three test corrals remained below 9.0 during the study (Figure 2). SD was also recorded at each site during each visit.

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



Post Monitoring

In order to remove the corrals from Barr and to satisfy the discharge permit, pH, DO, and $Al_{(PD)}$ standards all needed to meet specified water quality limits inside the three test corrals. The pH standard was met in all three corrals (Figure 2). Due to the low water depths in August and September, the DO in the test corrals was below 5.0 mg/L. The DO concentrations did increase due to cooler water temperatures. At the time of removal on 10/08/12, the water depth inside the corrals was only 1.3-m. DO in the open water near the corrals was measured before and after the removal of the corrals, and there were no measureable differences in DO after removing the corrals. Barr's dissolved oxygen saturation remained above 100% throughout the removal process.

The $Al_{(PD)}$ samples were collected on 08/14/12. Results were available from the laboratory by 09/20/12. The results showed an elevated concentration in two of the test corrals and also in the open water. The removal of the corrals was postponed. Additional aluminum samples were collected on 09/20/12. Again, there were mixed results with the open water exceeding the 87 µg/L standard (Table 6).

Based on communication with Andrew Neuhart on 10/04/12 from CDPHE, it was decided that the corrals could be removed based on the lower aluminum levels inside the corrals as compared with the surrounding open water aluminum concentrations. A possible explanation why the open water was high in aluminum is because of the drawdown of the reservoir and the re-suspension of the reservoir sediments.

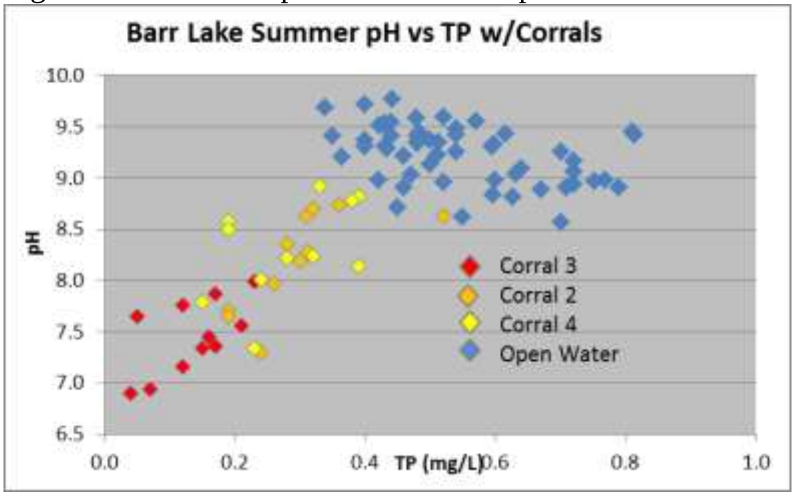
Table 6. Potentially dissolved aluminum data.

Location	Date	$Al_{(PD)}$ (µg/L)
Open Water	5/23/12	5.81
	8/14/12	127.0
	9/20/12	123.0
Test Corral 2	5/23/12	20.3
	8/14/12	74.0
	9/20/12	32.0
Test Corral 3	5/23/12	5.3
	8/14/12	112.0
	9/20/12	186.0
Test Corral 4	5/23/12	12.7
	8/14/12	176.0
	9/20/12	44.1

Results

The goal of this study was to determine the linkages between TP and various response variables. Previous to this study, there were no TP measurements below 400 µg/L. By using alum to reduce TP, data were collected on pH and Chl-a to better understand how the pH standard can be met at lower TP levels. pH data is now available at lower TP concentrations to determine what level of TP is necessary to bring pH below 9.0 (Figure 3).

Figure 3. Relationship between TP and pH.



TP & SRP

TP was reduced in the three test corrals but not lowered to the levels outlined in the pH TMDL, 100 µg/L maximum with an average of 40-60 µg/L. Due to potential internal loading and variablity between test corrals, the TP concentrations ranged from 40 – 390 µg/L. From table 5, corral 3 had the lowest TP values along with the lowest Alk, Chl-a, and pH and the highest SD and TN:TP ratio.

The readily available portion of the phosphorus, SRP, was the lowest in corral 3 also. The average SRP for corral 3 during the study was 80 µg/L.

Alk & pH

Alk was reduced in the test corrals due to the formation of sulfuric acid when the alum was added. The estimated background pH when Alk is 160 µg/L is close to 8.4. As the Alk was lowered, especially in corral 3, the background pH also was lowered.

Chl-a & Secchi Depth

Chl-a for the test corrals all remained under the goal of 25 µg/L. Water clarity is closely linked to Chl-a during the growing season. Again, corral 3 had the least Chl-a throughout the study; average Chl-a was 2.8 µg/L with a maximum concentration of 18.6 µg/L. The clarity in corral 3 was also the highest. The SD was visible to the bottom for most of the study. In contrast, test corral 4 had the highest Chl-a for the three test corrals; average Chl-a was 62.5 µg/L with a maximum concentration of 143 µg/L. Clarity was similar to the open water and the control corral. The average SD in corral 4 was 1.7-m.

It was obvious from the weekly sampling events that the three test corrals were responding differently to the same alum applications. Lower TP resulted in lower Chl-a, lower pH, lower Alk, and increased clarity.

Discussion

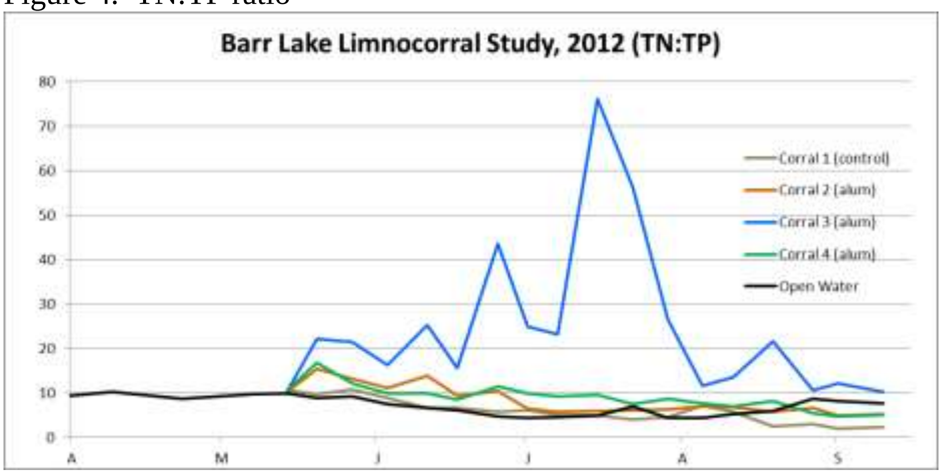
The variability among the three test corrals was unexpected. The reason for duplication in the study was to measure precision. The corrals were next to each other, they experienced the same environmental conditions, and they were sampled the same. The results should have been more similar.

There are no explanations why the three corrals produced three difference results. It took longer to position corral 4 in place, but all four corrals were assembled, anchored, and treated with the alum in the same way. Possibly the lake bottom sediments were different, but this is unlikely since the bottom of the reservoir is uniform in the area around the corrals.

Corral 3 had the best water quality while corral 4 had the worst water quality of the three test corrals. Corral 3 had the lowest Alk and the highest TN:TP ratio. Corral 3 was the only corral with a nutrient ratio higher than 10 (Figure 4). The average TN:TP ratio for corral 3 during the study was 32.4. Besides the lowest TP concentrations, corral 3 also had the highest nitrate/nitrite levels corresponding to the highest TN values.

The variability in the results helped populate the data gap in figure 3. By having a range of results, the graph was able to show a gradual increase in pH as TP went up. This variability will be tested in 2013 when new corrals are purchased and installed. The study will be repeated in 2013 to see if there are similar results when there is more water in the reservoir. Ideally, the data results between corrals should be comparable.

Figure 4. TN:TP ratio

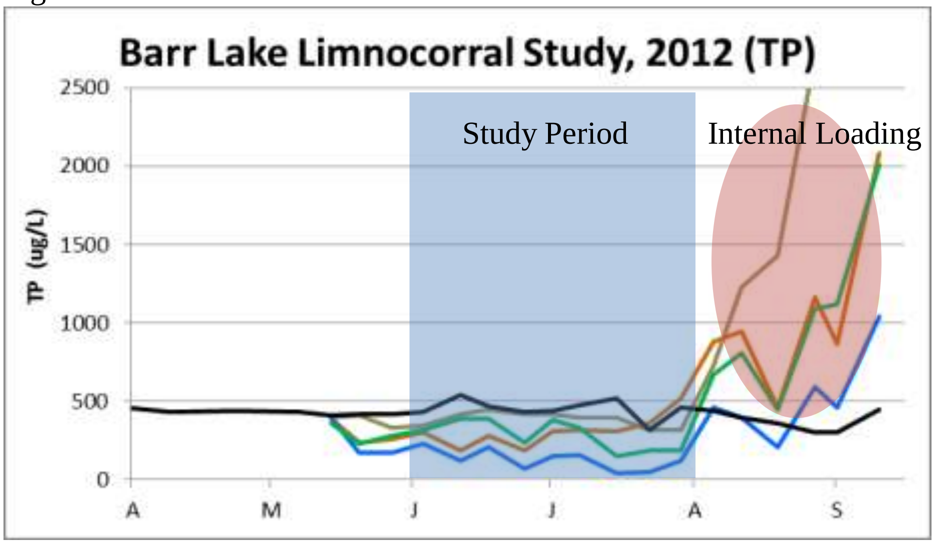


The TN:TP ratio and the Alk may have had a role in why corral 3 performed so well. The ratio of nitrogen to phosphorus >25 may play a major role in reducing the Chl-a. Phosphorus limitation will lower the pH by suppressing blue-green algae growth.

Clearly, the rapid decline in water elevation created an additional challenge. The study could have been more robust if additional data were available for August and September. For future limnocorral studies, it will be important to make sure the corrals are in the deepest area of the reservoir to maintaining maximum water depth and to minimize the potential for data variability.

For internal phosphorus loading, water less than 3-m in depth seems to trigger internal loading. The DO in the shallow, isolated corrals quickly dropped in August and September allowing the sediments to release phosphorus (Figure 5).

Figure 5. Barr Lake TP from 05/30/12 to 09/26/12



The TP in all four corrals significantly increased after 08/07/12, especially corral 1 that did not receive alum. Corral 1 went from 320 µg/L to 4,070 µg/L by 09/26/12. Corral 3 went from 50 µg/L on 08/07/12 to 1,040 µg/L by 09/26/12. The open water remained well mixed and oxygenated so the TP did not increase.

Conclusions

The goal to better understand the linkages between TP, Chl-a, Alk, SD, and pH in Barr was partially achieved. For the first time, water quality data were collected during the growing season when TP was below 200 µg/L.

As with many field studies, more questions were raised then answered. It would have been ideal to have all of the TP values below 100 µg/L but that was not achieved. Further studies will improve on the method to use alum to reduce TP below a desired amount. It is clear that the pH standard can be met in Barr when TP is reduced in a way that the TN:TP ratio favors a phosphorus limited system.

Besides the ratio of nitrogen and phosphorus, Alk plays an important role in keeping the pH below 9.0. Alk will need to be reduced along with TP. The Chl-a of 25 µg/L appears to be a reasonable upper boundary. With continued corral studies in 2013, it is hypothesised that a TP of 100 µg/L with Alk below 100 mg/L and a TN:TP ratio >25 will allow for the pH standard to be met.

For 2013, the corrals will be installed in a deeper area of Barr. The amount of time to get the TP results from the laboratory will be decreased, and the alum dosage of 11 mg of Al/L will be increased in order to maintain TP below 100 µg/L.