WATER QUALITY MANAGEMENT FOR pH CONTROL

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INTRODUCTION

In intensive aquaculture, high-density algal blooms can cause marked fluctuations in pH. As the bloom undergoes photosynthesis, the carbon dioxide concentration undergoes a diurnal cycle mirroring that of the dissolved oxygen. The relationship between photosynthesis and pH has been well documented (Tucker and Boyd, 1985). In some waters, the resulting evening pH readings have been observed at levels as high as 12.0, well into the lethal range for many species. Certain waters have been implicated as having a low buffering capacity and hence an increased probability of mortality due to high pH (Boyd, 1982; Durborow, 1986).

Boyd (1982) noted that in most natural waters, the pH during the high periods of photosynthesis will not exceed 9.5 to 10. He observed that the exception is those waters which have their alkalinity anions associated with sodium or potassium, rather than calcium. In water quality testing, this would be reflected by a calcium hardness which is low in comparison to the alkalinity.

Suggested methods of pH control in ponds have included injection of carbon dioxide; addition of acid-forming fertilizers; addition of strong acids (Boyd, 1982); and reduction of the algal bloom by use of flushing or herbicides. Most of these alternatives are too expensive, too dangerous, and too temporary to be practical. The most commonly accepted alternative is the addition of various salts in order to develop a good buffering system. Boyd (1979) tested a series of chemical additives for efficacy in controlling pH. Among those tested were lime, ammonia fertilizer, aluminum sulfate and calcium sulfate. Only calcium sulfate was recommended as feasible. The prescribed application rate was:

$$CaSO^4 \text{ (mg/l)} = (\text{Total Alkalinity} - \text{Total Hardness}) \times 2.2$$

Equation 1

This equation would increase the total hardness to a level equal to that of the total alkalinity.

After subsequent studies (Boyd and Mandel, 1980; Boyd, 1982). The equation was revised to:

$$CaSO^4 \text{ (mg/l)} = (\text{Total Alkalinity} - \text{Total Hardness}) \times 4.3$$

Equation 2

The doubling of the previously suggested level was intended to make the effects quicker acting and longer lasting. Boyd also stated that "further research on reducing pH in ponds is badly needed" (Boyd, 1982).

MATERIALS AND METHODS

Twenty-four plastic pools were constructed measuring 12 feet in diameter and 3 feet in depth (volume of 8800 1). The plastic pools were thoroughly leached with water to remove oils and received a 4 inch layer of mud from a cultured pond. The pools were then filled with well water which had characteristics typical of waters experiencing high pH fluctuations (Boyd 1982).

To insure that all pools would obtain adequate phytoplankton blooms, they were fertilized and inoculated with seed. Each pool was fertilized at a rate of eight pounds of phosphorus per acre. For the first testing period the fertilizer was not added until the twenty-second day of the experiment, due to the existence of adequate blooms in all of the pools at the beginning of the testing period. However, periods of low solar radiation and heavy rain decreased the blooms in some of the pools, resulting in a decision to fertilize the pools at that time. For the remaining experiments, the fertilizer was added at the beginning of the testing period. Twenty-five hundred milliliters of water from ponds containing heavy algal blooms was added to each pool to encourage algal bloom development within the pools.

An airstone was placed in each pool to prevent stratification and nocturnal oxygen depletion. After the completion of the first test, it was determined that the airstone failed to prevent stratification in some of the pools. To alleviate this stratification problem, airlifts were constructed. The airlifts were used for the remainder of the experiments conducted.

Water from the well and the pools was analyzed at the Agricultural Engineering Water Quality Laboratory located in the College of Veterinary Medicine Building. Analyses conducted at the laboratory included measuring temperature, pH, total alkalinity, calcium, and magnesium. The temperature and the pH of the pools were analyzed twice daily, once in the morning between 6:00 a.m. and 7:30 a.m. and once in the mid-afternoon between 1:30 p.m. and 3:00 p.m. during the testing periods. From the water sample taken in the mid-afternoon, analyses were periodically conducted for total alkalinity, calcium, and magnesium.

Testing Procedures. All analyses were performed according to Standard Methods for the

Examination of Water and Wastewater (1985). Determinations of metals in the water were conducted using atomic absorption spectrometry (Perkins-Elmer (1980) model 5000 atomic absorption spectrophotometer). Spectral analysis of the well water from the Aquaculture Research Unit agreed with a confirming analysis for calcium and magnesium conducted by the Mississippi Chemical Laboratory (Deliman, 1988).

Water pH was measured with a Fisher Accumet pH meter model number 825MP (Fisher, 1984). The Fisher pH meter values were checked with the values obtained with other pH meters.

Alkalinity values were obtained by using the electrometric titrator and procedures outlined in Standard Methods (1985). Periodic calibration checks were made during the testing periods to insure accurate results. Alkalinity values of the well water tested at the Agricultural Engineering Water Quality Lab agreed with the values obtained by Layne Central Company of Jackson, Mississippi.

Chemical Treatments. Previous studies by Boyd and Mandel (1980) indicated that agricultural gypsum showed a lasting effect in controlling pH of waters with low hardness and high alkalinity levels. The calcium contained in the agricultural gypsum would presumably increase the hardness to alkalinity ratio, thus eliminating the cause of the high pH. Based on this study, agricultural gypsum was selected as a chemical treatment. Other potential calcium sources, not tested by Boyd (1980), included calcium chloride and calcium carbonate. Calcium chloride and calcium carbonate would increase the hardness to alkalinity ratio due to the amount of calcium added as calcium chloride or calcium carbonate. Thus, calcium chloride and calcium carbonate were also selected as chemical treatments in the study.

Boyd and Mandel (1980) assumed that sediment absorbs a portion of the calcium added. For this reason several levels of each calcium treatments were tested.

Carbon Sources. It has been noted that ponds or lakes which receive their water from watersheds high in organic material (detritus) have the potential to experience low pH. The pH of humic acid, which is formed by the decomposition of carbon by microbes, may be as low as 4.0. Microbial activity within the pool is also a source of carbon dioxide due to respiration. The addition of carbon dioxide to the water results in the formation of carbonic acid, which lowers water pH, and also replaces carbon dioxide removed by photosynthesis. For this reason, different organic carbon sources were tested as a possible means of controlling pH.

The two carbon sources tested were glacial acetic acid and ground corn. The first carbon source, glacial acetic acid, was selected because of its ability to lower pH immediately. After the initial lowering of the pH, it was thought that microbial degradation of the acetyl fraction of the acid might help to maintain the pH at a lower level. The second carbon source selected was ground corn. Its selection was based entirely on its carbon content. Ground corn has one of the highest carbon and lowest nitrogen contents of ingredients used in feed mills. The ground corn was tested at different levels to determine its effectiveness.

Experiment 1. The first experiment was conducted to determine the effectiveness of calcium sulfate and calcium chloride in reducing pH. Each chemical was tested at three different calcium levels: 50%, 100% (both as $CaCO_3$); and 150% of the amount of calcium required to make the hardness and alkalinity equal. Each treatment was replicated three times. Three control pools were used with no added chemicals. These were fertilized and maintained in the same condition as the pools containing treatments throughout the experiments.

For the first test the difference between total alkalinity and total hardness was found to be 58.68 mg/l of $CaCO_3$. The chemical treatments were added on the morning of June 2, 1987 and concluded on July 1, 1987. Following the experiment, the pools were drained and then flushed twice to ready the pools for the next experiment.

Experiment 2. The second experiment was conducted to analyze the effects of calcium sulfate and calcium chloride at higher concentrations than those in the first test. Each chemical was tested at three different levels and replicated three times. Calcium sulfate and calcium chloride were added to levels 4x, 12x and 20x the difference between the total alkalinity and the total hardness. Since the same chemicals were tested as in the first experiment, the amount of chemical added for each treatment was calculated in the same manner.

A carbon source was also tested during the second testing period. Three pools (8800 1 each) received·500 milliliters of glacial acetic acid which contained 209.38 grams of carbon.

Again, three pools were used as controls and they received no chemical treatments. The treatments were added to the pools on July 22, 1987 and the experiment concluded on August 20, 1987. Following the experiment, the pools were drained and flushed twice to ready the pools for the next experiment.

Experiment 3. The third and final experiment was conducted to analyze the effects of calcium carbonate and ground corn. Three levels of calcium carbonate were tested and were replicated three times. Calcium carbonate was added to the pools at levels 1x, 2x, and 4x the difference between total hardness and total alkalinity.

The ground corn was added at three carbon levels and each level was replicated three times. The ground corn contained 71% nitrogen free extracts (National Academy of Sciences, 1971) which is usually interpreted to be carbohydrates. Based on this assumption, the amount of carbon contained in each treatment was calculated. The levels of carbon analyzed were 425 grams, 850 grams and 1700 grams in each 8800 1 pool.

The treatments were added on September 22, 1987. The calcium carbonate was put into solution before being added as a treatment. The ground corn was applied evenly across the surface. The experiment was concluded on October 16, 1987.

Experimental Design. All of the experiments were completely randomized according to the procedures outlined by Steele and Torrie (1980). The first and the third experiments were set up in a 2x3 factorial design. This was indicated by two chemicals being tested at three different levels and having each level replicated three times. The second test closely resembled a 2x3 factorial design, but cannot be classified as one due to additional testing of glacial acid. Since all of the experiments required taking data over a period of time, the experiments were further classified as repeated measurements and were analyzed as such. The common practice to analyze repeated measurement data from a completely randomized design is to use a split-plot-in-time analysis.

To conduct these tests all of the experimental data were initially entered onto a Lotus 1-2-3 (1985) spreadsheet. The data were then converted into an ASCII file so that it could be read by the SAS statistical program (1986). The data used for analyses are reported in Deliman (1988). The SAS (1986) statistical package was used to conduct all statistical analyses. In order to conduct statistical tests on the experimental data, each treatment was assigned an individual number. The numbers assigned to each treatment for each experiment are recorded in Table 1. In the results and discussion section, each treatment is referred to by the appropriate number.

RESULTS

Experiment 1. The sulfate and calcium chloride treatments were effective in increasing the total hardness (as $CaCO_3$) in the pools into which they were added. In most cases, both chemicals were effective in raising the total hardness to the calculated amounts. However, some of the treatments failed to reach the calculated total hardness levels. This supports Boyd and Mandel's (1980) suggestion that some of the calcium added is lost in the muds of the pools.

For each of the experiments, the treatments' evening pH values were converted to hydrogen ion concentrations, averaged, and then converted back into pH values.

All time periods tested for day and treatment interactions (1st week, 2nd week, 3rd week, 4th week, and overall effect of treatments), failed to conform to the sphericity test required in order to use a split-plot-in-time analysis. Therefore, the Greenhouse-Geisser adjusted degrees of freedom were used to determine the significance of the interactions. There was no significant interaction between day and treatments during any of the time periods tested ($\alpha<0.01$). Since there was no interaction between day and treatments, the Greenhouse-Geisser adjustment could also be used to test the significance of the treatments. There was also no significant difference between any of the treatments during any of the time periods tested ($\alpha<0.01$). The ranges of pH for the last day of the experiments are shown in Table 2.

Table 1. Treatment numbers as assigned to experiments

Experiment 1	Treatment Number
50% Calcium Sulfate	0
100% Calcium Sulfate	1
150% Calcium Sulfate	2
50% Calcium Chloride	3
100% Calcium Chloride	4
150% Calcium Chloride	5
Control	6
Experiment 2	**Treatment Number**
400% Calcium Sulfate	0
1,200% Calcium Sulfate	1
2,400% Calcium Sulfate	2
400% Calcium Chloride	3
1,200% Calcium Chloride	4
2,000% Calcium Chloride	5
500 ml Acetic Acid	6
Control	7
Experiment 3	**Treatment Number**
100% Calcium Carbonate	0
200% Calcium Carbonate	1
400% Calcium Carbonate	2
5,000g Ground Corn	3
7,000g Ground Corn	4
10,000g Ground Corn	5
Control	6

Experiment 2. In Experiment 2, the total hardness levels again increased after the addition of the treatments and in the pools which were treated with acetic acid. Treatments 2 and 3, the high and medium levels of calcium sulfate, never reached the hardness levels which were calculated. All other treatments were approximately in the desired ranges. This might be attributed to the loss of calcium sulfate to the mud in the pools, particularly at the high concentrations used. The average pH values during the experiment for the calcium sulfate and calcium chloride treatments are listed in Table 2.

The Greenhouse-Geisser adjustment factor was used to determine significance of day and treatment interactions due to the lack of sphericity among the data. The time periods tested for significant interactions included the 1st, 2nd, 3rd, and 4th week, and the overall effect of treatments (days 1,7,14,21,29). Using the Greenhouse-Geisser adjustment and testing for significance ($\alpha<0.01$), no significant day and treatment interactions occurred. Because of this, the treatments were also tested for significance using the Greenhouse-Geisser adjustment. All of the treatments tested during Experiment 2 failed to be significant during any of the time periods tested.

Experiment 3. The total hardness of the treatments tested during the third experiment produced unexpected results. The calcium carbonate treatments never reached calculated total hardness levels, and the treatments of ground corn experienced unusually high total hardness levels, although no additional calcium was added to the corn pools in the treatments. A possible explanation for this could be that corresponding low pH values during the experiment caused calcium to be released from the muds of these pools and that this calcium was put back in solution. The calcium dissolved from the muds could be either naturally occurring, or have been lost to the muds of some of the pools during previous experiments. The latter is less likely, since each pool was filled and rinsed between experiments.

Table 2. Ranges of pH for the last day of the experiments

Treatment Number	Range From	Range To
Experiment 1		
0	10.75	9.17
1	10.61	10.55
2	9.99	8.47
3	9.41	8.65
4	9.70	8.40
5	9.85	9.39
6	10.70	8.30
Experiment 2		
0	8.94	8.15
1	9.73	7.57
2	8.36	7.83
3	8.60	8.14
4	10.05	7.25
5	8.89	7.91
6	9.93	8.79
7	9.33	9.05
Experiment 3		
0	9.27	8.11
1	9.15	8.60
2	9.99	8.33
3	7.37	7.25
4	7.70	7.12
5	7.23	5.59
6	9.55	8.98

The pH values of the calcium carbonate treatments appeared to be below that of the control for most of the experiment. Most of the calcium carbonate treatments reached pH levels below the control by day 5. The exception was Treatment 2 which did not fall below the pH of the control until day 10 of the experiment. The ground corn treatments reached pH values well below that of the control by day 2 and continued to decline until day 8. The lowest pH achieved was in Treatment 5, where the largest quantities of corn were added, although the other corn treatments declined to near the same pH levels. The ground corn treatments maintained a lower pH from that of the control during the entire experiment.

Statistics conducted for day and treatment significance for the 1st, 2nd, 3rd, and 4th week, and overall effect (days 1,7,14,21,25) failed to conform to the sphericity test required to use split-plot-in-time analysis. Once again the Greenhouse-Geisser adjustment was used to test for day and treatment significance ($\alpha<0.01$). The statistical tests indicated that day and treatment interaction during the 1st, 2nd, and 4th week and overall effect were significant at an alpha value equal to 0.01. Therefore, these weeks were further analyzed to determine treatment significance using the procedure outlined. Since the 3rd week indicated that there was not a significant day and treatment effect during the time period, it was further tested for possible treatment effects by using the Greenhouse-Geisser adjustment. The treatment effects for the 3rd week proved to be significant. A Fisher's LSD test conducted on the treatments for the 3rd week indicated that the treatments which were significantly different were 3, 4 and 5 (the ground corn treatments).

Further analyses conducted on week 1, week 2, and the overall effect of the experiment indicated that only ground corn treatments 3 , 4, and 5 were significantly different. The combined treatment effect of 3, 4, and 5 versus the control was also significant ($\alpha<0.01$). At this alpha level the other treatment (calcium carbonate) tested was insignificant.

Additional analyses of week 4 data indicated that treatment 1 of the calcium carbonate treatments, and treatment 5 of the ground corn treatments were significant ($\alpha<0.05$). Treatments 3 and 4 of the ground corn treatments tested significant at both the alpha = 0.01 and 0.05 levels. The combined treatment effect of the calcium carbonate treatments versus the control was significant at the alpha = 0.05 level. The combined treatment effect of the ground corn treatments versus the control proved to be significant at both the alpha = 0.01 and 0.05 levels. This was the only week in which a calcium carbonate treatment was significant.

DISCUSSION

Despite the historical suggestion that the addition of calcium is an efficacious treatment for high pH in aquaculture waters, no statistically significant data supporting this practice were found in the study. Boyd (1982) recommended adding calcium sulfate at a rate of two times the amount required to equalize total hardness and total alkalinity. In this study, amounts of calcium sulfate were added at rates of 50%, 100%, 150%, 400%, 1200% and 2000% of the amount required to equalize total hardness and total alkalinity. All of the rates tested were not significant in controlling high pH ($\alpha<0.01$). The same amounts of calcium chloride were tested with the same results. Calcium carbonate was the only statistically significant calcium source in controlling high pH. It was significant ($\alpha<0.05$) only during the fourth week of the experiment in which it was tested.

While the calcium sources were not effective, the carbon sources were effective in controlling pH. Although not statistically significant, the glacial acetic acid was effective in immediately reducing the pH. However, this effect lasted only a few days. The ground corn treatments proved to be the most effective treatment in controlling pH. The ground corn was significant ($\alpha<0.01$) during all time periods tested with the exception of treatment 5 (1700 grams of carbon) during the fourth week. There are other potential sources of carbon, less expensive and perhaps longer lasting which should be tested.

Dissolved oxygen levels should be monitored in future experiments involving carbon sources as a possible solution to high pH problems. The pools in Experiment 3 which contained the highest levels of carbon became anoxic at the end of the testing period. When the pools were drained, an accumulation of ground corn was noticed. The accumulation of a carbon source on the bottom of a pond represents a potential threat to the dissolved oxygen levels. The low dissolved oxygen problems should be addressed in future experiments involving carbon sources.

Despite inoculating each pool with "seed" (water samples from other ponds) and fertilizing each with phosphorus, the concentration of algal blooms was extremely varied. Because high pH levels are usually associated with uptake of carbon dioxide during photosynthesis in pools containing heavy algal blooms, pools should be maintained with heavy algal blooms for experiments of this type. The experiments conducted indicated that the pools which contained the heaviest blooms were indeed the ones which achieved the highest pH levels for each treatment. An effort should be made in future experimentation to quantify photoplankton density present in each pool.

SUMMARY

1. Three different sources of calcium and two sources of carbon were tested to determine their effectiveness in controlling pH.
2. The different sources of calcium in Experiment 1, calcium sulfate and calcium chloride, were added at rates to increase the total hardness to levels of 50%, 100%, and 150% of the amount required to equal total alkalinity as $CaCO_3$.
3. The different sources of calcium in Experiment 2, calcium sulfate and calcium chloride, were added at rates to increase the total hardness to levels of 400%, 1,200%, and 2,000% of the amount required to equal total alkalinity as $CaCO_3$.
4. The source of calcium tested in Experiment 3, calcium carbonate, was added to increase the total hardness to levels of 100%, 200%, and 400% of the amount required to equal total alkalinity as $CaCO_3$.
5. 500 ml of glacial acetic acid was added as a carbon source (209 grams of carbon) in Experiment 2.
6. Three levels of organic carbon (425, 850, and 1700 grams) were added as ground corn in Experiment 3.
7. All of the calcium sources were successful in increasing the total hardness levels except for calcium carbonate.
8. The calcium sources that were successful in increasing the total hardness levels were also successful in maintaining the increased hardness levels for the duration of the experiment in which they were being tested.
9. Calcium sulfate and calcium chloride were shown to have no added treatment effects (control of high pH) at alpha = 0.01 level in Experiments 1 and 2 when tested for significance during the 1st, 2nd, 3rd, and 4th weeks, and for the overall effect of the treatments during the experiments.
10. The glacial acetic acid treatments proved to be insignificant during all time periods tested - 1st, 2nd, 3rd, and 4th week, and overall effect of the treatment during the experiment.
11. When the calcium carbonate treatments were tested for significance during the 1st, 2nd, 3rd, and 4th week, and overall effect of the treatments during Experiment 3, only treatment 1 (the 100% level) had a significant treatment effect at the alpha = 0.05 level during the 4th week.
12. The combined treatment effect of the calcium carbonate treatments were significant only during the 4th week at the alpha = 0.05 level during Experiment 3.
13. When testing the ground corn treatments for significance during the 1st, 2nd, 3rd, and 4th week, and overall effect of the treatments during Experiment 3, it was found that all of the ground corn treatments were significant at ($\alpha<0.01$) in all but i weeks data.
14. The combined treatment effect of the ground corn treatments were significant ($\alpha<0.01$) for all time periods tested except for the 4th week.
15. Since the calcium sources were not significant factors in controlling high pH, they should be abandoned and other methods of accomplishing this task should be examined.

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Acknowledgments. The research from which this material was derived was partially funded by the U. S. Geological Survey, Department of the Interior, as authorized by the Water Resources Act of 1984 (P.L. 98-242), the Mississippi Water Resources Research Institute, and Mississippi State University.