

ADJUSTMENT OF ALKALINE RESERVE OF LAKES AND PONDS BY ADDITION OF HYDRATED AND AGRICULTURAL LIME

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The various forms of carbonates function as the principal buffering agents in natural waters. The bicarbonate component in addition functions as a reservoir for carbon dioxide used by plants in photosynthesis. The relationship of liming to basic productivity has been demonstrated in several investigations (Ball, 1947; Maples, 1949; and Waters, 1957), although other investigations (Swingle, 1947; Johnson and Hasler, 1954) have failed to show an increase in fish production associated with liming.

The present work is especially concerned with the buffering activity of the carbonates. Schaeperclaus (1933) has investigated the relationship between the acid combining capacity (A.C.C.) of waters and their tendency to become too acid for fishes (Table 1). In two instances the authors have encountered A.C.C. values that Schaeperclaus classes as being low enough to permit water to "sour" and cause "fish-kills." The objective of the present work is to report the existence of waters of such unusually low A.C.C. and to demonstrate that it is practical to increase the A.C.C. values by the addition of hydrated and agricultural lime. Evidence of fish mortality resulting from low carbonate content is also presented.

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CHEMICAL METHODS

Water samples were taken with a one-liter Kemmerer sampler and chemical analyses were made immediately after collection. The pH values were determined by use of a Taylor colorimetric comparator.

Carbonates were measured in terms of the acid combining capacity of water, the method suggested by Schaeperclaus (1933). The determinations were made by titrating a 100 ml sample with 0.1N hydrochloric acid to the methyl orange end point. The A.C.C. values are equivalent to the number of milliliters used in titration. The relationship of A.C.C. values to total alkalinity is given in Table 1. These values may also be converted to total alkalinity by multiplying by 50.

ADJUSTMENT OF CARBONATES IN
HATCHERY PONDS

The first occurrence of water of unusually low A.C.C. was encountered at the Wheeler Minnow Hatchery, Murray, Kentucky. This hatchery consists of 30 one-third acre ponds supplied by water from a well 287 feet deep. The water is pumped to the ponds under 20 pounds of pressure throughout the summer and a portion of the winter. The flow into each pond is sufficient to give a flush rate of approximately four per cent of pond volume in 24 hours. The ponds are stocked at the rate of approximately 200,000 fingerling golden shiners (*Notemigonus crysoleucas*) per acre. The fish are artificially fed. Since construction and initial liming of the ponds in 1953, they received no further lime until the beginning of the present study. Thus ponds were not limed for approximately five years before the initiation of the study reported herein.

Investigations commencing February 18, 1959 revealed a combination of conditions to exist that produced extreme and changing pH values. First the well water supplying the ponds had a low buffering capacity (A.C.C. of 0.2), a high free carbon dioxide content (35 to 45 p.p.m.), and a corresponding low pH (5.0 to 5.5). Most of the ponds supported a pronounced bloom of unicellular algae. The low buffering capacity permitted the pH to fluctuate in proportion to the amount of free carbon dioxide accumulating in a particular pond. This carbon dioxide build-up, in turn, was controlled by the inflowing water of

high carbon dioxide content and, as a result of the removal of carbon dioxide, by photosynthesis during daylight hours. Thus the daytime sampling on February 18, 1959, following three days of complete overcast, revealed the following chemical conditions in four of the ponds: A.C.C., 0.2 to 0.5; free carbon dioxide 19-22 p.p.m., and pH 4.9 to 5.6. During a subsequent period of bright sunlight the pH values in mid-afternoon reached levels of 8.1 to 9.5.

The effects of the inflowing water of high carbon dioxide content upon the pH values of the poorly buffered water was demonstrated by nighttime pH values during and in the absence of normal flushing. When water was flowing into the ponds, the nighttime pH values were between 4.9 and 7.1, whereas 24 hours after inflow was stopped the values ranged from 6.3 to 7.0.

On February 20, 1959 experimental liming with hydrated lime ($\text{Ca}(\text{OH})_2$) was effected in six ponds with a view to raising the buffering ability of the water and stabilizing the pH. Hydrated lime was broadcast over the surface of the ponds at the rate of 50 pounds each. Water inflow to the ponds was stopped until the completion of observations on the addition of hydrated lime. Thirty days after the addition of hydrated lime (3/22/59) the A.C.C. values in the six treated ponds ranged from 0.6 to 1.0. The addition of hydrated lime successfully raised the buffering ability of the water and pH to levels suitable for fish, at least as long as the ponds were not flushed. The twenty-four untreated ponds, however, still had A.C.C. values less than 0.5 which

is in the danger zone for fish as shown by Schäeperclaus' evaluation (Table 1).

On the basis that finely-ground, agricultural lime might produce a more lasting buffering effect, even when the ponds are being flushed, all ponds were treated with agricultural lime (one ton per pond applied at the water's edge). This liming was done between March 23 and April 4, 1959. Water samples taken immediately after the liming (4/5/59) showed that 19 of the 30 ponds had A.C.C. values above 0.8, 10 ponds had values from 0.6 to 0.7, and only one pond had a value as low as 0.5 (Table 2). Seven days later the A.C.C. values ranged from 0.6 to 1.4, with the majority above 0.8. Without further liming, the A.C.C. values in all but one pond remained at or above 0.5 through 1959 and up to March of 1960 (Table 2).

The apparent success of agricultural lime in the above application might be attributable in part to the constant inflow of water of high carbon dioxide content and to the great extent of shoreline relative to the volume of water.

ADJUSTMENT OF CARBONATE CONCENTRATIONS IN LAKES

The second occurrence of an unusually low A.C.C. was found in Izaak Walton Lake at Christopher, Illinois. This lake has an average depth of seven feet and its water supply is entirely from surface runoff. The lake was constructed in 1938 and no liming had been done prior to the present study.

In July of 1959 the A.C.C. and pH values were found to be seriously low (Table 3). It was decided to attempt adjustment of the A.C.C. and pH by the addition of hydrated

TABLE 1.—Evaluation of Acid Combining Capacity (A.C.C.) and its Effects on Fishes (Modified from Schäeperclaus, 1933).

A.C.C. O or negative	Total Alkalinity p.p.m. CaCO ₂	Pond-cultural significance
	0-5	Water strongly sour, unusable for hatchery purposes; adding chalk (<i>i.e.</i> , lime) to the water unprofitable in most cases.
0.1-0.5 cc eq. 2-8 drops. (eq. 2.86-14 mg CaO per liter).	5-25	A.C.C. very low, pH rate mostly below 7. Great danger of water turning sour and of the pH rate reaching the acid danger point. Danger of dying off of fishes, pH rate variable, carbon dioxide supply poor, consequently water not very productive.
0.5 to 2 cc eq. 8 to 30 drops. (eq. 14 to 56 mg CaO per liter).	25-100	pH rate variable, carbon dioxide supply medium high, consequently mediocre productivity. No danger for the health of fishes, since a natural turning sour of the water is not to be feared.
2 to 5 cc eq. 30 to 75 drops. (eq. 56 to 140 mg CaO per liter).	100-500	pH rate varying only slightly, great optimal carbon dioxide supply, water very productive, health of fishes not endangered.
5 cc and above eq. 75 drops (eq. 140 mg CaO per liter).	500 and above.	Rarely to be found, pH rate very constant. An alleged decrease in productivity not proven. Health of fishes not endangered.

TABLE 2.—Effects of Adding Hydrated and Agricultural Lime on Acid Combining Capacity and pH of Pond Water at the Wheeler Minnow Hatchery, Murray, Kentucky.

Chemical Data	Condition of Ponds Before Treatment (2/18/59)		Condition of Ponds After Adding 50 lbs Hydrated Lime ¹		Condition of Ponds After Adding 2,000 pounds of Agricultural Lime Per Pond Between March 23 and April 4, 1959 ²					
	4	9-7.1	24 untreated	6 treated	4/5/59	4/12/59	1/9/60	2/6/60	3/8/60	3/28/60
pH		6.3-7.0	7.1-8.3		7.1-8.3	8.3-9.5	6.9-8.9	6.9-8.9	6.9-9.5	6.9-9.5
Range	0.2-0.5	0.2-0.5	0.6-1.0		0.5-1.4	0.6-1.4	0.5-1.0	0.5-1.0	0.5-1.0	0.5-1.2
A.C.C. Mean	0.8	0.8	0.8	0.7	0.7	0.8

¹ Water inflow was stopped for all ponds from 2/20/59, when hydrated lime was added, until 3/22/59 when water samples were taken. The stoppage of water inflow accounts for the increase in pH values of the untreated ponds.

² Water inflow was permitted following the addition of agricultural lime.

TABLE 3.—Effects of Adding Hydrated Lime on Acid Combining Capacity (A.C.C.) and pH, Izaak Walton Lake, Franklin County Illinois, 1959-1960.

Date	Station Number	Depth of Sample	pH	A.C.C.	Date	Station Number	Depth of Sample	pH	A.C.C.
1959					1960				
July 9	I	1 foot	7.4		May 21	I	1 foot	7.3	0.35
July 10	I	"	6.9		June 12	II	"	6.9	0.34
July 21	I	"	6.8	0.30	June 12	II	10 feet	6.9	0.28
July 25	I	"	5.8		June 19	Added 150 lbs lime.			
July 26	Added 500 lbs lime.				June 19	II	3 feet		0.38
July 26	I	1 foot	6.4		June 19	II	9 feet		0.43
July 28	I	"	5.9		June 25	Added 350 lbs lime.			
July 29	I	"	5.0	0.15	July 23	I	1 foot	7.7	0.48
July 30	II	"	5.2	0.18	July 24	Added 500 lbs lime.			
Aug. 6	I	"	7.7	0.45	Aug. 3	I	1 foot	7.7	0.48
Aug. 8	I	"	7.7	0.43	Aug. 13	I	"	7.5	0.48
Aug. 11	I	"	7.7	0.39	Aug. 21	I	"	7.7	0.48
Aug. 17	I	"	7.7	0.28	Aug. 28	I	"	8.0	0.48
Aug. 18	I	"	7.7	0.29	Aug. 28	Added 500 lbs lime.			
Aug. 21	I	"	5.2	0.20	Sept. 4	I	"	8.3	0.65
Aug. 22	Added 500 lbs lime.				Sept. 9	I	"	8.5	0.64
Aug. 24	I	1 foot	5.7	0.35	Sept. 11	I	"	7.5	0.48
Aug. 25	II	"	5.0	0.26	Sept. 19	I	"	8.0	0.80
TOTAL LIME ADDED IN 1959=1000 lbs					Sept. 25	I	"	8.0	0.80
MEAN A.C.C. (1959)=0.30					Oct. 3	I	"	8.5	0.80
1960					Oct. 5	Added 400 lbs lime.			
Jan. 9	I	3.0 feet	5.9	0.20	Oct. 9	Added 850 lbs lime.			
Jan. 9	II	10 feet	6.9	0.24	Oct. 9	I	1 foot	8.5	1.12
Feb. 28	II	"	6.9	0.24	Oct. 14	I	"	8.5	0.96
Mar. 6	II	1 foot	6.9	0.24	Oct. 23	I	"	8.5	0.96
Mar. 13	II	"	6.9	0.24	Oct. 30	I	"	8.0	0.96
Mar. 20	II	"	6.9	0.22	Nov. 6	I	"	8.0	0.96
Mar. 27	II	"	6.9	0.27	TOTAL LIME ADDED IN 1960=2,750 lbs				
April 3	II	"	6.9	0.28	MEAN A.C.C. (1960)=0.50				
April 10	II	"	6.9	0.28	1961				
April 17	II	"	6.9	0.28	Feb. 1	I	1 foot	7.5	0.75
April 24	II	10 feet	6.9	0.30	Feb. 1	I	3 feet	7.6	0.80
April 24	II	1 foot	6.9	0.28	Feb. 10	I	1 foot	6.9	0.70
April 25	II	"	6.9	0.28	Feb. 10	I	3 feet	7.0	0.75
April 25	II	10 feet	6.9	0.30					
May 14	II	1 foot	7.2						
May 14	II	10 feet	6.9						

¹ Station I at end of boat dock, maximum depth 3.6 feet; Station II middle of lake, maximum depth 10 feet.

lime. Hydrated lime, being readily soluble, could be applied over the total area of the lake. In the hatchery ponds it was necessary to accommodate for continuous flushing but this was not the case in Izaak Walton Lake.

The addition of 500 pounds of

lime on July 26, 1959 resulted in an increase in the pH and A.C.C. values for one week (Table 3). The second lime application on August 22, 1959 also produced a slight increase in pH and A.C.C. which was again followed by a drop in these values. By January of 1960 the lake

again had a low pH (5.9) and a low A.C.C. (0.2).

From January through June of 1960, the pH remained (for the most part) slightly below 7.0 and the A.C.C. remained at undesirably low levels.

A series of lime applications from June through October, totaling 2,750 pounds, resulted in pH values which remained above 7.0. The average of 17 A.C.C. determinations in 1960, before any lime was applied, was 0.28 whereas the average of 18 A.C.C. determinations after the lime application was 0.69. It is evident

from these data that the liming in 1960 established a more stable and desirable pH level (Table 3). Furthermore, the average of the A.C.C. values for 1960 was 40 per cent higher than in 1959, providing a level considered safe for fishes. Thus, at a cost of approximately forty dollars, the buffering ability of the water was brought to a desirable level.

EFFECTS OF LOW A.C.C. ON FISH SURVIVAL

In February 1959, the owner of the Wheeler Minnow Hatchery re-

TABLE 4.—Comparison of Acid Combining Capacity (A.C.C.), Carbon Dioxide, pH Values and Mortality of Golden Shiners in Laboratory Experiments.¹

A.C.C.		CO ₂ (p.p.m.)		pH	Per cent	Hour of
Range	Mean	Range	Mean	Range	Mortality	Mortality ²
0.40-0.90	0.54	4-35	23	5.7-6.8	0	73
0.40-0.90	0.54	6-58	28	5.6-6.8	0	73
0.46	0.46	71-73	72	5.4-6.7	50, 100	71, 96
0.40-0.54	0.44	6.12	9	7.5-7.7	0	48
0.28-0.82	0.41	6.70	15	6.9-7.0	100	142
0.38	0.38	3-10	7	6.9	0	25
0.32-0.40	0.36	8-11	9	7.1-7.3	0	16
0.29-0.57	0.36	5-53	30	25, 50	31, 55
0.25-0.40	0.34	4-54	33	5.5-7.2	0	73
0.20-0.45	0.33	5-19	10	50, 100	10, 25
0.22-0.48	0.32	3-113	16	6.9-7.0	25, 75	69, 247
0.21-0.45	0.30	3-33	20	5.6-6.9	50, 100	57, 70
0.29-0.30	0.30	5-53	31	5.5-6.5	25, 50	55
0.23-0.30	0.28	16-22	19	5.5-5.9	25, 100	24, 31
0.22	0.22	6-9	8	7.1-7.2	100	8
0.20-0.27	0.22	9-11	10	7.0-7.2	25, 50	8, 16
0.20-0.26	0.22	9-11	10	7.0-7.3	75, 100	8, 12
0.18-0.28	0.21	4-10	8	5.1-5.5	75	20
0.15-0.32	0.21	5-24	14	4.9-6.8	25, 100	20, 24
0.18-0.24	0.20	4-9	10	6.9-7.2	50, 75, 100	20, 24, 28
0.15-0.20	0.17	5-9	7	5.1	50	19
0.14-0.18	0.16	4-10	8	4.8-6.8	25, 100	20, 24
0.12-0.18	0.15	6-10	8	4.7-5.3	100	20
0.12-0.25	0.15	7-18	11	7.2-7.6	0	60
0.12-0.15	0.13	3-68	26	75	29

¹ Ten liters of water in glass aquarium were used in each experiment. Four golden shiners were placed in the aquarium at the start of each experiment and chemical data and mortality were checked approximately four times daily.

² In those cases where no (or incomplete) mortality occurred, the hour given represents the time the experiment was terminated.

ported the occurrence of a major "die-off" in several ponds of the hatchery. The fish formed dense aggregations at the pond surface and were covered with a white mucus. The owner also reported a similar occurrence in the spring of 1958, when nearly all the fish died.

The authors examined 40 fish, 10 from each of four ponds showing the highest mortality. Microscopical examinations revealed none of the common external parasites which frequently cause mortality among golden shiners. In the absence of surface parasites, the precipitated mucus present on the fish suggested a surface irritation which was apparently caused by an abiotic environmental variable.

Laboratory experiments were undertaken to simulate hatchery conditions. In these experiments, golden shiners were held in 10-liter aquaria which were continuously flushed with a small amount of water of specific carbonate and carbon dioxide levels. The results are given in Table 4.

Mortality was produced by the simulated conditions and was found to be inversely related to the A.C.C. The product-moment coefficient of correlation for this relationship was found to be -0.41 , significant at the 95 per cent level. A similar comparison between maximum carbon dioxide, mean carbon dioxide and minimum pH was not found to be significant.

The mortality produced in these experiments tended to confirm the belief that mortality in the ponds

was due to abnormal chemical conditions. The specific cause of death was a low pH resulting from the presence of a high carbon dioxide concentration in poorly buffered water.

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