HARDNESS, ALKALINITY, pH, AND POND FERTILIZATION

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Abstract: Many ponds in the southeastern United States have waters with less than 20 mg/l total alkalinity and should be limed to insure good response to inorganic fertilization. Water analysis is the only technique for determining if a pond needs liming, and the liming rate can best be estimated from a lime requirement determination of the bottom mud. In some waters total alkalinity may be high, but total hardness low. Such waters frequently develop dangerously high pH when fertilized. Alum rather than acid forming fertilizers should be used as emergency treatment to prevent fish kills during periods of high pH. Data on alkalinity and hardness are therefore needed when making fertilizer recommendations for individual ponds. Sufficiently accurate water analyses may be made with water analysis kits, provided reasonable care is exercised.

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Over the past 45 years, more than 1.7 million ponds have been built in the 16 member states of the Southeastern Association of Fish and Wildlife Agencies. Applications of inorganic fertilizer will greatly increase the production of sport fish in many of these ponds. H. S. Swingle and co-workers at Auburn University developed a popular pond fertilization program which consists of 8 to 12 periodic applications annually of 112 kg/ha of 8-8-2 or equivalent. This fertilization program has been used so widely over the past 30 years that many biologists give little or no thought to its efficacy. However, recent studies demonstrated that: (1) ponds in pastures often need little or no fertilization (Boyd 1976a); (2) current recommendations on pond fertilization call for about twice as much P_2O_5 as needed in woodland ponds with low or moderate fishing pressure (Dobbins and Boyd 1976; Lichtkoppler and Boyd 1977); (3) K_2O is not required for woodland ponds if waters contain more than 1.3 mg/l potassium (Dobbins and Boyd 1976); (4) nitrogen fertilization is not necessary in many sport fish ponds (Boyd and Sowles 1978). In addition, some ponds will not respond well to fertilization unless they are limed; and in some other ponds, fertilization leads to excessively high pH. The purpose of this paper is to discuss the importance of pH, alkalinity, and hardness in fertilized sport fish ponds.

DEFINITION OF TOTAL HARDNESS AND TOTAL ALKALINITY

Total hardness is a measure of the total concentration of divalent cations in water expressed in mg/l of equivalent calcium carbonate. In most natural waters, calcium and magnesium are the only divalent cations present in detectable concentrations. Total alkalinity is a measure of the total titratable bases in water expressed also in mg/l of equivalent calcium carbonate. Although many bases are present in water, bicarbonate and carbonate ions are responsible for nearly all the total alkalinity in most waters. Total alkalinity and total hardness values are normally similar in magnitude because calcium, magnesium, bicarbonate, and carbonate ions in water are usually derived from the solution of limestone in geological formations. In the following discussion, we will often use hardness and alkalinity to mean the same as total hardness and total alkalinity, respectively.

LIMING

Phytoplankton growth in soft, acid waters is limited by inadequate supplies of carbon dioxide or bicarbonate. The muds in soft water ponds are acid and strongly absorb the phosphorus added in fertilizer. Liming increases the pH of bottom muds making phosphorus more available, and increases the availability of carbon for photosynthesis by raising the bicarbonate ion concentration in the water (Boyd and

Scarsbrook 1974). Thomaston and Zeller (1961) reported that fertilized ponds in Georgia with less than 10 mg/l total hardness did not produce adequate plankton for good fish production unless they were limed. Responses to fertilization were variable in unlimed ponds with waters of 10 to 20 mg/l total hardness, but unlimed ponds with waters above 20 mg/l total hardness consistently produced adequate plankton after fertilization to provide good fish production. Boyd (1974) made similar observations on ponds in Alabama. The pH and concentration of free carbon dioxide in pond water is related to alkalinity rather than hardness. However, in many pond waters in the Southeast, hardness and alkalinity are of roughly the same magnitude (Boyd and Walley 1975). This was the situation in the ponds studied by Thomaston and Zeller (1961), but it is better to use alkalinity than hardness as an indicator of the need for lime. Some ponds may have hardness values that are smaller or larger than alkalinity values, and the use of hardness data can lead to erroneous conclusions regarding liming. Ponds having total alkalinity values above 20 mg/l, regardless of hardness, will seldom respond to liming, but the farther below 20 mg/l the alkalinity, the greater the response to liming. If ponds have total alkalinity values between 12 and 20 mg/l, the response to lime will not be great, and unless maximum fish production is the goal, the expense of liming may not be justifiable in some ponds.

In some physiographic areas, almost all ponds need lime while in other areas few ponds need lime. In the Black Belt Prairie region of Alabama and Mississippi, ponds typically have adequate alkalinities and few need lime (Boyd and Walley 1975). Ponds along the coast of Georgia normally have acid waters and need lime to promote survival and growth of fish. To illustrate, analyses of samples from 10 borrow pit ponds along Interstate 95 between St. Marys and Savannah are listed in Table 1. All of the ponds were

Table 1. Analyses of water samples from borrow pit ponds along Interstate 95 in Georgia.

Pond No.	*pH*	*Total hardness (mg/l as $CaCO_3$)*	*Calcium hardness (mg/l as $CaCO_3$)*	*Total alkalinity (mg/l as $CaCO_3$)*
1	4.40	9.14	4.96	0
2	5.20	12.02	6.95	2.0
3	4.35	29.49	13.50	0
4	5.05	30.98	22.14	1.3
5	4.40	15.09	6.36	0
6	6.50	8.34	5.46	1.4
8	4.85	11.42	4.17	0.6
9	4.80	5.16	1.99	0.4
10	5.50	5.36	3.18	3.6

too acid for good fish production and had alkalinity values below 5 mg/l. Low pH and total alkalinity values were caused by high concentrations of aluminum in the bottom muds. Data in Table 1 also illustrate that total hardness may not always be a suitable indicator for the need for lime as two of the ponds had hardness values above 20 mg/l and five had values above 10 mg/l, even though total alkalinity never exceeded 5 mg/l. The two examples given above are extreme situations, because in most physiographic regions ponds with alkalinities below 20 mg/l and ponds with alkalinities above 20 mg/l are encountered fairly frequently. This point is illustrated in Table 2 with data from ponds of the Piedmont Plateau Province and the Fall Line Hills belt of the Coastal Plain Province of Alabama. Ponds which contained more than 20 mg/l total alkalinity were often located within 1.6 kilometers or less of ponds which contained less than 10 mg/l alkalinity. In a series of samples from 390 ponds of all major physiographic regions of

Table 2. Distribution of total alkalinity values (mg/l as $CaCO_3$) in waters of ponds from the Piedmont Plateau Province and the Fall Line Hills belt of the Coastal Plain Province in Alabama.

	Total Number of samples	*Number below 10 mg/l*	*Number between 10 and 20 mg/l*	*Number above 20 mg/l*
Piedmont	51	16	21	14
Fall Line Hills	104	43	36	25

Alabama, 300 ponds had total alkalinity values below 20 mg/l. Analyses of samples from ponds in northern Florida, Georgia, Mississippi, and South Carolina also indicated that a large proportion of the ponds in these regions have total alkalinity values less than 20 mg/l. Nevertheless, the decision on whether or not a pond needs liming should be based on water analysis rather than guesswork.

When lime is added to a pond, it reacts with mud, and until enough lime is added to satisfy the lime requirement of the mud, little if any of the added lime will be available to increase the hardness and alkalinity of the water. A number of procedures are available for determining the lime requirement of agricultural soils (Pearson and Adams 1967; Yuan 1974) and these procedures are sometimes used to estimate the lime requirement of pond muds. Boyd (1974) modified the lime requirement procedure used by the Auburn University Soil Testing Laboratory (Adams and Evans 1962) so that it can be used to estimate accurately the amount of lime needed to raise the total alkalinity of the water in a pond to 20 mg/l or more. Few fisheries biologists have facilities for making lime requirement tests, so samples should be sent to a state soil testing laboratory for analysis.

Instructions for taking mud samples and applying lime are given by Boyd (1976b). Lime requirements of muds from shallow water are lower than those of muds from deeper water. Therefore, samples should be taken from different areas of the pond bottom and equal volumes of each sample composited and dried to give a single sample for lime requirement analysis. Adequate samples for most ponds require muds from 10 to 12 different sites. Agricultural limestone is the best liming agent to use in ponds. Hydrated lime(calcium hydroxide) and burnt lime (calcium oxide) have a higher neutralizing value than agricultural limestone, but if applied in large quantities, hydrated lime and burnt lime cause excessively high pH and fish mortality. Basic slag has a lower neutralizing value,than agricultural limestone, so extremely large applications of basic slag are needed. Although agricultural limestone can be easily applied to the bottom of empty ponds, application is more difficult when ponds are full of water. Best result may be achieved by broadcasting agricultural limestone evenly over the entire pond surface. Bags of limestone may be emptied from a moving boat. Bulk agricultural limestone is cheaper and may be applied from a plywood platform attached between two boats. Limestone should be applied during late fall or early winter so that it will react with water and bottom muds before fertilizers are applied in the spring. Agricultural limestone will precipitate phosphorus if applied at the same time as fertilizer. The residual effect of liming is governed by the rate of water loss to seepage and overflow. In ponds with normal rates of water loss, liming will usually last for 3 to 5 years. Once a pond has been limed, small annual applications (25% of the initial application) may be used to prevent the need for large applications of lime every few years.

HIGH pH

The pH of water increases rapidly when plants remove large amounts of carbon dioxide for use in photosynthesis. This results in an increase in carbonate concentration as carbon dioxide is removed as summarized in the following equation:

$$2HCO_3^- \rightleftharpoons CO_2 + CO_3^{2-} + H_2O$$

The pH is directly proportional to the carbonate ion concentration because carbonate hydrolyzes:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

Notice that the hydrolysis of carbonate ion only yields one bicarbonate ion while two bicarbonate ions must decompose to replace one carbon dioxide molecule. In most waters, pH will not exceed 9.5 or 10 in the afternoon because of the precipitation of carbonate by calcium ion. However, in some waters calcium hardness is much less than total alkalinity because alkalinity anions are associated with magnesium, sodium, or potassium rather than with calcium. Sodium and potassium carbonates are highly soluble, and magnesium carbonate is more soluble than calcium carbonate. Since large concentrations of carbonate may accumulate in waters where alkalinity is high and calcium concentrations are low, pH may rise to higher levels than encountered in waters of similar alkalinity, but with greater calcium concentration.

Well water sometimes has a high alkalinity, but low hardness, because of exchange of calcium and magnesium with sodium in the rocks and minerals of the aquifer (Hem 1970). For example, artesian well waters along the South Carolina coast often have alkalinities which are considerably higher than their hardnesses (Table 3), and ponds receiving the flow of the wells have alkalinity values considerably in excess of hardness values. The

Table 3. Analysis of well waters and of ponds filled by the well waters.

Sample	*Total Alkalinity (mg/l as $CaCO_3$)*	*Total hardness (mg/l as $CaCO_3$)*	*Calcium hardness (mg/l as $CaCO_3$)*
Wiggins, S.C.			
Well	313.2	37.4	11.3
Pond	93.2	26.9	17.1
Ruffin, S.C.			
Well	85.0	9.14	7.80
Pond	92.4	26.1	20.1
Williams, S.C.			
Well	60.1	14.1	12.5
Pond	59.2	17.1	11.9
Meridian, Miss.			
Well	136.0	21.8	17.1
Pond	93.0	15.1	11.5

alkalinity values of ponds are lower than those in well waters because of dilution by rainfall and surface runoff into the ponds. Fertilization of such ponds usually causes heavy plankton blooms and pH values are often high. Fish kills were observed in a number of these ponds in South Carolina when pH values exceeded 10 for prolonged periods. Well and pond waters at the National Fish Hatchery, Meridian, Mississippi, also have high total alkalinity and low total hardness (Table 3), and high pH and related fish kills occur periodically in ponds (Jack Frost, personnel communication). Waters with high alkalinity and low hardness do not occur frequently, but one should always analyze the water to make sure that the potential for problems with high pH does not exist when making fertilizer recommendations. Liming is of no benefit in ponds of this type.

Applications of ammonium fertilizers have been recommended to lower the pH of ponds waters (Swingle 1961). Ammonium ion from the fertilizer is nitrified with the production of hydrogen ion as follows:

$$NH_4 + 1\ 1/2O_2 \longrightarrow NO_2^- 2H^+ + H_2O$$
$$NO^2 + 1/2O_2 \longrightarrow NO_3^-$$

Not all of the ammonium will be nitrified and no research has been conducted to show that ammonium fertilizers will actually decrease the pH of pond water for prolonged periods. Ammonium sulfate used in South Carolina ponds at the rate of 224 kg/ha decreased the pH 2 to 3 units within 24 hours. However, intense algae blooms developed and the pH increased to near the original level within 3 weeks. Furthermore, at high pH, a large percentage of the ammonium ion from the fertilizer will be transformed to un-ionized ammonia which is highly toxic to fish (Trussell 1972).

Alum (aluminum sulfate) may be added to ponds to decrease pH. One can readily calculate the amount of filter alum($Al_2(SO_4)_3 \cdot 14H_2O$) needed to remove the measurable carbonate from water and cause the pH to fall to 8.34. Each molecule of filter alum yields 6 hydrogen ions in water (Sawyer and McCarty 1967) so each molecule of filter alum will convert 6 carbonate ions to bicarbonate or 6 hydroxide ions to water. The amount of filter alum needed to remove 1 mg/l of phenolphthalein alkalinity (expressed as mg/l $CaCO_3$) may be calculated as follows:

$$\begin{array}{lll} 594.14\text{ mg} & & 600.48\text{ mg} \\ Al_2(SO_4)_3 \cdot 14H_2O = 6H^+ & = & 6\ CaCO_3 \\ x & & 1\text{ mg/l} \end{array}$$

$$x = 0.99\text{ mg/l}$$

Therefore, approximately 1 mg/l of alum is needed to remove 1 mg/l of phenolphthalein alkalinity. Treatment with alum will cause an immediate reduction in pH. Alum treatment does nothing to alter the conditions responsible for excessively high pH, so if phytoplankton growth continues at a rapid rate following alum treatment, the pH will again rise to a dangerous level. However, alum treatment may be used to prevent a fish kill when the pH is too high.

The application of gypsum ($CaSO_4 \cdot 2H_2O$) will increase the calcium concentration in water. Gypsum treatment should decrease the likelihood of dangerously high pH during periods of rapid photosynthesis in waters with high alkalinity and low hardness, because the added calcium ion will precipitate carbonate as calcium carbonate. Experience indicates that gypsum application will moderate pH, but confirmatory research is needed. The amount of agricultural gypsum (80% purity) needed to increase the total hardness of water by 1 mg/l can be readily calculated as:

$$\begin{array}{ll} 172\text{ mg} & 100.08\text{ mg} \\ CaSO_4 \cdot 2H_2O = & CaCO_3 \\ 0.80x & 1\text{ mg/liter} \end{array}$$

$$x = 2.15\text{ mg/l}$$

Therefore, the amount of agricultural gypsum required to equalize total hardness and total alkalinity may be calculated by the equation:

Agricultural gypsum in mg/l = 2.15 (total alkalinity - total hardness)

Although agricultural gypsum will increase the total hardness of pond water, it is not a liming agent. Applications of gypsum will not neutralize acidity or increase the total alkalinity. this is important, because some biologists in the Southeast have incorrectly assumed that gypsum was a liming agent.

WATER ANALYSES

The discussion above illustrates the necessity for analyzing pond waters for alkalinity and hardness when making fertilizer recommendations. These data allow the biologist to make an intelligent decision regarding liming, and to identify ponds which may have problems with high pH. The standard procedures for these analyses are simple (American Public Health Association et al. 1975), but most biologists do not have access to a laboratory for preparing and standardizing the required reagents. Therefore, most biologists rely on water analysis kits. Boyd (1976c, 1977) recently demonstrated that Hach water analysis kits are suitable for obtaining data on hardness and alkalinity for use in pond management. For kits that employ the drop counting method of titrating samples, one drop of titrant equals a relatively large increment of alkalinity or hardness. For waters with low hardness or alkalinity, one should increase the sample size and proportionately reduce the factor which is multiplied by the number of drops of titrant in obtaining concentration. Determinations with water analysis kits employ small volumes of sample, so slight errors in measuring the volume of titrant are greatly magnified in the final results. Water samples should be analyzed as soon as possible after collection. The reagents in water analysis kits should be replaced annually to guard against deterioration.

Water analysis kits can also be used to obtain reasonably accurate estimates of pH (Boyd 1976c, 1977). However, the kits which employ color comparators usually read 0.5 to 1.0 pH units too high. Some biologists have portable pH meters. These workers almost invariably calibrate their meters with a buffer solution of pH 7.0. Meters which do not function properly can usually be set to pH 7.0 with the calibration controls. Therefore, one should periodically determine if the meter reads the pH of a second buffer (pH 5.0 or 9.0) correctly after it has been calibrated with a buffer of pH 7.0.

Reason must also be used in evaluating pH data. Fertilized ponds typically have high levels of photosynthesis and pH values may change by 2 or 3 pH units during a single day. The lowest pH values are in the morning and the highest in the afternoon. In ponds with heavy plankton blooms, pH is normally higher in the afternoon near the surface than at greater depths. It is not unusual to measure an afternoon pH of 9.5 to 10 in the surface water of any fertilized pond. This does not indicate that the fish are in danger of dying from high pH. They can seek refuge from the high pH in subsurface waters, and even if the entire pond has a pH of 10, the pH will usually decrease during the night. Fish kills because of high pH occur in ponds where the pH rises above 10 throughout the epilimnion and remains this high for a prolonged period.

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