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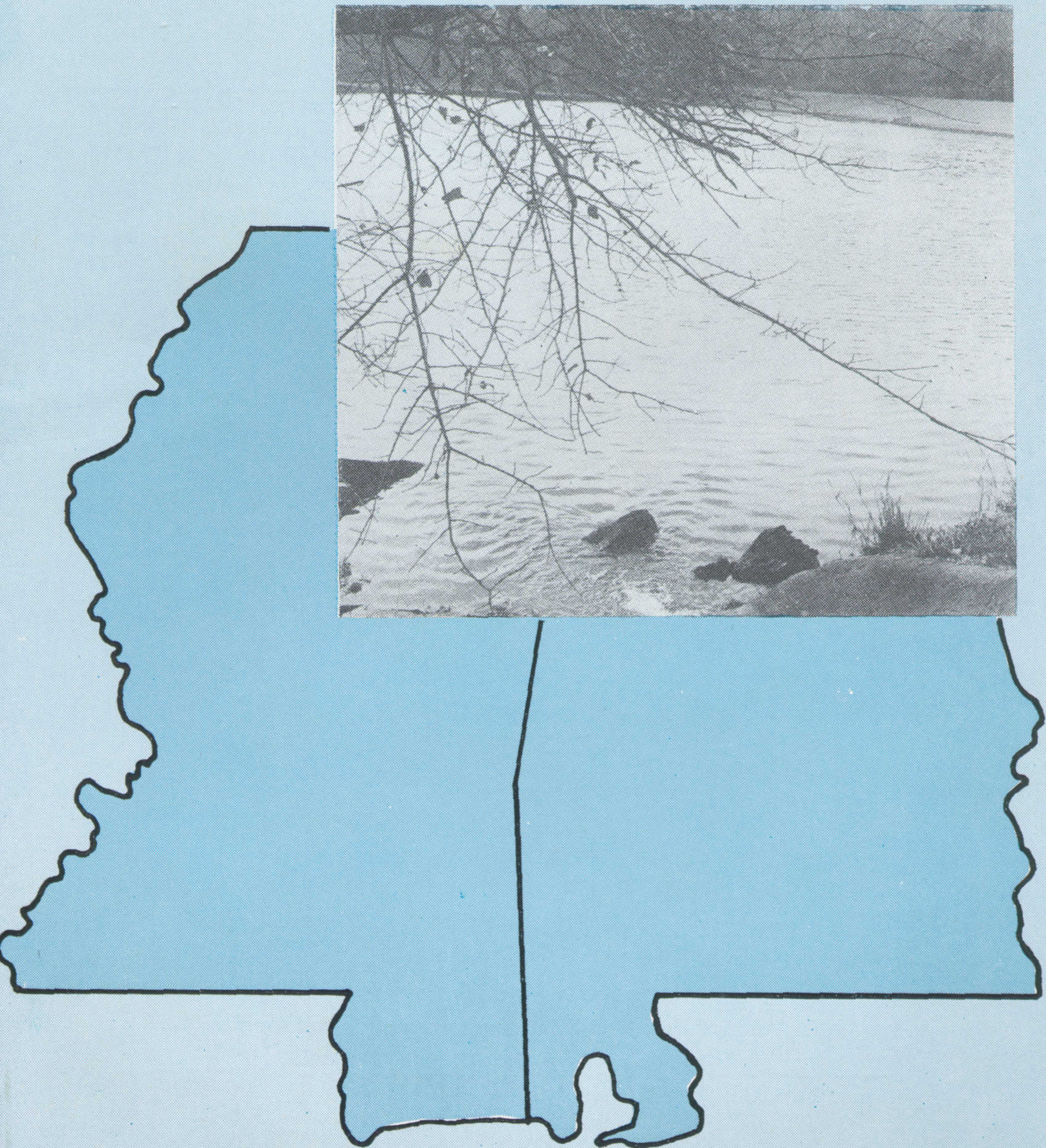
Total Alkalinity and Hardness of Surface Waters in Alabama and Mississippi



AGRICULTURAL EXPERIMENT STATION/AUBURN UNIVERSITY
R. Dennis Rouse, Director
Auburn, Alabama

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Total Alkalinity and Hardness of Surface Waters In Alabama and Mississippi

CLAUDE E. BOYD and W. WAYNE WALLEY*

A NUMBER OF WORKERS reported that fish production in unfertilized waters increased with increasing total alkalinity *(2,3,9, 10,18,19,25,26)*. The importance of total alkalinity as a limnological variable was discussed by Mairs *(16)*, who concluded that biological productivity was generally greater in waters with high alkalinity than in waters with low alkalinity. Generally, ponds with low alkalinity must be limed for fertilization to be effective in increasing plankton and fish production *(4,12,22,24,28)*. Alkalinity is also an important variable influencing the distribution of aquatic plants (7,17,27). Considerable data are available for total alkalinity of surface waters in the New England States where waters of high alkalinity are restricted to areas of extensive limestone *(6,16)*. Moyle *(19)* prepared an atlas to the total alkalinity of surface waters in Minnesota where the magnitudes of total alkalinity values were related to the types of geologic formations. Shoup *(21)* reported data for 371 streams in Tennessee, where levels of total alkalinity were generally correlated with the nature of geological formations comprising stream beds and soils. Zeller and Montgomery *(28)* reported that total hardness of pond waters in Georgia varied among soil regions and only ponds of the limestone belt in northwestern Georgia had hard waters. Total alkalinity was not measured.

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* Associate Professor, Department of Fisheries and Allied Aquacultures, Auburn University and Chairman, Department of Biology, Belhaven College, Jackson, Mississippi.

The present report contains data on total alkalinity, total hardness, and calcium hardness of surface waters from the major physiographic divisions of Alabama and Mississippi.

MATERIALS AND METHODS

Samples of surface water were collected from small streams (6 to 60 feet wide) and ponds during the summer and fall of 1965, 1971, and 1973. Some ponds of the Yazoo Basin were small bayous of natural origin, but all ponds in other areas were man-made. Ponds varied in size from 0.1 to 50 acres and most were filled entirely by direct precipitation and runoff. A small percentage of the ponds also received the flow of streams or springs. Collections were made only during periods of dry weather when streams were at low or medium flow and ponds were not swelled by recent runoff. Sampling sites were not selected unless their locations could be plotted accurately on highway maps and physiographic identities made with certainty.

Each body of water was sampled only once. However, since there are relatively small temporal changes in total alkalinity of most lakes and the alkalinity of streams does not fluctuate greatly with season in humid regions, this procedure seems justifiable *(15,16,20)*.

The physiographic map presented by Fenneman *(8)* was modified by deletion of some restricted belts of the Coastal Plain (Ripley Cuesta, Buhrstone Cuesta, and Hatchetigbee Anticline). This map was enlarged to the same scale as maps bearing locations of sampling sites and reproduced on transparent paper. Dots representing sampling sites were then accurately plotted on physiographic maps by tracing.

Samples were stored in polyethylene or glass bottles and analyzed as soon as possible (usually 2 days or less). Standard procedures were employed for chemical analyses *(1)*. Total alkalinity was estimated by titration to the methyl orange endpoint with 0.02 N (normal) sulfuric acid. Total hardness was determined by titration with 0.01 M (molar) EDTA (Ethylenediaminetetraacetic acid) using eriochrome black-T as the indicator. Calcium hardness was determined by EDTA titration to the murexide endpoint and approximate concentrations of calcium and magnesium ions were calculated from data on total and calcium hardness.

RESULTS AND DISCUSSION

The Coastal Plain province comprises almost all of Mississippi and about two-thirds of Alabama. The belted formations of the Coastal Plain are sedimentary in origin and of Cretaceous or younger age. Other physiographic provinces in the two states include the Interior Low Plateaus in the extreme northeast corner of Mississippi and the Piedmont, Ridge and Valley, Appalachian Plateaus, and Interior Low Plateaus in Alabama. Formations of these four provinces are Paleozoic in age. Underlying rocks of the Piedmont are metamorphic, while the other three provinces are underlain by sedimentary deposits. Geological data regarding these provinces were obtained from Fenneman *(8)*, Hodgkins *(13)*, and Hunt *(14)*.

Streams are numerous throughout Alabama and Mississippi, but with the exception of bayous in the Yazoo Basin of Mississippi, natural lakes and ponds are rare. Many ponds have been constructed in both states. The Alabama Department of Conservation estimates that Alabama has about 30,000 fish ponds with a total area of approximately 100,000 acres. Reliable estimates of the number and total area of ponds in Mississippi are not available. A number of large reservoirs (larger than 500 acres) have also been constructed in both states, but these reservoirs were not considered in this study.

The distribution of 729 total alkalinity values, 308 for streams and 421 for ponds, is illustrated in figures 1, 2, 3, and 4. Earlier reports accepted 40 mg. per l. total alkalinity as a reasonably good division between hard and soft waters for biological purposes *(16,17,18,19)*. However, the three illustrated intervals for soft waters between 0 and 40 mg. per l. total alkalinity, figures 1, 2, and 3, were chosen for convenience. Averages and standard deviations for total alkalinity values of each physiographic region are listed, tables 1 and 2.

The total alkalinity of stream waters was closely related to the nature of subsurface formations. Waters from streams of the Fall Line Hills, Pine Meadows, Southern Pine Hills, and Red Hills usually had less than 20 mg. per l. total alkalinity. These belts of the Coastal Plain are underlain primarily by sands. Calcareous formations of the Black Belt and the heavy clay alluvium of the Yazoo Basin yielded waters of high alkalinity. Values were usually above 100 mg. per l. and occasional samples had total

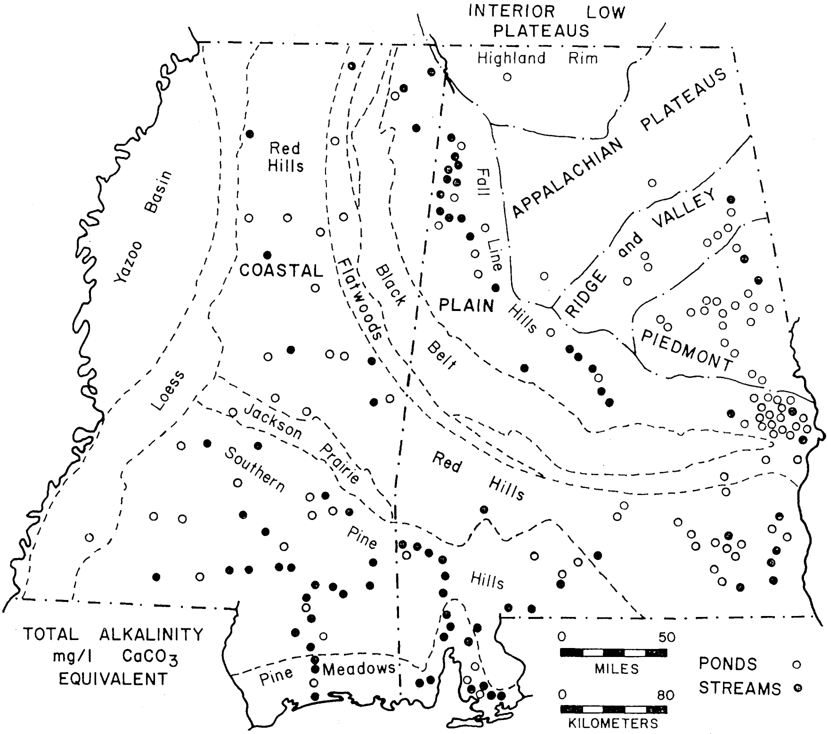

FIG. 1. Distribution of total alkalinity values less than 10 mg per l. in waters of ponds and streams of Alabama and Mississippi.

alkalinity levels above 300 mg per l. Subsurface formations of the Flatwoods, Jackson Prairie, and Loess Hills of the Coastal Plain usually have a high clay content. Waters from streams of these areas were intermediate in total alkalinity. Gneiss, schists, marble, and quartzite comprising formations of the Piedmont are relatively insoluble and stream waters of this province had low total alkalinity. Stream waters of high alkalinity were frequently encountered in the Ridge and Valley, Appalachian Plateaus, and Interior Low Plateaus, reflecting the extensive deposits of limestone in these provinces. Occasional soft water streams of these provinces apparently issued from local deposits of sandstone.

Along the Coastal Plain, total alkalinity of pond waters was greatest for ponds on fertile loam and clay soils and lowest for ponds on unproductive sandy soils. Ponds of the highly fertile

Yazoo Basin and Black Belt usually had waters with high alkalinity (greater than 40 mg. per l.), while most ponds of the Jackson Prairie, Loess Hills, and Flatwoods had waters of intermediate alkalinity (20 to 40 mg. per l.). Local areas of sandy or acid soils exist in the Black Belt where ponds contained between 20 and 40 mg. per l. total alkalinity. Likewise, a few ponds with water of very low alkalinity (less than 20 mg. per l.) were present on poorer soils of the Jackson Prairie, Loess Hills, and Flatwoods. Soils of the remainder of the Coastal Plain are often sandy, and as a rule, ponds had water of low alkalinity. Percentages of ponds with less than 20 mg. per l. total alkalinity were: Pine Meadows 87.5 percent, Fall Line Hills 76.2 percent, Southern Pine Hills 68.4 percent, and Red Hills 78.8 percent. However, ponds on the more fertile soils of these areas had waters with 20

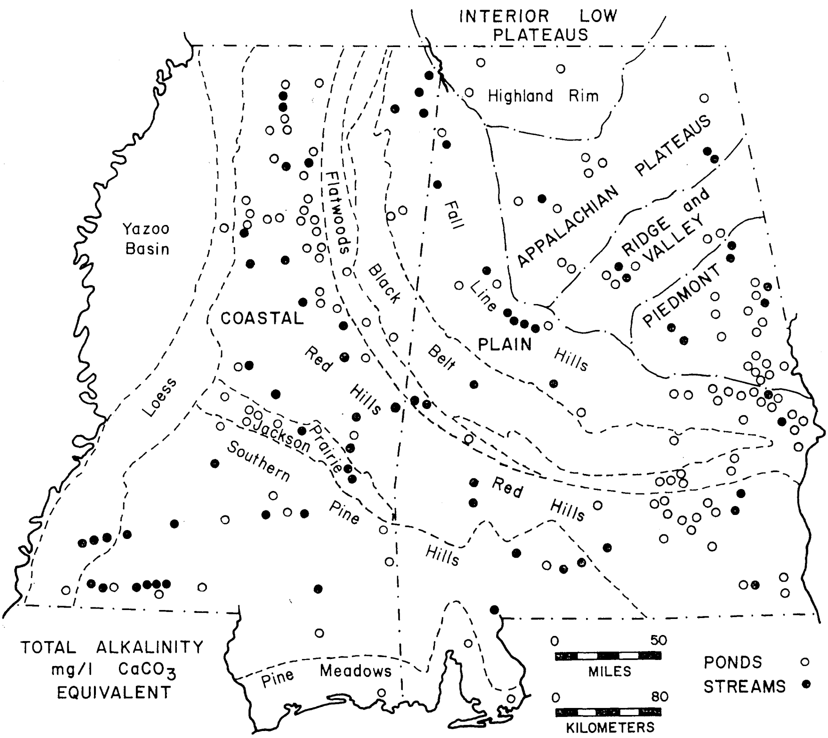

FIG. 2. Distribution of total alkalinity values between 10 and 19.9 mg per l. in waters of ponds and streams of Alabama and Mississippi.

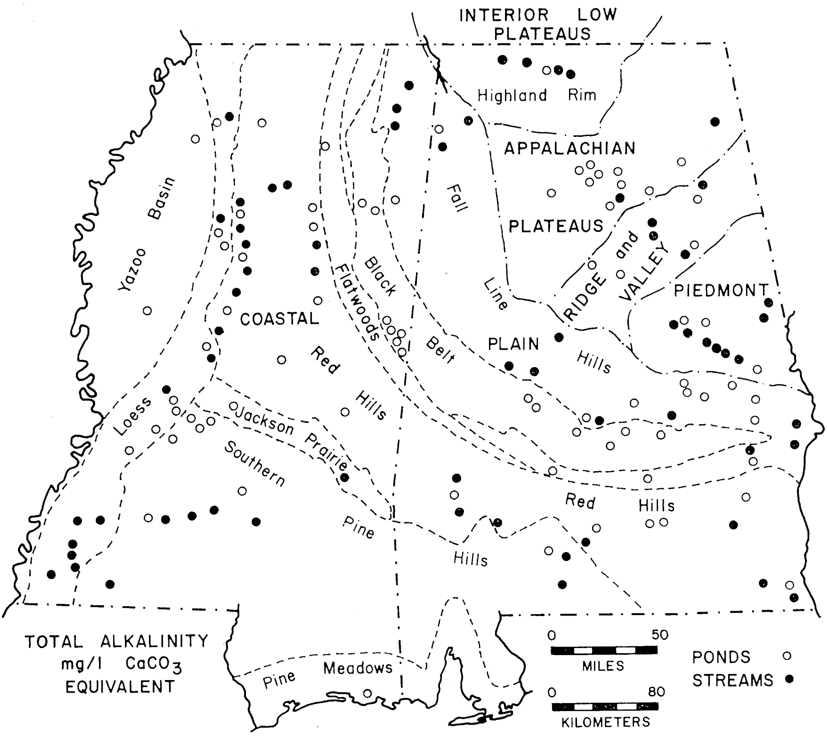

FIG. 3. Distribution of total alkalinity values between 20 and 40 mg per l. in waters of ponds and streams of Alabama and Mississippi.

to 40 mg. per l. alkalinity. A few ponds with distinctly alkaline waters (greater than 40 mg. per l.) were also located. These ponds either received runoff from local calcareous soils or were filled by flow from springs issuing from local deposits of limestone. For example, ponds near Auburn, Alabama, typically had water with less than 20 mg. per l. total alkalinity, but Palmer's Pond located 5 miles southeast of Auburn contained water with a total alkalinity of 81.5 mg. per l. Examination of the watershed revealed that Palmer's Pond received flow from a spring of a limestone deposit. All ponds located on the acid, base-deficient soils of the Piedmont province contained soft waters. Total alkalinity values for waters of ponds of the Interior Low Plateaus, Appalachian Plateaus, and Ridge and Valley provinces were distributed among all four illustrated intervals. This wide range in total alkalinity of pond waters reflected the great local variation in soils of these provinces.

In general, stream waters of a particular physiographic area had higher values for total alkalinity and total hardness than pond waters, tables 1 and 2. Waters of streams during periods of low flow consist primarily of ground water entering where streams cut below the water table. Ground water has relatively long contact with rocks and soils under reducing conditions and at high concentrations of carbon dioxide *(11,15)*. These circumstances favor solution of minerals, and ground water is normally more concentrated with ions than runoff, which has rather brief contact with surficial rocks and soils. Most of the ponds sampled in this study were filled largely or entirely by direct precipitation and runoff. Such waters were usually less concentrated with ions than ground water.

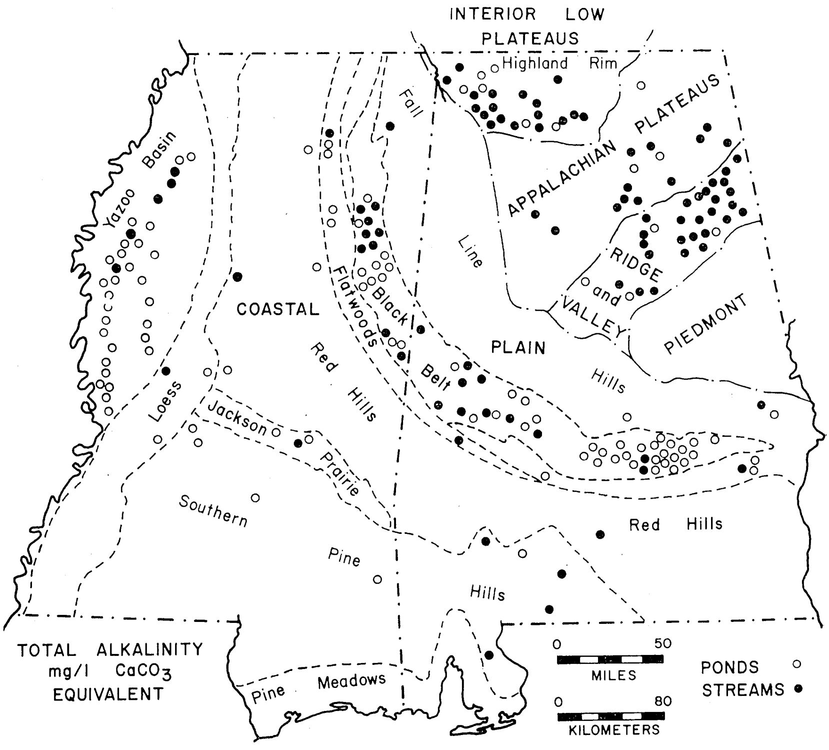

FIG. 4. Distribution of total alkalinity values above 40 mg per l. in waters of ponds and streams of Alabama and Mississippi.

There was usually a high correlation between total alkalinity and total hardness, tables 3 and 4, and values for total alkalinity and total hardness were usually of similar magnitude, tables 1 and 2. These observations suggest that both total hardness and total alkalinity in waters of most physiographic areas were de-

TABLE 1. AVERAGE ± ONE STANDARD DEVIATION FOR TOTAL ALKALINITY, TOTAL HARDNESS, AND CALCIUM HARDNESS VALUES FOR WATERS FROM PONDS AND STREAMS OF DIFFERENT BELTS OF THE COASTAL PLAIN PROVINCES OF ALABAMA AND MISSISSIPPI. CALCIUM TO MAGNESIUM RATIOS ARE ALSO PRESENTED

Description of samples		Total alkalinity	Total hardness	Calcium hardness	Ca/Mg ratio
		mg/l	*mg/l*	*mg/l*	
Pine Meadows	Streams	6.4 ± 4.1	----	----	----
	Ponds	10.6 ± 6.3	----	----	----
Southern Pine Hills	Streams	14.5 ± 13.2	16.7 ± 15.3	11.4 ± 12.6	3.53
	Ponds	18.9 ± 16.7	14.5 ± 15.4	10.8 ± 13.1	4.80
Jackson Prairie	Streams	40.9 ± 45.9	44.6 ± 49.7	38.7 ± 48.2	10.82
	Ponds	25.8 ± 19.9	25.9 ± 24.0	20.0 ± 21.3	5.80
Red Hills	Streams	20.3 ± 16.2	18.1 ± 10.5	11.8 ± 7.7	3.08
	Ponds	16.5 ± 15.2	14.5 ± 13.6	9.2 ± 7.1	2.85
Flatwoods	Streams	29.8 ± 39.3	77.7 ± 81.4	42.5 ± 40.8	1.99
	Ponds	34.4 ± 30.1	33.3 ± 30.0	25.7 ± 23.5	5.48
Black Belt	Streams	112.5 ± 73.6	113.8 ± 66.3	103.6 ± 65.0	16.93
	Ponds	56.8 ± 23.6	57.8 ± 26.8	53.3 ± 26.6	19.58
Fall Line Hills	Streams	21.9 ± 31.6	25.1 ± 46.7	16.7 ± 32.6	3.28
	Ponds	16.0 ± 12.5	14.6 ± 12.5	10.5 ± 11.1	4.24
Yazoo Basin	Streams	154.5 ± 117.8	88.5 ± 104.3	52.7 ± 55.7	2.43
	Ponds	101.2 ± 69.4	59.2 ± 42.4	37.1 ± 20.6	2.79
Loess Hills	Streams	40.1 ± 54.2	48.2 ± 58.3	28.4 ± 31.7	2.63
	Ponds	24.9 ± 18.3	14.4 ± 8.1	8.7 ± 5.7	2.52

TABLE 2. AVERAGE ± ONE STANDARD DEVIATION FOR TOTAL ALKALINITY, TOTAL HARDNESS, AND CALCIUM HARDNESS VALUES FOR WATERS FROM PONDS AND STREAMS OF FOUR PHYSIOGRAPHIC PROVINCES IN ALABAMA. CALCIUM TO MAGNESIUM RATIOS ARE ALSO PRESENTED

Description of samples		Total alkalinity	Total hardness	Calcium hardness	Ca/Mg ratio
		mg/l	*mg/l*	*mg/l*	
Piedmont	Streams	24.2 ± 17.0	17.9 ± 14.9	11.1 ± 11.9	2.69
	Ponds	12.8 ± 5.4	10.5 ± 5.4	6.9 ± 3.8	3.17
Ridge and Valley	Streams	84.6 ± 43.5	83.9 ± 45.5	60.2 ± 37.9	4.19
	Ponds	24.1 ± 19.7	22.0 ± 20.0	17.0 ± 16.5	5.63
Appalachian Plateaus	Streams	76.6 ± 48.3	81.6 ± 54.0	57.9 ± 43.6	4.03
	Ponds	24.6 ± 18.5	22.8 ± 19.0	17.3 ± 17.3	5.21
Interior Low Plateaus	Streams	96.8 ± 50.8	98.9 ± 51.6	87.1 ± 49.1	12.15
	Ponds	40.2 ± 28.2	40.8 ± 28.7	33.1 ± 24.9	7.09

rived from solutions of calcium and magnesium carbonates. Significant exceptions to relationships between hardness and alkalinity were noted in waters of streams of the Flatwoods, ponds of the Loess Hills, and ponds and streams of the Yazoo Basin, tables 1 and 3. In the case where total hardness greatly exceeded total alkalinity, sulfate ions were proportionally more abundant. Sodium and potassium were associated with alkalinity anions in situations where alkalinity greatly exceeded hardness.

Calcium was more abundant than magnesium in all waters and average Ca to Mg ratios of 2.0 to 6.0 were usual, tables 1 and 2. Waters of the Black Belt had especially high Ca to Mg ratios since the Selma Chalk formations of this belt are calcitic rather

TABLE 3. EQUATIONS FOR CALCULATING TOTAL HARDNESS ($\hat{Y}$) IN mg/l EQUIVALENT $CaCO_3$ FROM TOTAL ALKALINITY (x) IN mg/l EQUIVALENT $CaCO_3$. EQUATIONS ARE BASED ON SAMPLES FROM PONDS AND STREAMS OF DIFFERENT BELTS OF THE COASTAL PLAIN PROVINCE OF ALABAMA AND MISSISSIPPI

Description of samples		Equation	Coefficient of determination (r^2)
Southern Pine Hills	Streams	$\hat{Y} = 3.439 + 0.898x + 0.0007x^2$	0.65**
	Ponds	$\hat{Y} = 4.750 + 0.300x + 0.0066x^2$	0.72**
Jackson Prairie	Streams	$\hat{Y} = 9.316 + 0.564x + 0.0036x^2$	0.99**
	Ponds	$\hat{Y} = 5.727 + 0.288x + 0.0127x^2$	0.97**
Red Hills	Streams	$\hat{Y} = -2.647 + 1.319x - 0.0090x^2$	0.82**
	Ponds	$\hat{Y} = 1.457 + 0.761x + 0.0009x^2$	0.90**
Flatwoods	Streams	----------	0.04
	Ponds	$\hat{Y} = -2.428 + 1.100x - 0.0010x^2$	0.98**
Black Belt	Streams	$\hat{Y} = 9.126 + 1.064x - 0.0008x^2$	0.83**
	Ponds	$\hat{Y} = 7.584 + 0.694x + 0.0028x^2$	0.86**
Falls Line Hills	Streams	$\hat{Y} = 2.577 + 0.992x + 0.0006x^2$	0.53**
	Ponds	$\hat{Y} = 2.206 + 0.629x - 0.0058x^2$	0.96**
Yazoo Basin	Streams	$\hat{Y} = -197.384 + 4.550x - 0.0119x^2$	0.55*
	Ponds	$\hat{Y} = 1.311 + 0.890x - 0.0022x^2$	0.26
Loess Hills	Streams	$\hat{Y} = -11.983 + 1.993x - 0.0045x^2$	0.67**
	Ponds	$\hat{Y} = -7.120 + 1.482x - 0.0165x^2$	0.63**

* Significant at the 0.05 level of probability.
** Significant at the 0.01 level of probability.

than dolomitic *(8)*. Correlations between total hardness and calcium hardness were high for waters from all physiographic areas, tables 5 and 6.

Although a number of authors pointed out that plankton and fish production was normally greater in hard than in soft waters, this relationship must be qualified *(2,3,9,10,16,18,19,25,26)*. Studies mentioned above were conducted in natural waters which were not fertilized intentionally or polluted by human activity. Water with high total alkalinity or total hardness has a greater complement of most ions than water with low alkalinity *(11,15)*. Therefore, correlations between alkalinity and productivity were related to differences in phosphorus and nitrogen concentrations rather than to alkalinity *per se (18,19,25)*. Further support of the indirect nature of correlations between alkalinity and fish production is afforded by experience on pond fertilization. Fish production in fertilized ponds of the Black Belt is no greater than production in most fertilized ponds of the Piedmont, even though Black Belt ponds usually have waters with much higher alkalinities than Piedmont ponds, tables 1 and 2. Waters of ponds constructed on fertile soils were observed in the present study to have higher alkalinities than ponds constructed on sandy, infertile soils. Unfertilized ponds on fertile soils produce more fish than unfertilized ponds on poor soils *(12,22,23,25)*. Again, this

TABLE 4. EQUATIONS FOR CALCULATING TOTAL HARDNESS ($\hat{Y}$) IN mg/l EQUIVALENT $CaCO_3$ FROM TOTAL ALKALINITY (x) IN mg/l EQUIVALENT $CaCO_3$. EQUATIONS ARE BASED ON SAMPLES FROM PONDS AND STREAMS IN FOUR PHYSIOGRAPHIC PROVINCES IN ALABAMA

Description of samples		Equation	Coefficient of determination (r^2)
Piedmont	Streams	$\hat{Y} = 3.650 + 0.403x + 0.0053x^2$	0.97**
	Ponds	$\hat{Y} = 2.169 + 0.401x + 0.0167x^2$	0.81**
Ridge and Valley	Streams	$\hat{Y} = -7.564 + 1.163x - 0.0008x^2$	0.99**
	Ponds	$\hat{Y} = -3.391 + 1.110x - 0.0015x^2$	0.99**
Appalachian Plateaus	Streams	$\hat{Y} = -10.668 + 1.554x - 0.0033x^2$	0.91**
	Ponds	$\hat{Y} = -1.858 + 0.995x + 0.00021x^2$	0.97**
Interior Low Plateaus	Streams	$\hat{Y} = 1.008 + 1.008x + 0.00002x^2$	0.99**
	Ponds	$\hat{Y} = 1.579 + 0.910x + 0.0011x^2$	0.99**

** Significant at the 0.01 level of probability.

TABLE 5. EQUATIONS FOR CALCULATING CALCIUM HARDNESS ($\hat{Y}$) IN mg/l EQUIVALENT $CaCO_3$ FROM TOTAL HARDNESS (x) IN mg/l EQUIVALENT $CaCO_3$. EQUATIONS ARE BASED ON SAMPLES FROM PONDS AND STREAMS OF DIFFERENT BELTS OF THE COASTAL PLAIN PROVINCE OF ALABAMA AND MISSISSIPPI

Description of samples		Equation	Coefficient of determination (r^2)
Southern Pine Hills	Streams	$\hat{Y} = 1.140 + 0.442x + 0.0057x^2$	0.95**
	Ponds	$\hat{Y} = -0.407 + 0.730x + 0.0014x^2$	0.94**
Jackson Prairie	Streams	$\hat{Y} = -2.427 + 0.860x + 0.0007x^2$	0.99**
	Ponds	$\hat{Y} = -1.747 + 0.782x + 0.0013x^2$	0.99**
Red Hills	Streams	$\hat{Y} = 0.864 + 0.515x + 0.0036x^2$	0.90**
	Ponds	$\hat{Y} = -1.420 + 0.854x - 0.0044x^2$	0.90**
Flatwoods	Streams	$\hat{Y} = -12.910 + 1.342x - 0.0043x^2$	0.89**
	Ponds	$\hat{Y} = -2.594 + 0.946x - 0.0017x^2$	0.97**
Black Belt	Streams	$\hat{Y} = -0.242 + 0.851x - 0.0004x^2$	0.96**
	Ponds	$\hat{Y} = -11.582 + 1.272x - 0.0021x^2$	0.98**
Fall Line Hills	Streams	$\hat{Y} = -4.536 + 1.070x - 0.0020x^2$	0.82**
	Ponds	$\hat{Y} = 1.013 + 0.516x - 0.0052x^2$	0.94**
Yazoo Basin	Streams	$\hat{Y} = 1.656 + 0.652x - 0.0004x^2$	0.99**
	Ponds	$\hat{Y} = -2.589 + 0.828x - 0.0018x^2$	0.92**
Loess Hills	Streams	$\hat{Y} = 2.772 + 0.522x - 0.0001x^2$	0.99**
	Ponds	$\hat{Y} = 0.395 + 0.479x - 0.0051x^2$	0.94**

** Significant at the 0.01 level of probability.

increase in fish production is normally related to greater concentrations of nitrogen, phosphorus, and other nutrients derived from solution and exchange of substances in bottom muds *(12,25)*.

Ponds with less than 20 mg. per l. total hardness or total alkalinity may not respond to fertilization with nitrogen and phosphorus *(4,24,28)*. Phytoplankton growth in these waters may be limited by inadequate supplies of carbon dioxide or bicarbonate and low concentrations of calcium. Equilibrium concentrations of phosphorus are also lower in ponds with soft waters and acid bottom muds than in ponds with harder waters and neutral, or nearly neutral, bottom muds *(5)*. Therefore, ponds with waters of less than 20 mg. per l. total hardness or alkalinity should be limed to increase the availability of carbon for photosynthesis, supply calcium, and conserve phosphorus applied in fertilizer *(4, 5,24,28)*. Pond waters with less than 20 mg. per l. total alkalinity and hardness were commonly encountered in all areas of Alabama and Mississippi except the Black Belt and Yazoo Basin, figures 1 and 2. Ponds with more than 20 mg. per l. were not restricted from the typically soft water areas, figures 1 and 2. Therefore, any decision on liming a pond should be based on examination of water, rather than reference to data presented in this publication.

TABLE 6. EQUATIONS FOR CALCULATING CALCIUM HARDNESS ($\hat{Y}$) IN mg/l EQUIVALENT $CaCO_3$ FROM TOTAL HARDNESS (x) IN mg/l. EQUIVALENT $CaCO_3$. EQUATIONS ARE BASED ON SAMPLES FROM PONDS AND STREAMS IN FOUR PHYSIOGRAPHIC PROVINCES IN ALABAMA

Description of samples		Equation	Coefficient of determination (r^2)
Piedmont	Streams	$\hat{Y} = 3.032 + 0.232x + 0.0073x^2$	0.99**
	Ponds	$\hat{Y} = 0.795 + 0.518x + 0.0049x^2$	0.89**
Ridge and Valley	Streams	$\hat{Y} = 2.420 + 0.471x + 0.0020x^2$	0.90**
	Ponds	$\hat{Y} = 2.244 + 0.438x + 0.0060x^2$	0.96**
Appalachian Plateaus	Streams	$\hat{Y} = -4.088 + 0.811x - 0.0004x^2$	0.84**
	Ponds	$\hat{Y} = -0.224 + 0.666x + 0.0027x^2$	0.98**
Interior Low Plateaus	Streams	$\hat{Y} = -12.064 + 1.090x - 0.0007x^2$	0.99**
	Ponds	$\hat{Y} = -5.478 + 1.105x - 0.0027x^2$	0.98**

** Significant at the 0.01 level of probability.

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