CHEMISTRY OF ALABAMA DONDS

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Information contained herein is available to all persons without regard to race, color, sex, or national origin.

WATER CHEMISTRY of ALABAMA PONDS

R. G. ARCE and CLAUDE E. BOYD

THERE ARE approximately 60,000 man-made ponds in Alabama which comprise an estimated 180,000 acres. These ponds are used for many purposes including sport fishing, commercial fish production, irrigation, stock watering, fire protection, water sports, and landscaping.

The chemistry of water is especially important in ponds that are managed for sport fish, bait minnow, or food fish production. Boyd (4) indicated that ponds with soft, acid waters need to be limed to enhance the effectiveness of inorganic fertilizers that are applied to increase plankton and fish production. Ponds with hard waters may not respond well to certain fertilization techniques because phosphorus applied in fertilizer is quickly precipitated as calcium phosphate (6). Ponds with low hardness and high alkalinity are often unsuitable for fertilization because of high pH resulting from over abundant phytoplankton growth and associated carbon dioxide depletion (8). In unfertilized ponds, natural productivity is often a function of alkalinity (6, 16).

Soil scientists and other agriculturists have long recognized the importance of soil surveys as an aid to crop and land management practices. However, there have been few surveys of pond waters to provide data for use in fish management. Boyd and Walley (7) found that total hardness and total alkalinity of pond waters in Alabama were closely related to the geologic and edaphic characteristics of watersheds. Waters from some physiographic regions usually had higher alkalinity and hardness values than waters from other regions. Nevertheless, considerable variation in alkalinity and hardness was encountered within a particular

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region. Boyd (5) found that nitrate, total ammonia nitrogen, potassium, soluble orthophosphate, and total phosphorus concentrations in waters of Alabama ponds did not differ between physiographic regions. However, waters from ponds in pastures almost invariably had greater concentrations of nitrogen, phosphorus, and potassium than waters from ponds in woodlands.

Other than the aforementioned studies, few data are available on water chemistry of Alabama ponds. The present study was initiated to provide data on water chemistry in ponds of different soils areas in Alabama. The variables measured were total alkalinity, total hardness, calcium, magnesium, sodium, potassium, sulfate, chloride, total dissolved solids, specific conductance, iron, manganese, zinc, and copper. No attempt was made to measure pH, phosphorus, nitrate, and ammonia because the analytical values for these substances change quickly during sample storage.

MATERIALS AND METHODS

Water Samples

Water samples were collected from five of the seven soils areas of Alabama. The areas of collection were: Limestone Valleys and Uplands, Appalachian Plateau, Piedmont Plateau, Prairies, and Coastal Plains. Sampling did not include the major Flood Plains and Terraces and the Coastal Marshes because there are relatively few ponds in these soils areas. Ponds were usually located randomly from county maps provided by U.S. Soil Conservation Service workers in each county. However, in a few areas samples were simply located by sight from highways. The locations of ponds were recorded by distance and direction from landmarks (city limit signs, intersections of highways, etc.). These locations were then plotted as accurately as possible on a general soils map of Alabama (11). Ponds were not sampled unless they could definitely be assigned to a particular soils area of the soils map. The surface area of each pond was obtained from the pond owner and the type of watershed (pasture, woodland, or cropland) was recorded.

Samples were collected between March and September, 1979. Each pond was sampled one time. Water was collected by holding a 2-liter polyethylene bottle 10-cm beneath the surface and allowing it to fill. Samples were analyzed as soon after collection as possible, usually within 2 days or less.

Water Analyses

Procedures

All analytical work conformed to guidelines presented by the American Public Health Association et al. (3). Total hardness was determined by titration with 0.01M ethylenediamine tetraacetic acid (EDTA) using Eriochrome Black T as the indicator. Calcium hardness was measured by titration to the end point of murexide with 0.01M EDTA. Total alkalinity was estimated by titration to the methyl orange end point with 0.02N sulfuric acid. Calcium concentrations were calculated from calcium hardness (6). Magnesium hardness was taken as the difference between total hardness and calcium hardness and magnesium concentrations were calculated from magnesium hardness as suggested by Boyd (6). Specific conductance was determined with a YSI Model 31 conductivity bridge.

Samples for other analyses were filtered through glass fiber filters (Gelman Type A-E) to remove suspended particles. Sulfate was determined turbidimetrically by the barium chloride method, the barium sulfate turbidity being measured with a Coleman Model 9 Nepho-colorimeter. Chloride was titrated to the diphenylcarbazone end point with standard mercuric nitrate. Total dissolved solid concentrations were estimated from the weight of the residue remaining after evaporation of 100 ml of filtrate at 105 degrees C. Sodium, potassium, iron, manganese, zinc, and copper concentrations were determined on filtrates by the Auburn University Soil Testing Laboratory using Perkin-Elmer Models 373 and 460 atomic absorption spectrophotometers. A series of 40 samples was also analyzed for calcium and magnesium by atomic absorption spectrophotometry for comparison with titrametric data.

Quality Control

At the beginning of the study, five 12-liter water samples that covered the concentration ranges expected for each variable were each analyzed seven times by the methods listed above. These data were used to determine the precision of the procedures according to the U.S. Environmental Protection Agency (22). Afterwards, 10 percent of the samples were analyzed in duplicate. Spike-recovery tests for accuracy were not conducted. However, data for 32 randomly selected samples were subjected to two tests, anion-cation balance (12) and agreement between calculated and measured specific conductance (14), to provide estimates of accuracy.

RESULTS AND DISCUSSION

Samples were collected from 203 ponds, figure 1. These included 57 from the Coastal Plains, 39 from the Prairies, 34 from the Appalachian Plateau, 36 from the Limestone Valleys and Up-

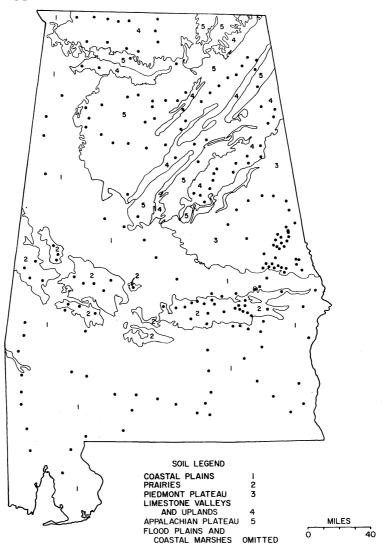


FIG. 1. Location of ponds in Alabama by soils area. Map after Hajek, Gilbert, and Steers (11).

lands, and 37 from the Piedmont Plateau. Ponds ranged in size from 0.25 to 20 hectares. Some of the ponds had received fertilizer applications, but none had been limed. The watersheds were of three types: row crops (16 ponds), pastures (98 ponds), and woodlands (89 ponds).

Quality Control

Precision estimates were based on analyses of five samples. The maximum standard deviations and 95 percent confidence intervals for individual measurements (6) for each variable are listed in table 1. For example, total alkalinity measurements were expected to have standard deviations of not more than \pm 0.24 mg/liter of means and individual measurements were expected to be within \pm 0.58 mg/liter of means. Duplicate analyses of samples for quality control always fell within the expected confidence intervals. Average coefficients of variation for all five samples are also presented in table 1.

Precision was relatively good for most procedures, and especially for total alkalinity, total hardness, and specific conductance, table 1. However, precision was poor for iron, manganese, zinc, and copper.

There was good agreement between calcium and magnesium concentrations determined by atomic absorption spectropho-

TABLE 1. PRECISION ESTIMATES FOR ANALYTICAL PROCEDURES. THE STANDARD DEVIATIONS
and 95% Confidence Intervals for Individual Measurements are the
HIGHEST FOR SEVEN REPETITIVE DETERMINATIONS ON EACH OF
FIVE SAMPLES. THE COEFFICIENTS OF VARIATION ARE THE
Averages for the Five Samples. Specific
CONDUCTANCE WAS MEASURED IN
VARIABLES WERE MEASURED
IN MG/LITER
FIVE SAMPLES. THE COEFFICIENTS OF VARIATION ARE THE AVERACES FOR THE FIVE SAMPLES. SPECIFIC CONDUCTANCE WAS MEASURED IN µmbos/cm WHILE ALL OTHER VARIABLES WERE MEASURED

Procedure	Maximum standard deviation	Maximum 95% confidence intervals for individual measurements	Average coefficient of variation (%)
Total alkalinity	0.237	0.58	0.64
Total hardness	0.450	1.10	0.69
Calcium	0.151	0.37	1.30
Magnesium	0.327	0.80	4.54
Potassium	0.181	0.44	5.53
Sodium	0.214	0.52	4.27
Chloride	0.275	0.67	3.06
Sulfate	0.345	0.84	5.36
Total dissolved solids	2.83	6.92	3.63
Specific conductance	2.41	5.90	0.49
Iron	0.048	0.12	19.3
Manganese	0.028	0.067	35.8
Zinc	0.015	0.036	19.9
Copper	0.009	0.022	39.1

tometry and by EDTA titration, figures 2 and 3. Therefore, data obtained by the titrametric technique were used throughout the study.

Good agreement was achieved between the summation in meq/liter of major anions $(CO_3^{2^-}, HCO_3^-, SO_4^{2^-}, and CI^-)^1$ and major cations $(Ca^{2^+}, Mg^{2^+}, K^+, and Na^+)$ for randomly selected samples, figure 4. The major ions account for almost all of the total ions in natural water and the summation of anions and cations must be equal because of the principle of electrical neutrality (13, 15, 17, 21, 23). Therefore, close agreement between the summation of anions and cations in the results of a water analysis for major ions suggests a high degree of accuracy in the analytical work (12).

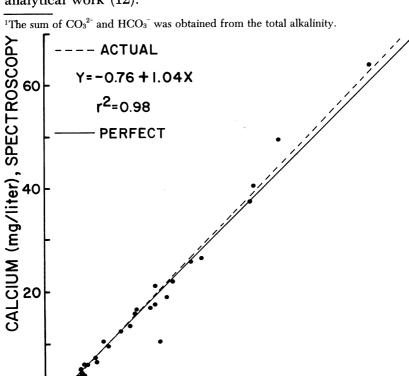


FIG. 2. Comparison between calcium concentrations determined by atomic absorption spectrophotometry and by titration with ethylenediamine tetraacetic acid. The solid line represents perfect agreement and the dashed line is the actual regression line.

40

(mg/liter), TITRATION

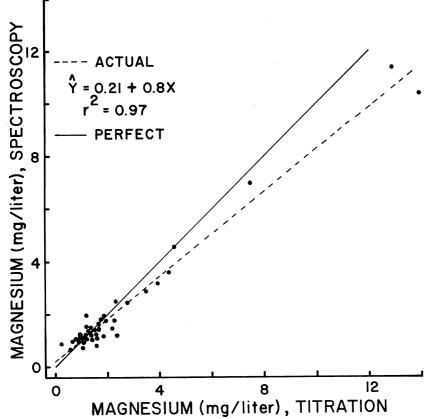
60

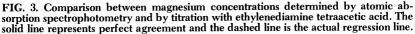
20

CALCIUM

0

O





The major cations and anions also account for essentially all of the electrical conductance of a water sample. The expected specific conductances for 32 randomly selected samples were calculated by the equations given by Laxen (14). These values agreed closely with measured specific conductance, figure 5, also suggesting that the analytical work was highly accurate.

Water Chemistry of the Soils Areas

A thorough description of the soils areas of Alabama is presented by Hajek et al. (11). Each major soils area is subdivided into different soil associations, but no attempt was made to identify the soil association or associations of the watershed of each pond. The Limestone Valleys and Uplands, Appalachian Plateau, and Prairies contain large areas of soils which developed

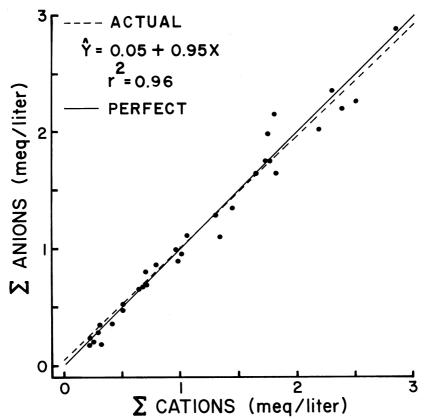


FIG. 4. Relationship between summation of anions and summation of cations for water samples from Alabama ponds. The solid line represents perfect agreement and the dashed line is the actual regression line.

in material weathered from limestone. Few soils in the Coastal Plains and none in the Piedmont Plateau developed in limestone. The soils in the Piedmont Plateau developed from the oldest surface rock in Alabama. Heavy clay surface soils are especially common in the Prairies while sandy surface soils are common in the Coastal Plains.

Data for each water quality variable from ponds of all soils areas were generally skewed, so standard deviations were of no value in describing the distributions. Frequency distributions were plotted for each variable by soils area, figures 6 to 16. Even though data were skewed, standard errors of the means were computed because skewedness does not invalidate the use of the standard error (19). Means and standard errors for each variable will usually be presented in the text rather than in tables.

WATER CHEMISTRY OF ALABAMA PONDS

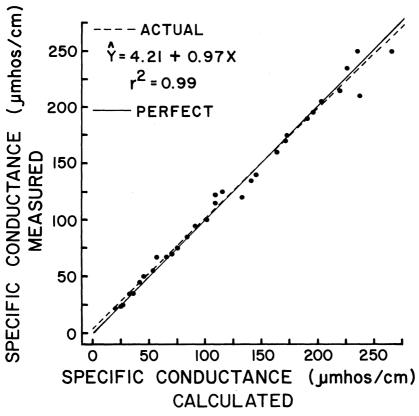


FIG. 5. Relationship between measured and calculated specific conductance values (14) for water samples from Alabama ponds. The solid line represents perfect agreement and the dashed line is the actual regression line.

Total Alkalinity

Total alkalinity is a measure of the total titratable bases in water expressed as mg/liter of equivalent calcium carbonate. In natural waters, HCO_3^{-} and $CO_3^{2^-}$ are the predominate bases and total alkalinity is considered a measure of the combined concentration of these two ions (3, 6, 12, 17, 21). Total alkalinity in mg/liter as CaCO₃ may be converted to meq/liter of $CO_3^{2^-}$ plus HCO_3^{-} by dividing by 50 mg of CaCO₃ per meq.

Means and standard errors for total alkalinity values (mg/liter as CaCO₃) for waters of the different soils areas were: Prairies, 51.1 ± 4.52 ; Limestone Valleys and Uplands, 42.2 ± 5.33 ; Appalachian Plateau, 18.9 ± 1.76 ; Coastal Plains, 13.2 ± 0.95 ; and Piedmont Plateau, 11.6 ± 0.79 . The greater concentrations of total alkalinity in waters of the Prairies and the Limestone Valleys and

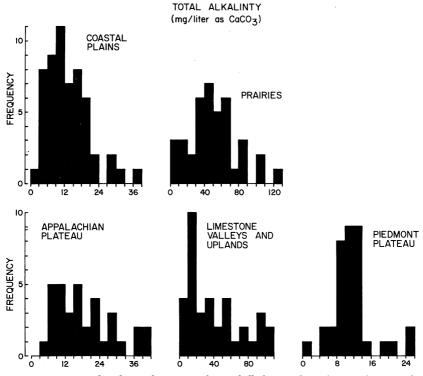


FIG. 6. Frequency distribution histograms for total alkalinity values of waters from ponds of different soils areas in Alabama.

Uplands reflect the frequent occurrence of limestone in soils of ponds and watersheds.

Few pond waters from the Prairies, figure 6, had less than 20 mg/liter total alkalinity, while a greater percentage of the pond waters from the Limestone Valleys and Uplands had less than 20 mg/liter. However, values above 40 mg/liter were common in both of these soils areas. Waters of ponds in the other three soils areas usually contained less than 20 mg/liter total alkalinity and many had values of 10 mg/liter or less. These observations on total alkalinity agree with results of Boyd and Walley (7).

Ponds with waters which contain less than 20 mg/liter total alkalinity need to be limed to ensure response to inorganic fertilization (4). Data presented in figure 6 suggest that the decision to lime a pond should be based on a water analysis for total alkalinity. For example, most waters of the Coastal Plains had less than 20 mg/liter total alkalinity, but a few had more than 20 mg/liter and would not need lime. Conversely, most pond waters of the Prairies had more than 20 mg/liter total alkalinity, but a few which were located on acid soils had less than 20 mg/liter and would need lime.

Total Hardness

Total hardness is a measure of the total concentration of divalent cations in water expressed as mg/liter as equivalent calcium carbonate. Since Ca^{2+} and Mg^{2+} are the primary divalent cations in most natural waters, total hardness is considered an estimate of the concentration of these two cations (6, 17).

Means and standard errors for total hardness values (mg/liter as CaCO₃) were: Prairies, 55.5 ± 5.19 ; Limestone Valleys and Uplands, 49.2 ± 6.20 ; Appalachian Plateau, 22.0 ± 2.25 ; Coastal

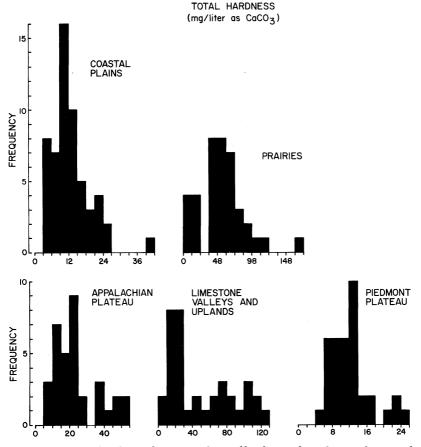


FIG. 7. Frequency distribution histograms for total hardness values of waters from ponds of different soils areas in Alabama.

Plains, 12.9 ± 0.92 ; and Piedmont Plateau, 12.3 ± 2.02 . As with total alkalinity, the high concentrations of total hardness in pond waters from the Prairies and the Limestone Valleys and Uplands reflect the large concentrations of limestone in soils. Most total hardness values were above 20 mg/liter in ponds of the Prairies, Limestone Valleys and Uplands, and Appalachian Plateau, figure

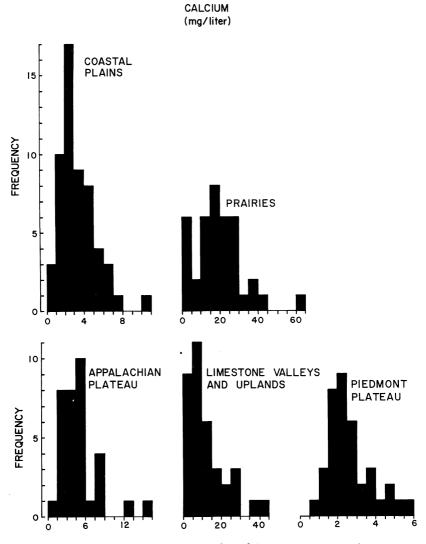


FIG. 8. Frequency distribution histograms for calcium concentrations of waters from ponds of different soils areas in Alabama.

7. However, most values were below 20 mg/liter for waters of the other two soils areas. These findings agree well with those of Boyd and Walley (7). Waters with less than 20 mg/liter total hardness should be limed for effective fertilization and sportfish production (4).

Calcium

Means and standard errors for calcium concentrations in mg/ liter were: Prairies, 19.7 ± 1.99 ; Limestone Valleys and Uplands, 11.9 ± 1.76 ; Appalachian Plateau, 5.0 ± 0.53 ; Coastal Plains, 3.40 ± 0.25 ; and Piedmont Plateau, 2.71 ± 0.19 . Most values were

MAGNESIUM

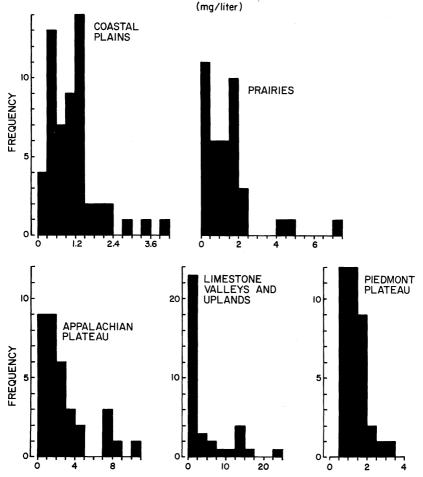


FIG. 9. Frequency distribution histograms for magnesium concentrations of waters from ponds of different soils areas in Alabama.

above 6 mg/liter for the Prairies and Limestone Valleys and Uplands, but below 6 mg/liter for other soils areas, figure 8. High concentrations of calcium resulted from abundant limestone in soils.

Magnesium

Means and standard errors for magnesium concentrations in mg/liter were: Limestone Valleys and Uplands, 4.7 ± 0.91 ; Appalachian Plateau, 2.8 ± 0.44 ; Prairies, 1.5 ± 0.22 ; Piedmont Plateau, 1.4 ± 0.10 ; and Coastal Plains, 1.1 ± 0.10 . Several samples from the Limestone Valleys and Uplands had more than 10 mg/liter of magnesium, figure 9. However, most waters from this soils area and from the other four areas had less than 4 mg/liter of magnesium.

Potassium

Means and standard errors for potassium in mg/liter were: Limestone Valleys and Uplands, 3.2 ± 0.84 ; Coastal Plains, 2.8 ± 0.34 ; Appalachian Plateau, 1.7 ± 0.37 ; Prairies, 1.5 ± 0.20 ; and Piedmont Plateau, 1.4 ± 0.12 . Distributions were relatively similar and differences in means resulted primarily from extreme values, figure 10. Almost all samples contained less than 4 mg/ liter potassium, but only 23 percent of the samples had less than 1 mg/liter potassium. When presented by soils areas, the percentages are: Prairies, 5; Coastal Plains, 16; Piedmont Plateau, 19; Limestone Valleys and Uplands, 33; and Appalachian Plateau, 47. Unless ponds contain more than 1 mg/liter potassium, fertilization with potassium fertilizers is probably advisable (9).

Sodium

Means and standard errors for sodium in mg/liter were: Prairies, 4.3 ± 0.46 ; Limestone Valleys and Uplands, 4.2 ± 1.81 ; Appalachian Plateau, 2.9 ± 0.27 ; Coastal Plains, 2.9 ± 0.24 ; and Piedmont Plateau, 2.6 ± 0.11 . Distributions were similar for the five areas and most samples had less than 5 mg/liter of sodium, figure 11. Differences in means for the five areas resulted primarily from the extreme values.

Chloride

Means and standard errors for chloride concentrations in mg/ liter were: Prairies, 6.8 ± 4.1 ; Limestone Valleys and Uplands, 6.6 ± 3.7 ; Coastal Plains, 5.5 ± 0.79 ; Appalachian Plateau, 3.2 ± 0.36 ; and Piedmont Plateau, 2.6 ± 0.29 . Most samples from the five areas had less than 6 mg/liter chloride, figure 12. A few

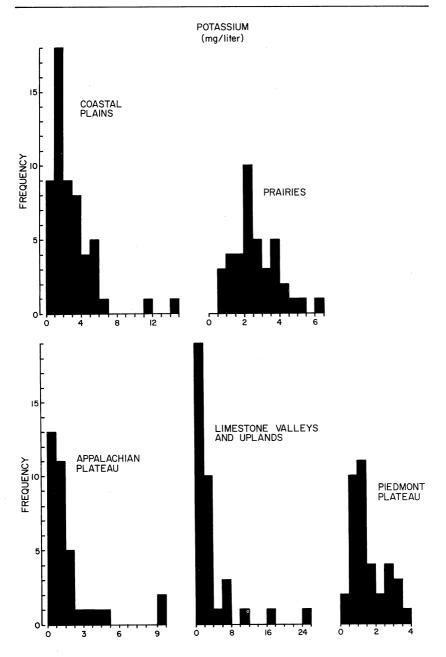


FIG. 10. Frequency distribution histograms for potassium concentrations of waters from ponds of different soils areas in Alabama.

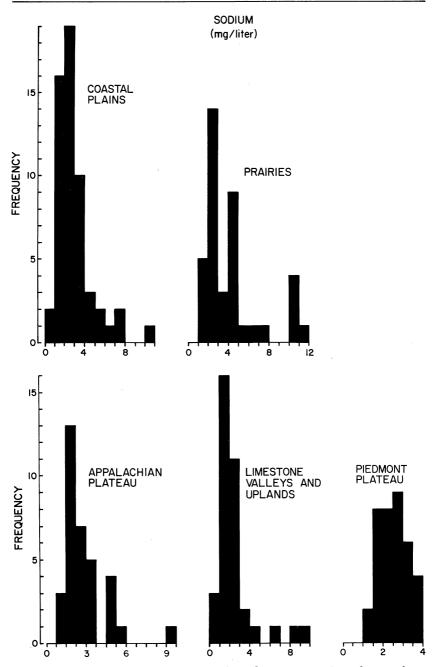


FIG. 11. Frequency distribution histograms for sodium concentrations of waters from ponds of different soils areas in Alabama.

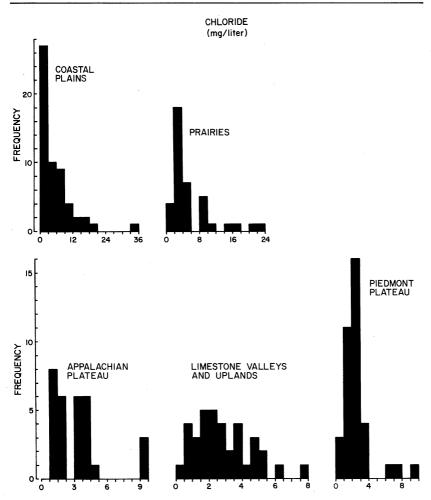


FIG. 12. Frequency distribution histograms for chloride concentrations of waters from ponds of different soils areas in Alabama.

samples from the Prairies and the Coastal Plains had 12 mg/liter or more of chloride. Variation between ponds was particularly great for the Prairies and the Limestone Valleys and Uplands.

Sulfate

Means and standard errors for sulfate concentrations in mg/ liter were: Appalachian Plateau, 6.6 ± 1.04 ; Prairies, 4.3 ± 0.80 ; Limestone Valleys and Uplands, 4.2 ± 0.78 ; Piedmont Plateau, 1.4 ± 0.31 ; and Coastal Plains, 1.8 ± 0.41 . A large proportion of the

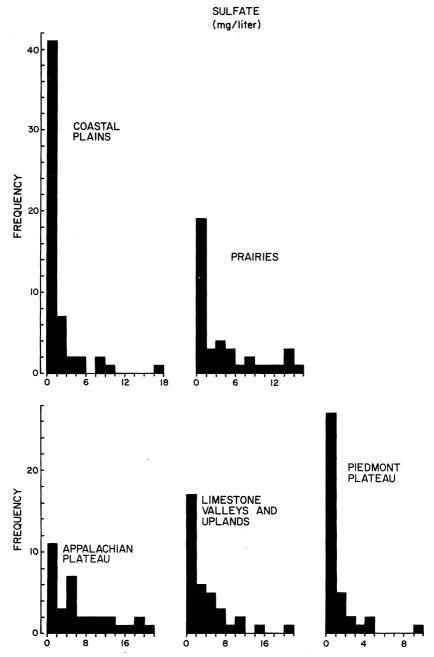


FIG. 13. Frequency distribution histograms for sulfate concentrations of waters from ponds of different soils areas in Alabama.

samples from all soils areas contained less than 2 mg/liter sulfate, figure 13. With a few exceptions, waters from ponds of the Coastal Plains and Piedmont Plateau contained less than 6 mg/ liter of sulfate. For the other three areas, an appreciable number of samples had sulfate concentrations of 6 to 22 mg/liter.

Iron, Manganese, Zinc, and Copper

There were no apparent differences between the mean values or distributions of these four trace elements for the five soils areas. Therefore, data for all soils areas were combined. The means and standard errors are presented in table 2 and the frequency distribution histograms in figure 14. Concentrations of iron were usually below 0.5 mg/liter and values for zinc were normally below 0.25 mg/liter. Most copper and manganese concen-

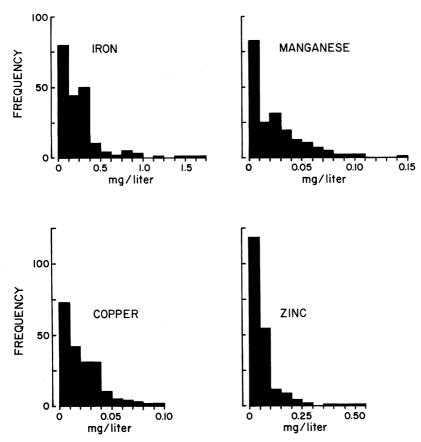


FIG. 14. Frequency distribution histograms for iron, manganese, copper, and zinc concentrations of water from ponds in Alabama (all soils areas combined).

Variable	Mean (mg/liter)	Standard error (mg/liter)
Iron	0.20	0.021
Manganese	0.03	0.003
Zinc	0.07	0.006
Copper	0.03	0.005

TABLE 2. MEANS AND STANDARD ERRORS FOR CONCENTRATIONS OF IRON, MANGANESE, ZINC, AND COPPER IN WATERS FROM 203 PONDS IN ALABAMA (ALL SOILS AREAS COMBINED)

trations were below 0.05 mg/liter. The values represent the total concentrations of the trace elements in filtrates of pond water. Large amounts of trace elements are complexed by inorganic and organic compounds (18, 20, 21), so the concentrations presented in this study are much greater than the true ionic concentrations of these trace elements.

Total Dissolved Solids and Specific Conductance

Means and standard errors for these two variables are presented in table 3 and frequency distribution histograms in figures 15 and 16. The greatest total dissolved solids and specific conductance values were for water from ponds of the Prairies and Limestone Valleys and Uplands, while the lowest values were generally for the Piedmont Plateau and Coastal Plains.

Specific conductance values were largest for samples with the greatest complements of ions, since the ability of a solution to conduct electricity is directly proportional to the ionic concentration. Total dissolved solid concentrations also increase as a function of ionic concentrations. Soluble organic substances which are largely uncharged contribute to the total dissolved solids. Thus, the amount of dissolved organic matter in water affects the relationship between total dissolved solids and specific

			dissolved (mg/liter)	cond	ecific luctance hos/cm)
Soils area	Number of samples	Mean	Standard error	Mean	Standard error
Piedmont Plateau Coastal Plains Appalachian Plateau Limestone Valleys	37 57 34	$34.5 \\ 44.3 \\ 60.2$	$2.25 \\ 3.13 \\ 6.06$	40.2 48.5 73.8	2.29 3.17 6.35
and Uplands	36 39	112 94.4	$\begin{array}{c} 10.9 \\ 18.2 \end{array}$	$\begin{array}{c} 146\\ 161 \end{array}$	28.9 33.9

TABLE 3. MEANS AND STANDARD ERRORS FOR CONCENTRATIONS OF TOTAL DISSOLVED SOLIDS AND SPECIFIC CONDUCTANCE VALUES FOR WATER FROM PONDS OF DIFFERENT SOILS AREAS IN ALABAMA

WATER CHEMISTRY OF ALABAMA PONDS

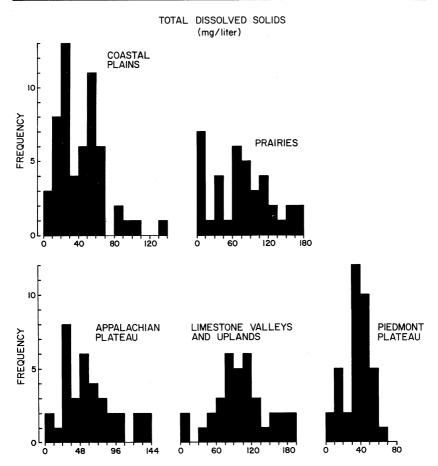
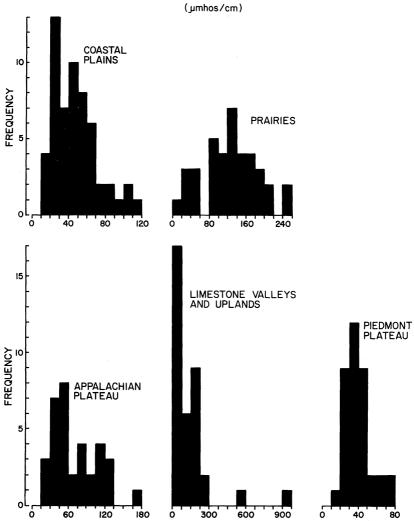


FIG. 15. Frequency distribution histograms for total dissolved solids concentrations of waters from ponds of different soils areas in Alabama.

conductance. Waters with low alkalinity (soft, acid waters) on wooded watersheds often contain high concentrations of tannins, lignins, and other organic substances. Such waters are heavily stained (have the appearance of tea or weak coffee) and often have fairly large concentrations of total dissolved solids in comparison to specific conductance values. Waters with high concentrations of divalent ions (hard waters) seldom contain high concentrations of organic substances because divalent ions favor precipitation of colloidal organic substances and the higher pH



SPECIFIC CONDUCTANCE

FIG. 16. Frequency distribution histograms for specific conductance values of waters from ponds of different soils areas of Alabama.

favors decomposition of dissolved and colloidal organic matter by bacteria $(\overline{23})$.

Relationships Between Variables

Pie diagrams (12) were prepared to give a visual comparison of the ionic concentrations (meg/liter) and the proportions of major

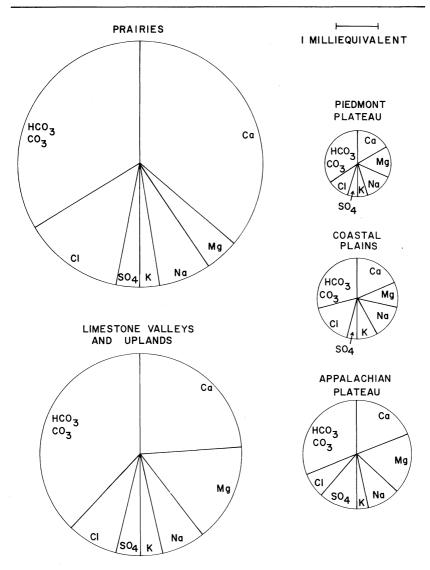


FIG. 17. Pie diagrams for the proportions of major ions in pond waters from five soils areas in Alabama. The diameters of the circles are proportional to the milliequivalents per liter of total ions.

ions in pond waters of the five soils areas, figure 17. The waters of the Prairies and the Limestone Valleys and Uplands had much greater concentrations of ions than the waters of the other areas. The waters of the Piedmont Plateau were the most dilute in ions.

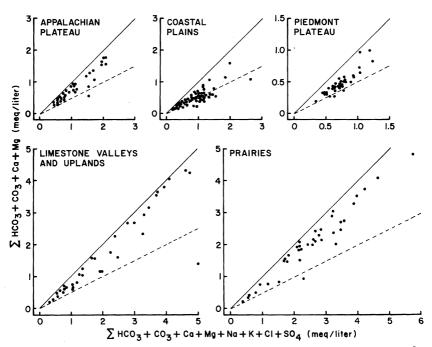


FIG. 18. Relationships between the summation of alkalinity anions $(HCO_3^{-1} and CO_3^{-2})$ and hardness cations $(Ca^{2^+} and Mg^{2^+})$ and the summation of all major ions for waters from ponds of different soils areas in Alabama. The solid line indicates the case where the Y-variable equals the X-variable and the dashed line represents the situation where the Y-variable is one-half of the X-variable.

Waters of the Coastal Plains and Appalachian Plateau were more similar in total ionic concentration to the waters of the Piedmont Plateau than to the waters of the other two areas.

Bicarbonate and carbonate (as calculated from total alkalinity) and calcium and magnesium comprised more than 50 percent of the total ions in waters of all five areas, figure 17. The proportions of the major ions were remarkably similar between soils areas. Therefore, pond waters from Alabama differ primarily in total concentrations of ions rather than in the proportions of different ions.

To further illustrate relationships between ions, the summations of all ions in meq/liter (X-variable) were plotted, figure 18, against the summation of HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+} in meq/ liter (Y-variable). The summation of HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+} may actually be obtained by summing total alkalinity and total hardness in mg/liter and dividing by 50. In figure 18 the solid line represents the case where HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+}

TABLE 4. RECRESSION EQUATIONS AND CORRELATION COEFFICIENTS FOR RELATIONSHIPS
BETWEEN THE SUMMATION OF HCO ₃ , CO ₃ ²⁻ , CA ²⁺ , AND MG ²⁺ IN MEQ/LITER ¹
(X-variable) and the Summation of Total Major Ions in meo/
LITER (Y-VARIABLE). DATA FOR WATERS FROM PONDS OF
DIFFERENT SOILS AREAS IN ALABAMA

Soils area	Number of samples	Regression equation	Correlation coefficient (r)
Piedmont Plateau Coastal Plains	37 57	$\begin{array}{l} Y = 0.227 + 1.037 \ X \\ Y = 0.227 + 1.333 \ X \end{array}$	$\begin{array}{c} 0.95\\ 0.91\end{array}$
Appalachian Plateau Limestone Valleys	34	Y = 0.11 + 1.198 X	0.97
and Uplands	36 39	$\begin{array}{l} Y = 0.332 + 1.046 \ X \\ Y = 0.345 + 1.075 \ X \end{array}$	0.86 0.98

 1 Total alkalinity plus total hardness (in mg/liter as CaCO₃) divided by 50 gives summation of HCO₃ , CO₃²⁻, Ca²⁺, and Mg²⁺ in meq/liter.

are the only ions in water and the dashed line represents the situation where the summation of HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+} is exactly one-half of the summation of the major ions. A number of data points for the Coastal Plains fell below the dashed line, indicating that the summation of HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+} comprised less than one-half of the total major ions. However, with five exceptions, the summation of HCO_3^- , $CO_3^{2^-}$, Ca^{2^+} , and Mg^{2^+} comprised one-half or more of the total major ions in waters from ponds of the other four soils areas. Thus, by measuring total hardness and total alkalinity in waters of Alabama ponds, one may obtain a fair estimate of the total concentration of major ions in Alabama pond waters. Regression equations for calculating the summation of total ions in meq/liter from total alkalinity plus total hardness are given in table 4.

The analytical data in mg/liter were used to calculate ratios between variables, figure 19. The ratio, total alkalinity: total hardness ranged from 0.8 (Appalachian Plateau) to 1.4 (Coastal Plains). Except for the Coastal Plains, alkalinity was slightly less than total hardness. Linear correlation coefficients between total hardness (X) and total alkalinity (Y) were Piedmont (r = 0.79; P < 0.01), Limestone Valleys and Uplands (r = 0.97; P < 0.01), Coastal Plains (r = 0.90; P < 0.01), Prairies (r = 0.89; P < 0.01), and Appalachian Plateau (r = 0.92; P < 0.01). It is easier in the field to make total hardness than total alkalinity determinations. For practical purposes, total hardness multiplied by 1.4 would give an estimate of total alkalinity for Coastal Plains waters, while total hardness multiplied by 0.9 would give a better estimate of total alkalinity for waters of other soils areas.

The undesirable combination of high alkalinity and low hardness was seldom encountered. Only one pond had an alkalinity

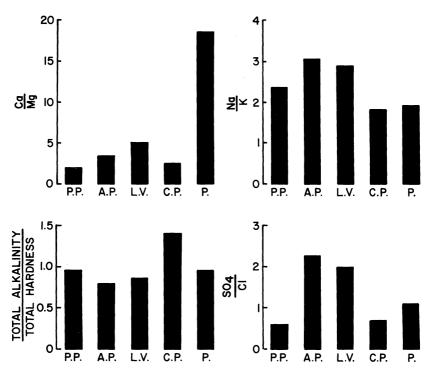


FIG. 19. Ratios between concentrations (mg/liter) of various chemical constituents in waters from ponds of different soils areas in Alabama. Legend: P. P. (Piedmont Plateau), A. P. (Appalachian Plateau), L. V. (Limestone Valleys and Uplands), C. P. (Coastal Plains), P. (Prairies).

value that was at least twice as great as hardness values. Boyd et al. (8) reported high alkalinity and low hardness in certain ponds which were filled by well water that had been softened by exchange of calcium in water with sodium in the geological deposits of the aquifer.

The ratio of calcium:magnesium, figure 19, was 18 for waters of the Prairies, but the ratios were 2 to 5 for other areas. This difference undoubtedly reflects a greater proportion of calcium to magnesium in Prairies soils as compared to other soils of Alabama.

Sodium concentrations were 2 to 3 times greater than potassium concentrations, figure 19. Sulfate concentrations were about twice as high as chloride concentrations in waters of the Appalachian Plateau and Limestone Valleys and Uplands, figure 19. However, in the other areas, sulfate concentrations were less than or approximately equal to chloride concentrations.

Soils area					Correla	ation coeff	ficients1			· · · · · · · · · · · · · · · · · · ·
	Number of samples	Total alkalinity	Ca ²⁺	Mg ²⁺	K⁺	\mathbf{Na}^{\star}	C1 ⁻	SO4 ²⁻	TDS ²	Specific conductance
Piedmont Plateau Coastal Plains Appalachian Plateau	37 57 34	0.91** 0.90** 0.92**	0.73** 0.94** 0.87**	0.91** 0.84** 0.70**	0.19 0.39** 0.08	0.35* 0.23 0.53**	$0.25 \\ 0.22 \\ 0.26$	0.08 0.09 0.47**	0.41** 0.42** 0.45**	0.92** 0.72** 0.78**
Limestone Valleys and Uplands Prairies	36	0.97 ** 0.89 **	0.88** 0.96**	0.79°° 0.44°°	$0.05 \\ 0.22$	0.27 0.08	0.23 0.58 °°	0.03 0.29	0.57 °° 0.12	0.38°° 0.75°°

TABLE 5. CORRELATION COEFFICIENTS (I) FOR RECRESSIONS OF TOTAL HARDNESS (X-VARIABLE) AND OTHER WATER CHEMISTRY VARIABLES (Y-VARIABLES) FOR WATERS FROM PONDS OF DIFFERENT SOILS AREAS IN ALABAMA

¹Significance at the 5% and the 1% probability levels indicated by one and two asterisks, respectively.

²Total dissolved solids.

TABLE 6. CORRELATION COEFFICIENTS (r) FOR REGRESSIONS OF SPECIFIC CONDUCTANCE (X-VARIABLE) AND OTHER WATER CHEMISTRY VARIABLES (Y-VARIABLES) FOR WATERS FROM PONDS OF DIFFERENT SOILS AREAS IN ALABAMA

		Correlation coefficients ¹								
Soils area	Number of samples	Total alkalinity	Total hardness	Ca ²⁺	Mg ²⁺	K⁺	Na^{+}	C1 ⁻	SO4 ²⁻	TDS ²
Piedmont Plateau Coastal Plains Appalachian Plateau	37 57 34	0.77** 0.81** 0.82**	0.93** 0.72** 0.78**	0.82°° 0.67°° 0.53°°	0.72** 0.60** 0.57**	0.32 0.63°° 0.38°	0.39° 0.65°° 0.56°°	0.37° 0.34° 0.52	0.03 0.01 0.39*	0.46°° 0.67°° 0.41°
Limestone Valleys and Uplands Prairies	36 39	0.32 0.53**	0.38° 0.75°°	0.42°° 0.72°°	0.14 0.37°	0.51 °° 0.09	0.46°° 0.38°	0.45°° 0.97°°	0.58 ** 0.02	0.62°° 0.89°°

¹Significance at the 5% and 1% probability levels indicated by one and two asterisks, respectively.

²Total dissolved solids.

TABLE 7. REGRESSION EQUATIONS FOR RELATIONSHIPS BETWEEN TOTAL HARDNESS (X-VARIABLE) AND SELECTED WATER CHEMISTRY VARIABLES (Y-VARIABLES) FOR WATERS FROM PONDS OF DIFFERENT SOILS AREAS IN ALABAMA. SPECIFIC CONDUCTANCE VALUES ARE IN µMHOS/CM AND OTHER DATA IN MC/LITER. CORRELATION COEFFICIENTS (r) ARE LISTED IN TABLE 5, BUT ALL WERE ABOVE 0.86

Soils area	Y-variable	Equation
Piedmont Plateau	Total alkalinity Magnesium Specific conductance	$\begin{array}{l} Y = \ 1.440 + 0.827 \ X \\ Y = \ 0.121 + 0.102 \ X \\ Y = \ 5.736 + 2.797 \ X \end{array}$
Coastal Plains	Total alkalinity Calcium	Y = 1.073 + 0.935 X Y = -0.038 + 0.242 X
Appalachian Plateau	Total alkalinity Calcium	Y = 1.473 + 0.722 X Y = -1.009 = 0.236 X
Limestone Valleys and Uplands	Total alkalinity Calcium	Y = 1.294 + 0.832 X Y = 0.223 + 0.238 X
Prairies	Total alkalinity Calcium	Y = 8.169 + 0.772 X Y = -2.520 + 0.401 X

Since total hardness and specific conductance are both easily measured under field conditions, regression analyses were conducted to ascertain if concentrations of other ions could be estimated from either of these determinations. The regression coefficients (r) are summarized in tables 5 and 6.

The majority of the regression coefficients were statistically significant. This was expected since specific conductance is related to total ionic concentration, and because total hardness is closely related to total alkalinity and the ions of hardness and alkalinity usually comprised more than 50 percent of the ions in Alabama pond waters. However, a regression coefficient of 0.87 is required if a regression equation is to account for at least 75 percent of the variation in the dependent variable, so many of the regression equations are of little predictive value. The regression equations for regression analyses with r > 0.86 are tabulated in tables 7 and 8.

 TABLE 8. REGRESSION EQUATIONS FOR RELATIONSHIPS BETWEEN SPECIFIC CONDUCTANCE (X-variable) and Selected Water Chemistry Variables (Y-variables)

FOR WATERS FROM PONDS OF DIFFERENT SOILS AREAS IN ALABAMA.

Specific Conductance Values are in μ mhos/cm

AND OTHER DATA ARE IN MC/LITER. CORRELATION

COEFFICIENTS (r) ARE LISTED IN TABLE 6,

BUT ALL WERE ABOVE 0.86

Soils area	Y-variable	Equation
Piedmont Plateau Coastal Plains Appalachian Plateau Limestone Valleys	Total hardness None None	Y = 0.012 + 0.306 X
and Uplands	None Chloride Total dissolved solids	Y = -27.08 + 0.259 X Y = 17.42 = 0.479 X

Effect of Watershed Cover

Analytical data were averaged across all soils areas for the three types of watersheds: row crops, pasture, and woods, figure 20. Although differences were noted for all variables, only the differences in potassium have practical significance. Results in figure 20 show that potassium concentrations were roughly twice as great in waters of ponds on row crop or pasture watersheds as in waters from ponds on wooded watersheds. Thus, the need for potassium fertilization is less for ponds on row crop or pasture watersheds.

Four basic types of water were noted in Alabama ponds as follows: clear water (rather unusual except in certain areas with abundant limestone), waters turbid with suspended soil particles

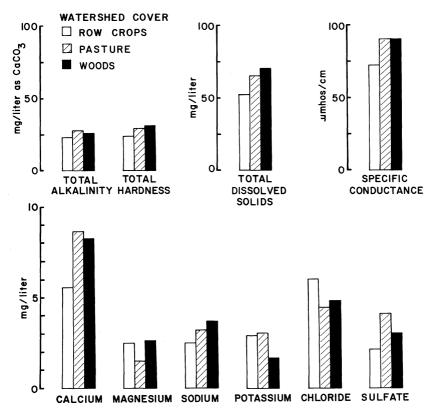


FIG. 20. Average concentrations of water chemistry variables for waters from ponds on different types of watersheds in Alabama (all soils areas combined). Samples sizes were: row crops, 16; pastures, 98; and woods, 89.

(ponds with row crops on watersheds), waters turbid with plankton (fertilized ponds or ponds in well-managed pastures), and waters stained with organic substances (ponds with wooded watersheds or pasture ponds with soft, acid waters). Obviously, there was some mingling of the types. For example, fertilized ponds with heavily stained waters often contained plankton blooms.

Ionic Concentrations and Activities

Calculations involving the methods of thermodynamics (equilibrium calculations) require that measured ionic concentrations be reduced to ionic activities. The simplest technique for converting ionic concentrations to ionic activities for equilibrium calculations is the use of the Debye-Huckel equation (1, 10) to calculate the activity coefficients of the ions of interest. The activity coefficients are then multiplied by the measured molar concentrations to give activities. The Debye-Huckel equation is

$$-\log \gamma_{i} = \frac{(A) (Z_{i})^{2} (\mu)^{1/2}}{1 + (B) (a_{i}) (\mu)^{1/2}}$$

where A and B are temperature dependent constants, Z_i = ionic charge, a_i = the effective ion size, μ = ionic strength, and γ_i = the activity coefficient of the ion. Values for A, B, and a_i are given by Garrels and Christ (10) and ionic strength can be calculated as

$$\mu = \Sigma \frac{(m_i) (Z_i)^2}{2}$$

where m_i = the measured molar concentration of the given ion.

A fraction of the anions and cations in aqueous solutions are strongly attracted to each other and behave as un-ionized species called "ion-pairs." Adams (11) demonstrated that ionpairing affects ionic strength, ionic concentration, and activity coefficients. The effect of ion-pairing on the calculated activity increases with increasing concentrations of ions and is appreciable in soil solutions (2). The method for correcting for ionpairing involves (a) measuring the ionic concentrations and calculating ionic strength assuming no ion-pairing, (b) calculating ionic activities, (c)-calculating ion-pair concentrations, (d) revising ionic concentrations and ionic strength based on the calculated ion-pair values, and (e) repeating steps (b), (c), and (d) until all ionic concentrations remain unchanged with succeeding calculations. This iterative process is slow unless it is programmed into a computer.

			Ion			
HCO ₃ ⁻	Ca ²⁺	Mg^{2+}	Na⁺	\mathbf{K}^{*}	$\mathbf{C1}^{-}$	SO4 ²⁻
0.23	0.061	0.054	0.11	0.035	0.071	0.013
0.23	0.061	0.054	0.11	0.035	0.071	0.013
0.26	0.076	0.040	0.12	0.070	0.15	0.01⁄6
0.26	0.076	0.040	0.12	0.070	0.15	0.016
0.36	0.11	0.10	0.12	0.071	0.087	0.058
0.36	0.11	0.10	0.12	0.071	0.087	0.058
0.81	0.25	0.16	0.18	0.078	0.18	0.036
0.80	0.24	0.16	0.18	0.078	0.18	0.034
0.97	0.40	0.051	0.18	0.066	0.12	0.036
0.96	0.39	0.051	0.18	0.066	0.12	0.034
	0.23 0.23 0.26 0.26 0.36 0.36 0.36 0.81 0.80 0.97	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

TABLE 9. COMPARISON OF ACTIVITIES (MEQ/LITER) CALCULATED BY THE DEBYE-HUCKEL EQUATION WITHOUT (INITIAL) AND WITH (CORRECTED) CORRECTION FOR ION-PAIRING

The influence of ion-pairing on calculated activities of major ions was determined for hypothetical samples assigned average concentrations of major ions for each of the five soils areas. Activities calculated from initial data (assuming no ion-pairing) and by the iterative procedure of Adams (1) were the same for the Piedmont Plateau, Coastal Plains, and Appalachian Plateau, table 9. There were only slight differences for the two methods of calculating activities for the Limestone Valleys and Uplands and Prairies, table 9. Therefore, the Debye-Huckel procedure may be used without correcting data for ion-pairing to convert analytical values for waters from Alabama ponds to activities. It is important to convert analytical concentrations to activities since, for the hypothetical samples, activity coefficients were as low as 0.819 for divalent ions and 0.952 for monovalent ions.

CONCLUSIONS

The average concentrations of total ions in waters of Alabama ponds differed with soils areas as follows: Piedmont Plateau < Coastal Plains < Appalachian Plateau < Limestone Valleys and Uplands < Prairies. Waters were essentially dilute solutions of alkaline earth carbonates and bicarbonates with low concentrations of sodium, potassium, chloride, and sulfate and with minute amounts of iron, manganese, zinc, and copper. Concentrations of nitrogen and phosphorus were not measured. The major differences in ionic concentrations in waters from the different areas resulted from variable amounts of alkaline earth carbonates and bicarbonates (total hardness and total alkalinity). Soils of areas in which ponds had high alkalinity and hardness had developed in limestone. Total ionic concentrations in waters of Alabama ponds can be estimated accurately by regression equations using the sum of total hardness and total alkalinity as the independent variable (X-variable).

For a given soils area, waters differed considerably in concentrations of all variables. Values were highly skewed, so data were presented in frequency distribution histograms. Means and standard errors for each variable and soils area were presented, but these values have limited practical value because of the great variation among individual samples.

Concentrations of total dissolved solids and values for specific conductance were often correlated with concentrations of individual ions. However, regression equations had little predictive value.

Management practices on watersheds did not greatly affect concentrations of major ions. However, ponds on wooded watersheds often had organically stained waters, ponds with row crops on their watersheds were often turbid with suspended soil particles, and pasture ponds frequently had plankton blooms.

The effect of ion-pairing on the calculation of activities from analytical data was not appreciable for waters from Alabama ponds.

LITERATURE CITED

- (1) ADAMS, F. 1971. Ionic Concentrations and Activities in Soil Solutions. Soil Sci. Soc. Amer. Proc., 35: 420-426.
- (2) _____. 1974. Soil solution, p. 441-481. In W. E. Carson (ed.), The Plant Root and Its Environment. Univ. Press of Virginia, Charlottesville, Virginia.
- (3) American Public Health Association, American Water Works Association, and Water Pollution Control Federation. 1975. Standard Methods for the Examination of Water and Wastewater, 14th ed. APHA, Washington, D.C. 1193 pp.
- (4) BOYD, C. E. 1974. Lime Requirements of Alabama Fish Ponds. Auburn Univ. (Ala.) Agr. Exp. Sta. Bull. 459. 20 pp.
- (5) _____. 1976. Water Chemistry and Plankton in Unfertilized Ponds in Pastures and in Woods. Trans. Amer. Fish. Soc., 105: 634-636.
- (6) _____. 1979. Water Quality in Warmwater Fish Ponds. Auburn Univ. (Ala.) Agr. Exp. Sta. 359 pp.
- (7) BOYD, C. E. AND W. W. WALLEY. 1975. Total Alkalinity of Surface Waters in Alabama and Mississippi. Auburn Univ. (Ala.) Agr. Exp. Sta. Bull. 465. 16 pp.

- (8) BOYD, C. E., J. W. PREACHER, AND L. JUSTICE. 1978. Hardness, Alkalinity, pH, and Pond Fertilization. Proc. Ann. Conf. Southeastern Assoc. Fish Wildl. Agencies 32: 605-611.
- (9) DOBBINS, D. A. AND C. E. BOYD. 1976. Phosphorus and Potassium Fertilization of Sunfish Ponds. Trans. Amer. Fish. Soc., 105: 536-540.
- (10) GARRELS, R. M. AND C. L. CHRIST. 1964. Solutions, Minerals, and Equilibria. Harper and Row, New York. 450 pp.
- (11) HAJEK, B. F., F. L. GILBERT, AND C. A. STEERS. 1975. Soil Associations of Alabama. Auburn Univ. (Ala.) Agr. Exp. Sta., Agronomy and Soils Departmental Series No. 24. 30 pp.
- (12) HEM, J. D. 1970. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geol. Survey, Water-Supply Paper 1473. U.S. Gov. Printing Office, Washington, D.C. 363 pp.
- (13) HUTCHINSON, G. E. 1957. A Treatise on Limnology. Vol. I. Geography, Physics, and Chemistry. John Wiley and Sons, New York. 1015 pp.
- (14) LAXEN, D. P. H. 1977. A Specific Conductance Method for Quality Control in Water Analysis. Water Res., 11: 91-94.
- (15) LIVINGSTONE, D. A. 1963. Chemical Composition of Rivers and Lakes. U.S. Geol. Survey, Prof. Paper 440-G. U.S. Gov. Printing Office, Washington, D.C. 64 pp.
- (16) MOYLE, J. B. 1946. Some Indices of Lake Productivity. Trans. Amer. Fish. Soc. 76: 322-334.
- (17) SAWYER, C. N. AND P. L. MCCARTY. 1967. Chemistry for Sanitary Engineers. McGraw-Hill Book Co., New York. 518 pp.
- (18) SCHINDLER, P. W. 1967. Heterogenous Equilibria Involving Oxides, Hydroxides, Carbonates, and Hydroxide Carbonates, p. 196-221. In R. F. Gould (ed.), Equilibrium Concepts in Natural Water Systems. Amer. Chem. Soc., Adv. Chemistry Series 67.
- (19) STEEL, R. G. D. AND J. H. TORRIE. 1960. Principles and Procedures of Statistics. McGraw-Hill Book Co., New York. 481 pp.
- (20) STIFF, M. J. 1971. The Chemical States of Copper in Polluted Freshwaters and a Scheme of Analysis to Differentiate Them. Water Res., 5: 585-599.
- (21) STUMM, W. AND J. J. MORGAN. 1970. Aquatic Chemistry. John Wiley and Sons, New York. 583 pp.
- (22) United States Environmental Protection Agency. 1972. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. Analytical Quality Control Laboratory, Cincinnati, Ohio. 97 pp.
- (23) WETZEL, R. G. 1975. Limnology. W. B. Saunders Co., Philadelphia. 743 pp.

Alabama's Agricultural Experiment Station System AUBURN UNIVERSITY

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- 2. Sand Mountain Substation, Crossville.
- 3. North Alabama Horticulture Substation, Cullman.
- 4. Upper Coastal Plain Substation, Winfield.
- 5. Forestry Unit, Fayette County.
- 6. Foundation Seed Stocks Farm, Thorsby.
- 7. Chilton Area Horticulture Substation, Clanton.
- 8. Forestry Unit, Coosa County.
- 9. Piedmont Substation, Camp Hill.
- 10. Plant Breeding Unit, Tallassee.
- 11. Forestry Unit, Autauga County.
- 12. Prattville Experiment Field, Prattville.
- 13. Black Belt Substation, Marion Junction.
- 14. The Turnipseed-Ikenberry Place, Union Springs.
- 15. Lower Coastal Plain Substation, Camden.
- 16. Forestry Unit, Barbour County.
- 17. Monroeville Experiment Field, Monroeville.
- 18. Wiregrass Substation, Headland.
- 19. Brewton Experiment Field, Brewton.
- 20. Solon Dixon Forestry Education Center, Covington and Escambia counties.
- 21. Ornamental Horticulture Field Station, Spring Hill.
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