ENVIRONMENTAL FACTORS AFFECTING THE PROPERTIES AND PRECIPITATION OF COLORING COLLOIDS IN AQUATIC HABITATS

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University in
New Orleans
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Biological Sciences

by

Billy Ray Bordelon
B.S., Louisiana State University in New Orleans, 1970
August, 1973

ACKNOWLEDGEMENTS

I would like to thank the Louisiana Water Resources Research Institute for the two years of funding for this study. I gratefully acknowledge my major professor, Dr. Michael A. Poirrier, for his guidance and assistance throughout the study. The help of my other committee-men, Dr. J. S. Rogers and Dr. J. O. Snowden, is also appreciated. Gratitude goes out to Y. M. Arceneaux who was extremely helpful in some problems associated with this study. Sincere thanks goes out to Marie LeBlanc whose speed and accuracy in typing channeled this thesis to its completion.

TABLE OF CONTENTS

LIST OF FIGURES

ABSTRACT

The coloring colloids of aquatic habitats from southeastern Louisiana are the same as those reported by other workers throughout the United States. The coloring colloids are polymeric aromatic hydroxy-carboxylic acids. These acids are fulvic, hymatomelanic, and humic acids. Color in southeastern Louisiana ranges from 0 to 5150 units. Ferric iron is associated with the colloidal complex which assists, along with their negative charge, in stabilizing the complex. The percentage of ferric hydroxide in the colloidal complex varied from 0.2 to 97.3%. The particle size has a range of 5-35 $m\mu$. In freshwater habitats fulvic acid is dominant followed by hymatomelanic then humic acids. In brackish-water to sea water habitats the fulvic acid component precipitates. At these habitats, hymatomelanic acid is dominant followed by humic acid. An infrared analysis of fulvic acid demonstrates that the functional groups associated with this acid have a high adsorptive capacity and are easily ionizable.

Color varies with both habitat and seasonal differences. Precipitation of color is accomplished by redox shifts and salinity increase. The coloring colloids are responsible for many ecological ramifications, such as altering chemical parameters, pollutant transport along with pollution bioaccumulation, in aquatic habitats.

INTRODUCTION

Natural waters having a yellow to brown color are common throughout many parts of the world (Kaufmann, 1969). Colored waters are associated with swamps, tundra, marshes, and bogs throughout the world, and are ubiquitous to streams, lakes, and ponds of the pinelands of the southeastern United States. They have been referred to in the literature as swamp, humic, colored, or brown waters.

Water of this type retains variable concentrations of iron in colloidal (Black and Christman, 1963a) complexation with a broad class of polyhydroxy-methoxy, aromatic, carboxylic acids (Lamar, 1968) of plant origin. These acids have been placed in three groups on the basis of their differential extraction. Fulvic acid is soluble in an acidic solution; hymatomelanic acid is soluble in alcohol; while, humic is not soluble in either.

There have been investigations into the nature of colored water, including its chemical and physical properties, but no field oriented studies which use recently developed techniques. Additionally, no Louisiana studies have been recorded. Information is needed on the nature of Louisiana colored waters so that sound recommendations concerning recreational, industrial, and domestic use and treatment can be formulated.

The American Water Works Association Research Committee on Color Problems Report (1966) indicated that color in water may produce the following adverse conditions:

(1) It is objectionable on aesthetic grounds

(2) It may cause taste in water

(3) It interferes with chlorination and induces bacterial growth

(4) It is objectionable to certain industries due to the possible effects on their products

(5) High concentrations limit productivity of water through its capacity to absorb photosynthetically active light

(6) It tends to foul anion exchange resins and interferes with other constituents of natural waters

(7) It influences corrosion and tends to hold iron and manganese in solution.

The Federal Water Pollution Control Administration (1968) stated that color in excess of 50 units limits productivity and may have a deleterious effect on aquatic life. Color values in Louisiana usually range between 200-300 units (U.S. Geological Survey, 1965) and can be as high as 5150 units (personal observation).

The coloring colloids produce other adverse effects which exclude aquatic organisms, especially game and commercial fish, from many habitats and limits their growth and abundance in most highly colored habitats. These include a pH range of 3.2 to 5.2, low dissolved oxygen concentrations, and high free carbon dioxide concentrations.

Another problem posed by colored water lies in its ability to hold undesirable materials as sol complexes in apparent solution. Symons et al. (1969) has shown that the colloidal acids readily adsorb iron and manganese. Poirrier et al. (1972) demonstrated that the coloring colloids adsorb C^{14} DDT and that C^{14} DDT can become concentrated by precipitation of the coloring material to at least 15,800 times its concentration in the water phase. Also, coloring colloids have the potential to adsorb heavy metals. Pilot studies in our laboratory indicated that the coloring colloids adsorb mercury and lead. These metals became highly concentrated in the tissues of oysters as the coloring material precipitated from the water phase.

Samples were restricted to southeastern Louisiana because of the numerous colored water habitats available for study. These included acid streams, ponds, and lakes in the pinelands of the Florida parishes; alkaline sloughs, swamps, drainage canals, and marshes along the Mississippi River floodplain; and brackish ponds, canals, and bayous in the coastal marshes. This area, diverse in habitats, provided an ideal location for studies on the properties and dynamics of coloring colloids.

Bayou Lacombe, a small, highly colored acid stream in St. Tammany Parish was studied in detail. This stream has a gradient of environmental conditions from the acid swampy headwaters, through the fast flowing mid-coarse areas, to the alkaline and brackish waters of Lake Pontchartrain at the mouth. Since this stream is highly colored, concentration of the coloring substance was easier, and any changes which occur in the substance would be more pronounced. Bayou Lacombe was not influenced by domestic or industrial pollution and is close to the University.

Habitat and seasonal differences in the following properties of the coloring colloids were investigated: color values on the U.S. Geological Survey scale, the buffering capacity of the colored water habitats, the particle size of the coloring colloids, an infrared investigation of the functional groups of the fulvic acid component, per cent iron in the colloidal complex, particle charge, and relative per cent of the different organic components in the complex. Aside from field research, experimental procedures were devised in the laboratory to test field data and resulting theories. Data from these studies would provide information as to what environmental factors affect the stability of the coloring colloids. An insight into their dynamics, i.e., accumulation, stabilization, and precipitation, provides necessary data for the evaluation of additional procedures for color removal. Understanding their dynamics would allow evaluation of their significance as a factor which influences the concentration and availability of nutrients and pollutants.

There has been some laboratory research concerning the structure and chemistry of the coloring colloids. No work, however, has been done on environmental factors affecting their properties, or seasonal and habitat differences of their properties.

Black and Christman (1963a, b) examined the chemical characteristics of colored waters. As researchers for water purification and treatment plants, they revealed some properties of the coloring materials which would assist the treatment for color removal.

Shapiro (1964) inspected the effect of iron and other metals on the "yellow" organic acids. Although his work showed an interaction with iron, he failed to detect any interactions with manganese, copper, or zinc.

Packham (1964) separated the three organic acid constituents of the coloring material and analyzed their relative abundance. These acids are fulvic, hymatomelanic, and humic. He indicated that fulvic acid was dominant followed by hymatomelanic acid then humic acid. His samples were freshwater, two from rivers and five from reservoirs.

Molecular weights of the humic substances are difficult to determine and many of the reported data may be unreliable. Gel filtration profiles obtained by Ghassemi and Christman (1967) indicated that the color producing molecules are mostly in the apparent molecular weight range of 700-10,000 relative to dextrans. Molecular weights up to 50,000 have been reported for humic acid (Black and Christman, 1963b) with equivalent weights in the range of 150-400. No work has been done on fulvic acid although it is frequently assumed (Packham, 1964) to have a lower molecular weight than humic acid. Kononova (1961) reported the molecular weight for hymatomelanic acid as 800.

Lamar (1968) reviewed the research on infrared analysis and provided definite evidence that the coloring colloids are aromatic. He also mentioned that the coloring "sols" precipitate under natural changes in the environment.

METHODS AND MATERIALS

Chemical and physical data were collected from six stations along Bayou Lacombe in St. Tammany Parish, Louisiana, because it is a typical acid stream abundant in coloring colloids. This stream was studied in the past by Bick and Hornuff (1953) and Gegan (1963). The same Stations (Figure 1) were sampled as the above workers, thus previous chemical data were comparable. Samples for water chemistries were taken every month for one year. Samples for relative proportions of the three colloidal acids were taken bi-monthly for one year. Samples were taken periodically for iron determinations, redox shifts, particle size and charge, and infrared analyses.

Although this stream represented diverse habitats, a variety of other sites (Figure 2) were chosen for unscheduled collections to further study the properties and precipitation of the colloidal acids. These included: two gravel pit lakes, three ponds, ten freshwater marsh canals, six seasonal swamps, ten tidal bayous, eleven polluted habitats, seven lake sites, eleven swamps, and ten stream sites.

Physical and Chemical Field Procedures

Water samples for pH, RpH, Eh, water temperature, alkalinities, free carbon dioxide, color, and hardness were collected a short distance below the surface with a three liter PVC water sampler. Water collection methods as given in Welch (1948) were followed. Water samples for laboratory analyses were collected in the same manner and stored in polyprophylene bottles at 5°C.

A Beckman Model G battery-operated pH-Eh meter was used for the measurements of pH, RpH, and Eh. RpH is the measured pH of a sample after shaking in a jar for one minute to drive off the free CO_2. The Beckman Model G meter was always standardized before each reading with buffers of pH 4.4 and/or pH 7.0. Eh (redox potential) was measured using a nonreactive bright platinum electrode. The results were expressed in millivorts (mv). The meter was calibrated monthly, if needed, against a Beckman Expandomatic laboratory pH meter.

Air and water temperatures were taken with a mercury-filled centigrade thermometer as instructed in Standard Methods (American Public Health Association, 1971).

Alkalinity and free carbon dioxide were measured according to procedures in Welch (1948), phenolpthalein and bromcresol green-methyl red mixed indicators were used.

Dissolved oxygen was measured with a battery-operated Yellow Spring Instrument Model 51A oxygen meter, which was calibrated prior to use according to the methods given by the Yellow Springs Instrument Co. (1970). The oxygen meter was standardized on a bi-weekly basis against the Winkler method of dissolved oxygen given in Standard Methods (American Public Health Association, 1971).

Unfiltered and filtered color was determined using a Hach AC-DR Colorimeter (Hach Chemical Co., 1969). One standard color unit is produced by a solution containing one mg/l platinum and twenty-five hundreths mg/l cobalt (Rainwater and Thatcher, 1960). Water transparency was determined with a Secchi disc.

Chemical Laboratory Procedures

All tests on water samples were run within five hours after collection.

Conductivity was determined by a Yellow Spring Instrument Model 31 conductivity bridge using either 0.1 or 10.0 conductivity cell for fresh or brackish water respectively.

Chloride was measured by using the argentometric method accompanied by the addition of aluminum hydroxide to counteract the error of color on the endpoint (American Public Health Association, 1971).

Total dissolved solids and loss on ignition was measured by procedures given in Standard Methods (American Public Health Association, 1971).

The following parameters were examined using reagents and methods prepared by the Hach Chemical Co. (1969): orthophosphate, silica, sulfate, nitrate, tannins and lignins, ferric iron, ferrous iron, and manganese.

In situations in which the organic acids were to be digested to release the total metal concentration, the procedures of Standard

Methods (American Public Health Association, 1971), and Masri and Friedman (1972) were followed.

Analytical Techniques for Concentration and Isolation of the Coloring Components

Coloring colloids are usually very dilute in natural habitats and must be concentrated from large volumes of water to obtain sufficient amounts for study. My sampling plan differed from all previous workers in that I had to process many more samples. As many as six samples were collected on the same day and processed simultaneously in the laboratory. Concentration procedures of all prior workers were examined and evaluated in terms of my project needs.

Black and Christman (1963b) used flash evaporation and freeze concentration to concentrate the color in the water samples. The flash evaporation procedure was very time consuming and required large samples. Their color values were not indicated but were probably low based on a sample size of 80 liters. Freeze concentration was eliminated due to expense of a 16 cubic ft. freezer and the time consuming nature of the method. Neither technique allowed for the concentration of many samples simultaneously.

Shapiro (1964) also used flash evaporation of 160 liter samples. He concluded that evaporation temperatures above 45°C would alter the structure of the acids. I found that evaporation at this temperature took two days for one liter of water. So again, flash evaporation under 45°C was time consuming and of little use for large sample sizes.

Packham (1964) used a strongly basic anion exchange resin, Amberlite IRA-904, with a high affinity for organic acids and with an open structure enabling the organic matter to be removed when the resin was eluted with sodium chloride. In terms of percent recovery of the three acids, I felt this procedure to be superior to other workers techniques. However, I found that there were disadvantages to this procedure. The concentration procedure lasted 100 hours, volumes of water as high as 200 gallons were needed, and equipment, such as, column, resins, batteries, pumps, etc., posed an expense and transportation problem. Of course, this procedure did not allow for many samples to be concentrated simultaneously.

Aschan (1909) precipitated the coloring material with ferric chlorite (amount not stated). Although some chemical properties were analyzed, the coloring acid components were not separated. Prior work in our laboratory demonstrated that coloring colloids could be removed by addition of 0.25 ml of 0.1<u>M</u> ferric chloride per 100 ml sample. This concentration was optimum for all color values of water. This method of concentration of color by precipitation with ferric chloride was ideal for this study. It allowed for a small samples (20 liters) because the water was highly colored and many samples could be processed simultaneously.

The precipitation method has been analyzed as to the chemical mechanics of the coagulation-precipitation process. As the coagulant dissolved and the trivalent ferric ions became available, they neutralized the negative charge on the particles of color (Pilipovich, et al., 1958). When the positively charged ferric ions have neutralized a considerable portion, perhaps most, of the negatively charged colloidal particles of color (Pilipovich, et al., 1958). The resultant particles may be called microflocs, since they are still beyond the limits of visibility and far too small to settle by gravity (Langelier and Ludwig, 1949). Tiny microflocs cluster together and agglomerate with the formation of floc particles which steadily grow in size until they are in proper condition for sedimentation. During this phase of floc growth surface adsorption takes place (Matijevic, 1961). The amount of surface area exposed by the innumerable particles of floc is very great.

The ferric chloride concentration method was compared to Packham's (1964) method using water from seven different sites of water. After the isolation of the three acids, there was no difference in humic acid recovery, two percent increase in fulvic acid recovery, and a twelve percent increase in the hymatomelanic acid recovery using the ferric chloride method was used.

Once the coloring materials were concentrated, they have to be purified and isolated into the three separate coloring components. The separatory isolation scheme used was the same as Packham's (1964). He found that Shapiro's (1957) method led to incomplete separation and total loss of the humic fraction, and Black and Christman's (1963b) method was time consuming and could not separate the fulvic fraction from other organic compounds. Samples were collected in five gallon polyprophylene containers. In the laboratory, 20 liters of water were removed from the container and filtered by vacuum filtration with Reeve Angel 201 filter paper, Millipore filter membrane (AA WG C-47-00), and then Sartorious filter membrane (S-111 06-047). The purpose of filtering down to 450 mμ was to remove any substances which would interfere with the purification scheme. The filtered water was then placed in 10 gallon containers. A 50 ml aliquot of 0.1M $FeCl_3$ was added to the water and agitated. After ten hours a precipitate formed.

The precipitate was removed by vacuum filtration and dissolved in concentrated NaOH and the supernatant was discarded. After approximately four hours another precipitate developed, i.e. $Fe(OH)_3$. The precipitate was removed by vacuum filtration and the supernatant solution contained the unpurified humic, hymatomelanic, and fulvic acids. This solution was filtered by vacuum filtration with Reeve Angel 201 filter paper, Millipore, then Sartorious filter membranes.

The solution was acidified to a pH of 1 with concentrated HCl. The sample was agitated and allowed to set for 24 hours. A subsequent precipitate (humic and hymatomelanic acids), and supernatant (fulvic acid) evolved. The two phases were separated by vacuum filtration.

Five-hundred ml aliquots of the fulvic acid solution were extracted with 100 ml then twice with 50 ml of n-butanol using separatory funnels. The organic extracts were then combined and evaporated to dryness under reduced pressure at a temperature not exceeding 45°C. The fulvic fraction was then separated from any impurities, if present, by extraction with acetone. The acetone extract was filtered and evaporated to dryness under reduced pressure, the solid residue of fulvic acid being scrapped from the flask and stored in a desicator.

The humic-hymatomelanic precipitate was digested with ethyl alcohol at 40°C. Hymatomelanic acid was coerced into solution and the insoluble humic acid remained. The hymatomelanic solution was evaporated to dryness under reduced pressure at 40°C. The humic precipitate was dissolved in a minimal volume of 5N NH_4OH and re-precipitated with HCl after filtration of the ammonical solution. The precipitate was filtered, washed with 0.1N HCl and dried at a temperature not exceeding 45°C.

After separately weighing the three acids, their concentrations and relative proportiones were computed.

PROPERTIES OF THE COLORING COLLOIDS

Color:

Color values of all the stations throughout the year are found in Appendix III. This data consisted of 153 measurements from 65 various sampling stations of which the color value range was 0-5150 units. The color of waters in southeastern Louisiana depended on habitat and seasonal differences.

In areas with abundant leaf litter, such as swamps and forests, the color values ranged from 250-300 units. When pine needles were abundant among the leaf litter this range increased to 300-400 units. Streams and bayous in which peaty soil was abundant typically had the highest color values which ranged from 500-700 units. In one location (Little Woods Canal) the color value was 5150 units which was the highest color value measured. Streams with sandy bottoms typically had low color values (0-75 units) unless the color was allochonthous, i.e., coming from another area of the stream with different bed characteristics.

Most stations in the Florida Parishes had a reddish soil (Mississippi Alluvial Fan). This soil was found to be acidic and contained large amounts of iron. Water in these areas were colored about 200 units regardless of bed type. The majority of this color was due to the presence of iron.

In areas of brackish water such as tidal marshes and estuaries color values were low (0-50 units). The color of water at polluted habitats did not differ from unpolluted habitats.

During various occasions the coloring material was found precipitated on the stream bed and shore and often on aquatic plants. During this phenomenon the color of the water drastically decreased.

It was noted that the color of water at any given station had a seasonal variation. The color of water from Bayou Lacombe along with other pertinent chemical characteristics (Appendix III) was measured one year on a monthly basis. As seen from these data an increase in color was found after periods of rainfall. This was due to the leaching effect of the rainwater as it percolated through the soil and leaf litter. The increase in color was associated with lowered dissolved oxygen, pH, and bicarbonates, and increased the free carbon dioxide and naturally the coloring colloid concentration. During periods of drought, the water level dropped and Bayou Lacombe was principally fed by ground water. At the same time, the color of water drastically decreased with associated floc formation on the aquatic plants. The decrease in color was associated with increased dissolved oxygen, pH, and bicarbonates, and decreased free carbon dioxide and coloring colloid concentrations.

The color of water was relatively stable when stored in the laboratory. A one gallon sample of water was collected in August, 1971, at station 2 (Bayou Lacombe) and stored in a glass jar for one year. Monthly color values were obtained and plotted in Figure 3.

This graph shows that the color remained within five units of the original color.

The pH of colored waters is usually acidic since the coloring colloids are acids. It was found that as the pH increased the color increased. Figure 4 is a plot of color vs pH. The graph indicates a linear relationship. Black and Christman (1963a) also reported that color increases with pH. The authors attributed the color increase to an increase in the molecular size of the color colloids as the pH increased.

The poorly buffered characteristics of colored water habitats is illustrated in Figures 5 and 6. Water was collected from Station 2 (Bayou Lacombe) at two different times of the year, once when it was highly colored (245 units) and once when it was hardly colored (40 units). Monitoring the pH, successive 0.5 ml aliquots of 0.01<u>N</u> NaOH were added to each solution. These graphs are also supported by the works of Gegan (1959) and Shapiro (1957). The lack of buffering capacity when the water was colored accounts for the extreme pH variations not only from station to station, but from month to month. In the late summer and early fall the pH is affected by the concentration of free carbon dioxide present, an inverse relationship which is characteristic of poorly buffered streams (Giddings and Monroe, 1972). Since no carbonates and a small amount of bicarbonates is present there is only limited buffering capacity from this source. However this capacity increases when the water is not as colored.

Ferric-Ferrous Iron and Percent Iron in Colloidal Complex

It is well known (Swain, 1963) that iron is transported in waters rich in organic matter, evidently as stable "humic" complexes in the form of a protected colloid. Coloring colloidal acids have carboxyl and hydroxyl functional groups which form chelates in natural waters (Stumm and Morgan, 1970). These substances coordinate and form complexes, mostly with iron since iron is so abundant. Such substances bind ferric hydroxide and at high concentrations are capable of preventing the precipitation of both the ferric hydroxide and the organic colloid.

Approximately 153 samples (Appendix) were processed for the determination of ferric and ferrous iron throughout selected habitats of southeastern Louisiana. Forty-five samples were anlyzed for percent iron complexed with the colloids. During collection of samples, field observations of flocculant material in water was noted. This data contributed to the examination of the stability of the ferro-organo complex. The flocculant materials were the precipitated coloring colloidal complex. Precipitation of the complex had habitat and seasonal differences. Precipitation usually took place in the unbuffered, usually acid, highly colored habitats. During dry seasons precipitation was more abundant than rainy seasons.

Iron concentrations were measured with a Hach Colorimeter (Hach, 1969). The amount of iron bound with the colloidal complex was calculated by measuring the iron concentration before and after the organic matter was destroyed (Gjessing, 1964). The organic digestion consisted of boiling a 50 ml filtered water sample for 15 min with two ml of concentrated HCl, cooling and then adding four ml of ten percent (w/v) sodium acetate solution. The pH was then adjusted to between four and five with ammonia. The percentage of iron in the complex was taken as the ratio of complexed iron to organic matter (Welsh, 1948).

The iron concentrations in samples before acid digestion ranged from 0-3.0 ppm. The percentage of ferric hydroxide in the colloidal complex varied in samples analyzed from 0.2 to 97.3%. The percentages were high where either iron or organic matter was abundant in soil.

The ferric hydroxide concentration associated on the colloids varied with different habitat conditons. As the pH of a colored water habitat increased (Figure 7) large amounts of ferric hydroxide were generated. The colloidal acids binded as much of this ferric hydroxide as possible. Any ferric hydroxide increase beyond this saturation point of the colloids precipitated as flocculant ferric hydroxide.

There was a direct relationship between increasing color and increased percentage of ferric hydroxide in the colloidal complex. As the color of the water in the habitat increased (Figure 8) there was increased surface area for the binding of the ferric hydroxide. Since surface runoff and leaching were responsible for increased color, they were also responsible for the greater abundance of available iron.

It was interesting to examine the effects of reducing ground water to the percentage of ferric hydroxide in the colloidal complex. During the dry months, the ratio of ground water to rain water supply increases for many habitats in southeastern Louisiana. The ground water used in the following experiment was from a 1600 foot artesian well near Talisheek, Louisiana. It had a dissolved oxygen of 0.2 ppm and an Eh of -221 mv. As seen by Figure 9, when the percentage of ground water increased the percentage of ferric hydroxide complexed decreased due to the reduction of the ferric to ferrous species.

The ferrous-ferric relationship was unique in acid water habitats as seasons progressed. Figure 10 is a plot of the ferric and ferrous relationship in Bayou Lacombe. During rainy seasons, the rain percolated the soil and leached large quantities of minerals and organic material. Thus the color values were high due to high colloid and ferric concentrations. The ferrous concentration at this time was low. When the drier months came, streams were mostly fed by reducing ground water which increased the ferrous concentration. At that time floc formation on vegetation and shore was high and consisted of coloring colloidal acids and ferric iron.

Symons _et al_., (1969) concluded that manganic ion was unstable in aqueous solution because it was subject to disproportionation. Strong complexing agents, such as the colloidal acids of natural surface waters, stabilized manganese in the trivalent state. This was witnessed, in my study, by the increase in concentration of available manganic ion after digesting the organic matter. In Bayou

Lacombe as well as other southeastern Louisiana habitats the manganese concentrations were present in very small amounts.

Redox Potential

As I waded through many habitats the bottom would become disturbed. At the same time, the Eh of the water fluctuated and the precipitation of the coloring colloids was noted. This happened in many habitats but was prevalent in colored eutrophic ponds with non-circulating reducing bottoms. Henceforth the Eh shift was a potential mechanism for the precipitation of the coloring colloids.

An analysis of the redox (oxidation-reduction) shifts of colored water habitats was then undertaken. These shifts were found to be important since the 153 habitats sampled showed a wide range of Eh measurements. This parameter was found important to the stability of the coloring colloids.

The Eh measurements in selected habitats ranged from -200 to -500 mv. This range showed both habitat and seasonal differences. The unbuffered, acidic, highly colored habitats were slightly oxidizing. The buffered, alkaline slightly colored habitats were strongly oxidizing with reducing bottoms. Most polluted habitats were slightly reducing. At many streams, e.g. Bayou Lacombe, the Eh measurements differed from the headwaters to the mouth by 200 to 300 mv.

Many habitats showed both diurnal and seasonal variation. The diurnal differences were usually found after a rainfall which agitated the bed. Seasonal variation was usually prominent in habitats where ground waters fed the system at different times of the year. During these times there were even transectional differences in the Eh readings. I found reducing conditions in the middle deeper waters and oxidizing conditions at the shoreline and on vegetation. Precipitation of the coloring substances were evident at this time.

Many factors affect the Eh at any given habitat. Factors such as hydrogen sulfide, methane, ground water, oxygenation, dead organisms, rainfall, and pH shifts were found in this study to affect the Eh.

In many cases, precipitation of the coloring colloids in nature was noted after the Eh shifted. Since this happened frequently in nature, an investigation of this phenomenon was prompted. This investigation consisted of placing filtered water in three-liter jars, altering various parameters and checking the samples periodically for precipitation or color reduction.

Water from Filmore Pond in City Park, Louisiana, was used for these experiments. This local pond was colored, free from pollution, typical of other colored water habitats, and close to the University. The water was always filtered down to 450 mμ. In Table I the water chemistry is given.

The first experiments were to analyze what conditions caused reduction. The Eh, color, and oxidation state of iron were monitored. The contents of the jars are given in Table II. These consisted of natural reducing substances, such as dead organisms, H_2S, CH_4, artesian water, pH shifts, and reducing substances not found in nature such as dextrose and hydroxylamine hydrochloride. The Eh, color, and state of iron was measured after 24 hours of reducing conditions. Table III shows the results. It was well demonstrated that many substances altered the redox equilibrium which shifted the ferric state to the soluble ferrous state. No precipitation occurred.

Two questions then became important. First, in the reduced state, was there any association of iron with the coloring colloids? Secondly, did the particle size of the complex changed? Two experiments were prepared to demonstrate whether or not there was association between the colloidal acids and the soluble iron. First, four-25 ml samples of filtered Filmore Pond water were obtained (A_1, A_2, B_1, B_2). Samples B_1 and B_2 were reduced with H_2S as in the above experiment. Iron determinations were done on A_1 and B_1 which showed 0.26 ppm ferric (no ferrous) and no ferric (0.32 ppm ferrous) respectively. A_2 and B_2 were treated to digest the colloidal acids (Gjessing, 1964). Iron determinations were then done on A_2 and B_2 which showed 0.32 ferric (no ferrous) and no ferric (0.32 ppm ferrous). Hence, in the normal oxidized condition iron is held associated with the coloring colloids and in the reduced state there seemed to be no such association.

One test for fulvic acid (Oldham and Gloyna, 1969) is that it is fluorescent in ultraviolet (UV) light. Fulvic acid is the predominant acid in the Filmore Pond water and has higher adsorptive characteristics for iron than either humic or hymatomelanic acids (Stevenson, 1972). An experiment was devised to further show the lack of an association of ferrous iron with coloring colloids.

Six-25 ml aliquots (A-F) of filtered Filmore Pond water were obtained. The solutions were reduced with H_2S as in the above experiments. An analysis of the first three solutions (A, B, C) showed no ferric iron, was UV positive, and had 0.32 ppm ferrous iron before and after acid digestion. Solutions, D, E, and F were centrifuged at 17,500 rpm for 30 min at 25°C. Supernates and precipitates developed. The supernates (D_s, E_s, F_s) were removed and the precipitates (D_p, E_p, F_p) were washed several times, then resuspended in 0.05M NaOH. An analysis of the supernates in solutions. D_s, E_s, and F_s showed no UV transparency, no ferric iron, and 0.32 ppm ferrous iron before and after digestion. The precipitates (D_p, E_p, F_p), however, contained the coloring colloidal fraction. D_p, E_p, and F_p showed UV transparency, and no ferric or ferrous iron before or after digestion.

The colloidal nature of the coloring acids proved not to change under reducing conditions. A particle size analysis before and after reducing conditions were applied showed that the size was 10-20 mμ.

Jar tests were performed to determine the effects of oxygenation upon coloring colloids. Filtered Filmore Pond water was used again. Table IV shows the contents of the jars. Oxidixing conditions used were air, oxygen, turbulence, and pH shifts. After 24 hours the Eh, color and form of the iron was measured (Table V). The results indicated that oxidation alone does not cause precipitation of coloring colloids or of iron. The iron remained in the ferric state. Color did not differ much from the control. Only precipitation in the last jar occurred. That jar had no coloring colloids. When oxygenation occurred, ferric hydroxide was generated and precipitated. The coloring colloids kept the ferric hydroxide from precipitating in the other jars.

Oxidation-reduction shifts were common in colored, unbuffered aquatic habitats, as well as alkaline eutrophic habitats with reducing bottoms. Thus, using this principle, jar tests were constructed to monitor redox shifts. Again, filtered Filmore Pond water was used. Table VI shows the contents of the jars. The Eh, UV, color, and form of iron was measured (Table VII). Solutions to which H_2S was added for 12 hours was then oxidized with O_2 for 12 hours.

Precipitation only occurred in jars which were reduced and then oxidized. The flocs were very similar to those seen on the stream beds and vegetation. In jars with precipitated solutions both the supernates and precipitats were analyzed. The upper 2.950 liters of supernate were removed from solutions B, D, F, H, and J. The floc and 0.50 liter of supernate was filtered through Reeve Angel 201 filter paper. The 0.05 liter of supernate was returned to the rest of the supernate. Three liters of 0.05<u>N</u> NaOH extracted and resuspended the floc from the filter paper.

Under reducing conditions the iron became solubilized and was unassociated with the coloring colloids. When oxidizing conditions occurred the iron and coloring colloids precipitated, resulting in a colorless solution. An analysis of the precipitate demonstrated that both ferric iron and the coloring colloids were present. This experiment was repeated twice. First, well water (10%) and mechanical shaking were the reducing and oxidizing agents. The second time, a pH shift of two units acidic (0.05M HCl) then two units basic (0.05N NaOH) were used. While it is true that a pH change is not necessarily a redox shift, it has been shown that the Eh is directly proportional to the pH of an acid water system (Overbeck, 1952). Since Eh, as well as pH, drastically changes in colored water habitats, a pH shift would logically attribute to precipitation in nature. In both repetitions the results were the same as the initial experiment.

An experiment was also devised to test what effect different oxidizing then reducing agents would have on the dynamics of the colloidal complex. Once oxidized the complex remained stable, as seen in a previous experiment. When the solutions were then reduced, they merely remained unassociated as the ferrous iron went into solution. No precipitation occurred. Thus it seemed that only a reduced then oxidized system created precipitation.

This finding did not derivate from field observations of naturally occurring precipitation. Much precipitation took place on submerged vegetation along the streams and shoreline areas where there is an interaction with oxygen. This occurred when reducing ground water entered these habitats. Much precipitation occurred on the stream beds when algae and other plants were present. Reduction can occur by means such as H_2S, other swamp gases, dead organisms, etc. Turbulence is also a major factor in the oxygenation of aquatic habitats.

Relative Percent of the Coloring Colloids and Salinity

Since color varied in all habitats selected, it was suspected that the concentration of coloring colloids and perhaps the relative percentages of the three coloring acids also varied.

The habitats selected included lakes, ponds, fresh and salt water marshes, swamps, bayous, and streams. A total of 118 samples were processed for this parameter. Bayou Lacombe was analyzed monthly for color and bimonthly for relative percentages of the three colloidal acids.

The concentration of coloring colloids was measured by the amount of organic matter that was loss on ignition from a filtered water sample. No loss on ignition was ever recorded when the filtered samples were centrifuged at 17,506 rpm for 30 min at 25°C. If any other organic matter remained it had to be in trace amounts. Nevertheless, the loss on ignition was taken as the concentration of coloring colloids. These values ranged from 100-900 ppm (Appendix III).

The concentration of the coloring colloids had habitat differences. In areas where the rate of decomposition was high, such as streams in forests and swamps, and acid ponds, the coloring colloids were abundant. Also, in areas where the soil had a high percentage of peaty material, the coloring colloids were also abundant. Many temporary habitats such as roadside ditches or small, shallow ponds typically had low concentrations of coloring colloids.

Although research has been done on the isolation of the coloring colloids (Black and Christman, 1963a; Lamar, 1968; Shapiro, 1957), Packham (1964) was the only worker who discussed their relative percentages in nature. In samples from three reservoirs, two lakes, and two rivers he found that fulvic acid was the most abundant followed by hymatomelanic then humic acids.

Although the concentrations of the coloring colloids varied in my study, the relative percentages of the three acids at any given freshwater habitat were the same as reported by Packham (1964) and were extremely stable. The only time the relative percentages differed was when freshwater flowed into brackish water causing a decrease in the fulvic acid concentration. Hymatomelanic and humic acids, however, were stable. Poirrier (personal communication) and Hopkins (1961) have both observed the changing (decrease) color of water as it approached an estuary. No one, however, has examined which constituent of the coloring materials was responsible for the color change.

There was a distinct pattern of the distribution of the three coloring acids along Bayou Lacombe. Stations 1, 2, and 4 have fulvic acid as the most predominant (83%) followed by hymatomelanic acid (13%) then very little humic acid (4%). Contrarily, Stations 5 and 6 have hymatomelanic acid as the most predominant (85%) followed by humic (15%) then fulvic (4%) acids. Figure 11 shows how fulvic acid decreases substantially from the above stations. At the same time, hymatomelanic and humic acids remained relatively unchanged throughout all stations (Figures 12 and 13). Since Stations 5 and 6 are tidal bayous, with intrusion of brackish-water from Lake

Pontchartrain, salinity was suspected to influence the concentration of the coloring acids.

In an analysis of other sampling sites (Figure 2) throughout southeastern Louisiana for colloidal acid concentration relationships, the same pattern developed: freshwater habitats consisted of very high fulvic acid concentrations (Figure 14). When the relative percentages of the acids were computed (Figure 15), the fulvic and hymatomelanic values were in contraposition while the humic acid values differed slightly. The answer as to why this happened in nature may best be answered by a structural chemist. In a private communication with Stevenson (U. of Illinois, Agricultural Experimental Station), he stated that "the COOH groups of the humic and hymatomelanic acids originate from side chains of an aromatic ring, whereas those of fulvic acid have been formed largely by partial oxidation of phenolic and/or enolic moieties, and the greater mobility of fulvic acid rather than humic or hymatomelanic acids in water was due to a combination of lower molecular weight and higher concentrations of acidic functional groups, particularly COOH."

Jar tests were devised to study the effects of increasing salinity upon acid components in the laboratory. The water used was filtered Filmore pond water. Centrifugation was performed at 17500 rpm for 30 min at 25°C. Salinity was increased by using Instant Ocean sea salts to give salinities of 5, 10, and 15 ppt (Table VIII).

Before the solutions were stored, salinity was measured (Table IX). The solutions were allowed to set for three days. Only tests containing fulvic acid (B, C, D, F, G) precipitated. To all tests, salinity and color were measured. To those that had no precipitation, only a total acid (coloring) analysis was performed. In tests that had a precipitate, the supernate was collected down to 0.050 liters. The floc and associated supernate was filtered through Reeve Angel 201 filter paper. The small supernate portion was added to the rest of the supernate. Fulvic acid was extracted from the precipitate using the n-butanol flash evaporation method.

These tests indicate that with increasing salinity there was increasing precipitation (color removal) of the fulvic acid fraction, whereas the humic and hymatomelanic acids are stable. It was interesting to note the change in salinities. The salinity of all solutions containing fulvic acid decreased over the three day period.

Thus it has been demonstrated that as colored freshwater mix with brackish waters, there was color reduction, decrease in fulvic acid concentration, and a decrease in the salinity.

Particle Size

Natural color in water has been reported by Shapiro (1957) to be in true solution. According to Black and Willimas (1961), natural color exists mainly as a colloidal dispersion. The theories of particle size proposed by the above authors was backed up by no experimental evidence on particle size. The size range of a colloid is defined as 1-1000 mμ (Sienko and Plane, 1966).

Black and Christman (1963b), using electrodialysis, indicated that most of the color in their water samples was colloidal in nature, that there was a range of particle sizes, and that most of the particles were in the 3.5-10 mμ diameter range.

I used membrane vacuum filtration techniques to measure particle sizes. A Millipore (Model 5KH32EG-550T) vacuum pump was used as the vacuum source. The filter papers or membranes employed are given in Table X. The method consisted of vacuum filtering a sample (100 ml) of colored water succesively using filters of decreasing porosity. After each filtration, an optical density measurement was taken. The optical density was read on a Bausch and Lomb spectronic 20 at 390 mμ (Datski, 1940). When the optical density reading was 80-100% less than that of the prior reading (Black and Christman, 1963b), it was assumed that 80-100% of the color was removed and the particle size was the same as the porosity of that filter or membrane.

The results from 67 samples demonstrated that the particle size was in the range of 5-35 mμ. Optical densities for the 4.8 mμ and 3.5 mμ membranes were never lower than the 5.0 mμ membrane. The particle size range is slightly different than Black and Christman's range of 3.5-10 mμ. The discrepancy of the ranges may be in the fact that the procedures of size estimation were different or there may be some geographical differences in the particle size range. Nevertheless, the size range by both methods show the coloring substances to be colloidal in nature.

An interesting observation from this study was that the particle size was pH dependent. For each particle size measurement taken, the pH of that sample was obtained. Figure 16 plots particle size versus pH. It is shown that as the pH increased the particle size also increased, and that at certain pH increments the colloids may consist of two sizes which accounts for the overlapping at the extremes of the particle sizes.

Since particle size was pH dependent there was habitat differences in the size of the coloring colloids. Highly colored acid habitats, in the Florida Parishes exhibited the smaller particle sizes, whereas the alkaline, slightly colored habitats, such as the Mississippi River Floodplain stations consistently showed larger particle sizes.

The Bayou Lacombe stations showed seasonal differences in the particle sizes throughout all stations. These differences, again, were associated with the changing pH. After periods of rain, color in Bayou Lacombe increased and pH decreased. During dry or drought conditions, alkaline artesian water fed the bayou and caused the pH to increase. The particle sizes of color throughout these stations were affected by the pH shift. As the pH decreased the particle size decreased, and as the pH increased the particle size also increased.

Ghassemi and Christman (1967) postulated that the particle size increase can be attributed to an increase in the molecular radius due to an increase in the ionization of the functional groups. Under highly alkaline conditions, the color molecules appear much larger, presumably due to complex formation with iron or other metalo-hydroxy complexes.

Infrared Spectra of Fulvic Acid Component

The functional groups of fulvic acids were studied by Shapiro (1957), Black and Christman (1963a), and Lamar (1968). Shapiro (1957) stated that the structure was only aliphatic. His isolation procedure, however, did not involve purification of his sample. Black and Christman (1963a) and Lamar (1968) demonstrated that most of the functional groups were aromatic. Fulvic acid was chosen to study the functional groups due to its high absorption characteristics and its solubility in organic solvents. It is also abundant in nature and can be compared to other workers.

Twenty-three samples were analyzed from habitats which included eight acid streams, three alkaline ponds, six tidal marshes, and six bayous. The stations were sampled at different times of the year. Fulvic acid was isolated from humic and hymatomelanic acids and dissolved in spectrograde n-butanol to give a ten percent fulvic acid solution (Lamar, 1968). A Beckman IR-8 double beam spectrophotometer-recorder was used. The optical cells were made of silver chloride. Due to the photosensitivity of the cells, handling was always done in a darkroom.

Spectrographic results (Figure 12) indicated that the functional groups of the fulvic acid component of habitats samples were the same as those reported by Black and Christman (1963a) and Lamar (1968).

Although Shapiro (1957) reported that the basic structure was aliphatic, I found aromatic structures throughout all selected habitats with no seasonal variation.

Carboxylic acids and carbonyl groups typically showed absorption bands over the 3.33-4.00 μ range. This was a result of the relative proximity of the associated OH and normal C-H stretching frequencies (Shriver et al., 1965). These bands were observed on the spectra of all fulvic acid samples. Two important bands on every spectrum were located at 5.92 μ and 6.18 μ. The former was the carboxyl group stretching frequency, and the latter was the characteristic stretching frequency of doubly bound carbon atoms in conjugated phenyl groups, indicative of unsaturation. Absorption at the 7.40 μ range in all samples was probably due to alkane groups. The absorption peak in the 8.30 μ region was due to C-O bonding as with carboxyl or ester groups.

The infrared data obtained promotes the conclusion of other workers that the organic component of the coloring colloids are aromatic hydroxy carboxylic acids. Since they are acids, they significantly influence the pH of water. The presence of functional side groups such as amines, aldehydes, alkanes, and esters of carboxylic acids demonstrated the complexity of the colloids.

Particle Charge

Postma (1967) indicated that elementary particles of colloidal or semi-colloidal dimensions usually contain an electric charge which influences their behavior in suspension. Their charge may be explained by: (1) preferential adsorption of anions, especially, hydroxyl ions, (2) catonic substitutions within the crystal lattice, and (3) residual valences (broken bonds) at particle edges.

Aschan (1909) first demonstrated the association of the negative charge with the organic color. Black and Christman (1963b) after analysis of infrared spectra, indicated that the negative charge on particles of coloring colloids may arise from ionization of the carboxyl and aromatic hydroxyl groups.

To determine if there was a negative charge associated with the colloidal acids of Bayou Lacombe, an electrophoretic experiment was devised. One hundred ml of water (240 units) were collected from Station 2 and filtered. The water was placed in a U-tube with a height of 158 mm and a diameter of 28 mm. Positive and negative electrodes were placed on either side of the tube. The electrodes were connected to a Heathkit IP-17 power supply unit at 10 volts and 25 milliamps. In 16 min the color on the negative side of the U-tube dropped to 30 units and the positive side increased to 450 units. This corresponded to over a 50% increase in color on the positive side. The negative nature of these colloidal acids stabilizes them in the water column through repelling forces.

The negative charge would show no habitat or seasonal differences since the infrared spectra of the functional groups, responsible for the charge, showed no difference.

DYNAMICS

Color in water depends primarily on iron. Iron is abundant in nature in both the ferric and ferrous state. Only the ferric state is associated with the coloring colloids and the ferrous state, when present, is soluble. The ferric association is vital to the stability of the colloidal complex. In all habitats studied there was always ferric iron associated with the coloring colloids (0.2-68.3%). The iron, along with the negative charge, keeps the coloring colloids in the water column. Without this association both the coloring material and iron would precipitate. Color is also contingent upon pH, Eh, and particle size. An increase in particle size and pH increases the color. Certain Eh shifts cause the coloring colloids to precipitate. The Eh shift indirectly precipitates the coloring colloids by directly affecting the state of iron.

The state of iron in water is dependent on Eh. In most cases, the Eh of the water column is oxidizing, but many conditions can occur to alter this. The Eh fluctuation of an aquatic habitat is one mechanism by which the coloring colloids and iron precipitate. Eh ranges are normally found between -400 mv and +500 mv. The basic mechanism of precipitation involves a reduction then an oxidation shift. Upon reduction, the iron changes its state to the soluble ferrous form where it is no longer associated with the coloring colloidal complex. However, upon oxidation, the iron and coloring colloids readily precipitate in a flocculant manner.

Many parameters are responsible for reducing conditions in aquatic habitats. Swamp gasses (H_2S, CH_4) are usually found in colored water habitats since the organic decomposition producing the gas also produces the color. The gasses are usually sealed in the muds and when disturbed they have a reducing effect on the aquatic system. Values between -250 and -110 mv were typically recorded in such habitats. Bacterial decomposition of dead organisms causes reducing conditions as low as -400 mv. Ground waters have a tremendous influence on the reduction of colored water habitats. These waters are low in dissolved oxygen and usually contain substantial amounts of H_2S. During dry periods, these ground waters supply the water for many aquatic habitats in southeastern Louisiana. Henceforth, reducing conditions prevail giving the streams and other bodies of water their seasonal precipitation of the coloring colloids.

Once reduction occurs in an aquatic habitat, oxidation usually follows. The upper layers of water are usually oxidized due to atsmospheric interaction. Thus, when reduced water is circulated, oxidation occurs readily at the water surface and shoreline areas. Differences as high as 550 mv were recorded between the bottom and surface waters. Aquatic vegetation significantly contributes to oxygenation. Another natural mechanism is turbulence. Since colored streams have a low buffering capacity there is substantial pH fluctuation. Small pH shifts (2-3 units) occur naturally and alter the oxidation-reduction system, which is another natural means of precipitation.

In any case, it is apparent that many variations can occur in nature to cause a redox shift which allows the iron and coloring colloids to precipitate. This process does not appear to be selective of any acid component. Although Eh affects the total concentration of coloring colloids, the relative percentages of the three colloidal acids are not influenced. Also, Eh does not appear to affect the particle size.

The pH of a colored water habitat does affect certain parameters. The pH is usually acidic since (1) the coloring colloids have acid functional groups and (2) the presence of certain soil and floral types are responsible for acidic conditions. The acidic nature of these habitats keeps the particle size of the colloids small (5 mμ) by way of deionization. In alkaline habitats the particle sizes are at their maximum (35 mμ) and the functional groups are ionized. In this manner, pH affects the overall charge on the colloids. These alkaline habitats are also colored and usually eutrophic. This process causes the reducing muds to be sealed off from the water column and subject to Eh shifts when disturbed. The pH does not seem to affect the relative percentages of the different colloidal acids.

Particle size and charge are related and most dependent on pH. The particle size is directly affected by pH while the charge is indirectly affected by pH and directly by particle size. The particle charge comes from ionization of functional groups such as carboxylic acids and aromatic compounds. Increased color increases the particle size and charge. Eh, however, affects neither.

The last, but probably the most important, mechanism of precipitation occurs in brackish-water habitats. In freshwater, there is a very stable relative proportion of the three coloring acids. It was found the fulvic acid was the most prominent (83%), followed by hymatomelanic acid (13%), then humic acid (4%). In freshwater habitats fulvic acid significantly contributes to the color of the water. I found that in polluted habitats, at least one fraction of the coloring colloids, i.e., fulvic acid, is stablized by heavy metals. Precipitation occurs when highly colored freshwater habitats enter brackish waters. There tends to be a substantial decrease in fulvic acid concentration. This alters the relative percentages to 85% hymatomelanic acid, 15% humic acid, and little, if any, fulvic acid. Since fulvic acid initially composed about 80% of the freshwater coloring material, this precipitation is noted by color decrease as brackish-waters increase (Hopkins, 1961).

CONCLUSION

Physical and chemical parameters have shown that the coloring colloids of southeastern Louisiana are the same as reported by other workers in various areas of the United States. The chemical data indicate that these materials are polymeric, aromatic, hydroxy, carboxylic acids. Iron, in the ferric state, is associated in the colloidal complex in various amounts. The iron and possibly other metals serve to stabilize the coloring colloidal complex and keep it in the water column. The infrared spectrographs of fulvic acid, the prominent acid in freshwater habitats, are very consistent and change neither with habitats nor with seasons. The functional groups are varied and give it a high adsorptive capacity. The particle size range (5-35 mμ) indicates that the coloring materials are colloidal in nature. The size increase is due to an increase in the molecular radius as the increasing pH ionizes the functional groups associated with the coloring colloids. The three components of the coloring organic substance are fulvic acid, hymatomelanic acid, and humic acid. In freshwater habitats their relative percentages are 83% fulvic acid, 13% hymatomelanic acid, and 4% humic acid. This ratio is quite consistent throughout all freshwater habitats.

There are two mechanisms which seem to naturally precipitate the coloring materials in aquatic habitats. These mechanisms are Eh and salinity induced precipitation. The first is the Eh (redox) shift which usually occurs on a seasonal basis. As the highly colored waters of the rainy seasons receed, the ground waters feed the stream. This ground water is reducing and is supplied to aquatic habitats at many sources. Once reduction takes place, immediate oxygentation is inevitable through various mechanisms. This reducing-oxidizing shift causes precipitation of the coloring colloidal complex. The precipitation is particularly noticed on the shoreline and aquatic vegetation throughout the stream. This process removes the color and allows increased light penetration to occur which thereby increases the productivity of the habitats. The presence of artesian water also accounts for favorable conditions for increased productivity. This precipitation is also found in isolated areas where mechanisms of reduction then oxygenation in a colored water habitat prevail. It is especially noticed along shoreline areas where plants and maximum water-atmosphere oxygen exchange takes place.

The second mechanism of natural precipitation occurs in brackish-water habitats. Before the colored water reaches these habitats, fulvic acid is prevalent (83%), followed by hymatomelanic acid (13%) then humic acid (4%). When these waters meet estuarine conditions (salinity > 3 ppt) the fulvic acid precipitates from the colloidal complex. At this time there is an evident decrease of color in these habitats due to the precipitation of fulvic acid. At these stations the relative percentages shift to 85% hymatomelanic acid, 15% humic acid, and little, if any, fulvic acid. This mechanism is probably in all estuarine habitats which receive discharge from colored freshwater habitats.

The presence or absence of the coloring colloids have direct effects on water resources and wildlife. The National Technical Advisory Committee (1969) stated that color in excess of five units inhibits photosynthesis by absorbing photosynthetically active light. The average color value in the habitats selected was 400 units, with maximum color values of 5150 units. With color values this high the productivity of aquatic habitats is extremely low. This results in little dissolved oxygen and high concentrations of free carbon dioxide. With this condition there is little buffering capacity and large fluctuations in pH occur. The pH usually remains low (4.2-5.8) due to the acidic functional groups and other plant and soil constituents. This causes low carbonate and bicarbonate alkalinities. During periods of natural precipitation, i.e., redox shifts, the coloring colloids are removed from the water column. As this happens, the phytoplankton and aquatic plants are able to increase photosynthesis. The clear water then takes on the characteristics of a more eutrophic habitat. As the material precipitates, the water sustains a relatively strong buffering capacity, the pH increases, and there is substantial carbonate and bicarbonate alkalinities. Organisms usually can cope these chemical changes. In fact, the precipitated particulate form of the coloring colloids are probably used as a food source for many organisms.

Adverse effects also occur in alkaline eutrophic habitats that are colored and also have a substantial buffering capacity. These habitats are susceptible to high degrees of bacterial decomposition at the bottom where it is sealed from the upper layers. Any disturbance of the sealed bottom layers will cause a redox shift in the system. This would cause hazardous reducing conditions that would affect the aquatic life, beside precipitating the coloring material.

With a knowledge of the limnological mechanism of color precipitation, treatment of farm ponds should be taken into consideration to increase the productivity. Farm ponds are found throughout the United States and many are highly colored. They are stocked with organisms such as catfish, bluegill, bass, crayfish, and many other organisms of commercial importance. Application of ferric chloride to remove color, as was done in this study, along with the addition of lime to increase pH would support a very productive phytoplankton community if nutrients were present.

Just as iron and manganese are bound to the colloidal complex in freshwater habitats, other nutrients may be associated with them and in this form would be unavailable to organisms. However, I have found no complexation with nitrates or phosphates. As the redox shift causes precipitation of the coloring colloidal complex in nature, the precipitated form may be used as a food source for many organisms. The nutrients in this case would be available to organisms in a concentrated form.

As seen from the infrared spectra, the fulvic acid component of the coloring colloids have many functional groups that partcipate in and adsorptive capacity. This mechanism is enhanced when the pH increases and the functional groups are ionized. Fulvic acid has also been shown to precipitate as the coloring colloids enter brackish water. Recent investigations, not part of this study, has demonstrated that (1) fulvic acid is the only coloring acid to participate in heavy metal adsorption, (2) heavy metals remain associated with the fulvic acid component, even after precipitation in brackish water habitats, (3) the fulvic acid-heavy metal precipitate is ingested by typical filter feeders of estuarine habitats, and (4) the heavy metal is incorporated, i.e., digested, as an integral part of the organism's tissue. It was demonstrated in aprior work (Poirrier et al., 1972) that DDT was adsorbed by the coloring colloids and concentrated over 15,000 times its concentration in the water phase. Thus, when these coloring materials precipitate they are a source for the concentration of pollutants. Any pollutant (heavy metals, trace metals, DDT, etc.) associated with the coloring colloids becomes greatly concentrated when the material shifts from the stable colloidal state to the concentrated particulate state. This mechanism whereby such pollutants, by way of the coloring material, accumulate and concentrate in their tissue is a hazard to organisms such as shrimp, oysters, clams, lobsters, and fish. Concentration factors of heavy metals occur around 100,000 times even when the initial concentration of the heavy metals in the water phase are harmless.

Thus there is the increase from harmless concentrations to harmful or lethal concentrations in the precipitated particulate form.

Prakish and Rashid (1968) indicated that "humic" substances influenced the growth of marine dinoflagellates. It is very plausible that some aspect of the coloring colloids have some effect on the red tide blooms which occur intermittently in the Gulf of Mexico. This phenomenon is produced by the dinoflagellate, *Gymnodinium brevis*. Possible aspects may be: (1) trace metal stabilization, (2) altering trace or heavy metal ratios, (3) using the colloidal material as a food source, or (4) some combination of these. Collier (1958) indicated that aqueous soil extracts stimulated laboratory blooms. A significant portion of soil extracts are the solubilized portion of plant decomposition products, which are basically tannin and lignin units. This fraction is in the same class as the coloring colloids of natural surface waters. The natural precipitation of the coloring colloids probably also involves in the co-precipitation of other materials such as silt and clays in estuarine waters.

In the future, local sources of water will have to be used to supply water for some municipalities. These will include domestic, recreational, and industrial uses for the water. The first problem water treatment plants will encounter is removal of the color of the water. This study provides necessary data, techniques, and mechanisms which would be invaluable to any investigations of color problems in aquatic habitats.

APPENDIX

I. Figures and Graphs

II. Tables

III. List of Stations and Their Water Chemistries

APPENDIX I. Figures and Graphs

Figure 1

Locations of Stations along Bayou Lacombe, St. Tammany Parish, Louisiana

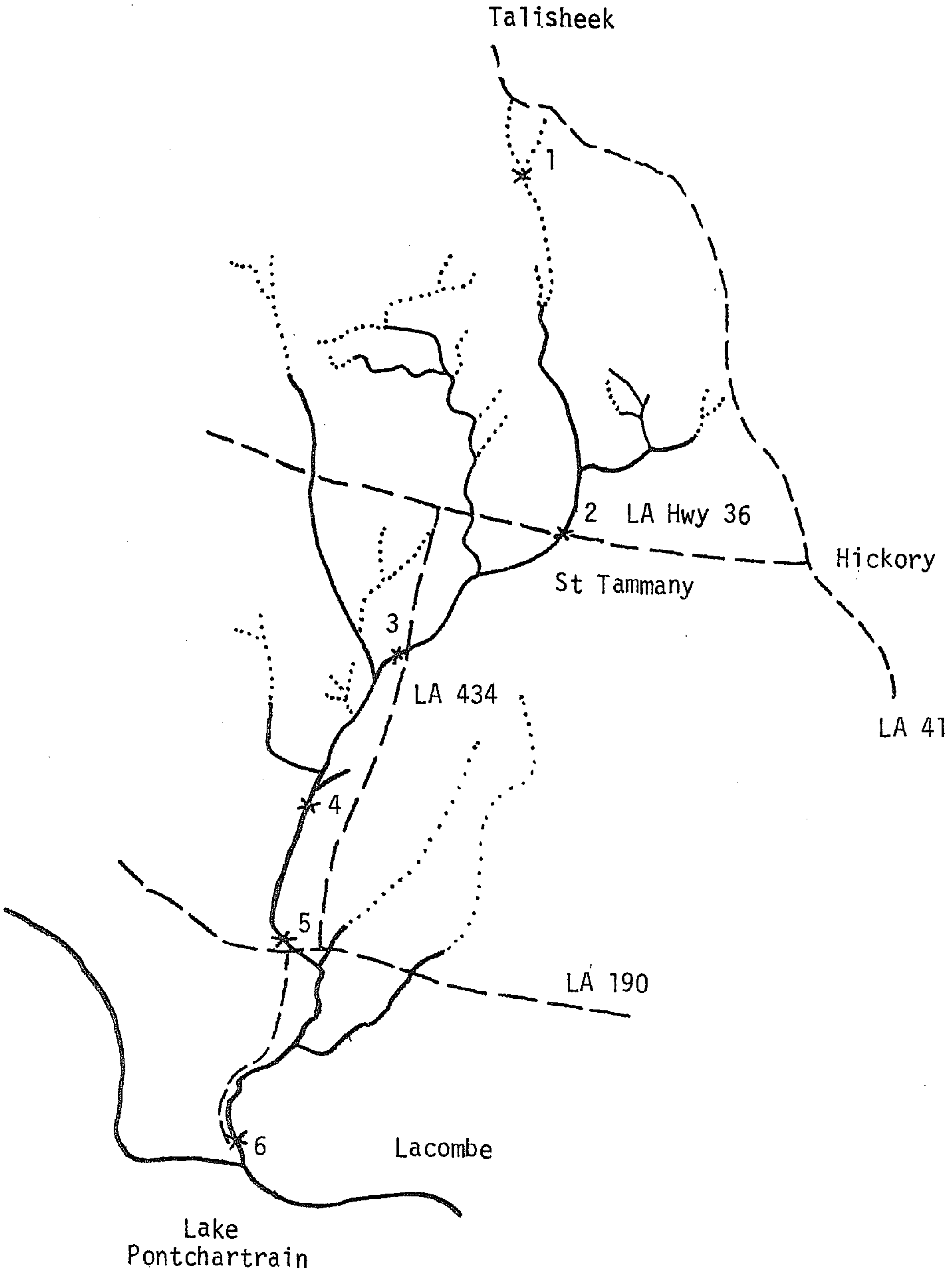

Talisheek
1
2
LA Hwy 36
Hickory
St Tammany
3
LA 434
LA 41
4
5
LA 190
6
Lacombe
Lake
Pontchartrain

Figure 2

Location of sampling sites in southeastern Louisiana

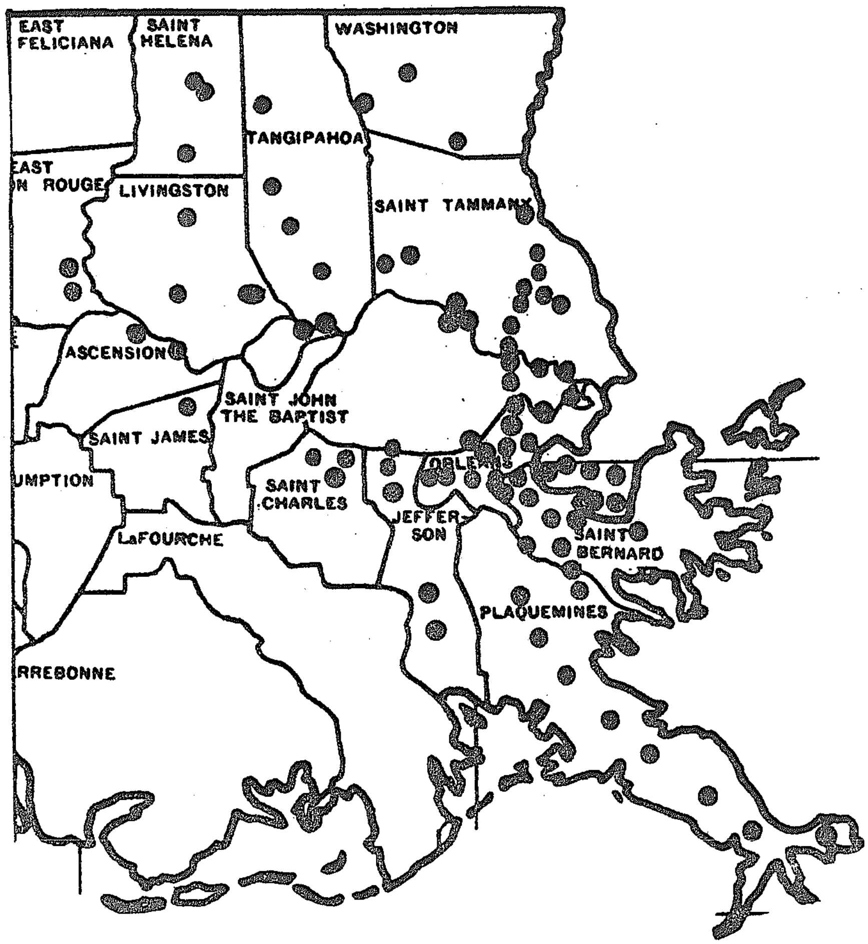

EAST FELICIANA
SAINT HELENA
WASHINGTON
TANGIPAHOA
EAST
N ROUGE
LIVINGSTON
SAINT TAMMANY
ASCENSION
SAINT JOHN THE BAPTIST
SAINT JAMES
UMPTION
SAINT CHARLES
ORLEANS
JEFFERSON
LaFOURCHE
SAINT BERNARD
PLAQUEMINES
RREBONNE

Figure 3

Color versus time when stored at 5°C

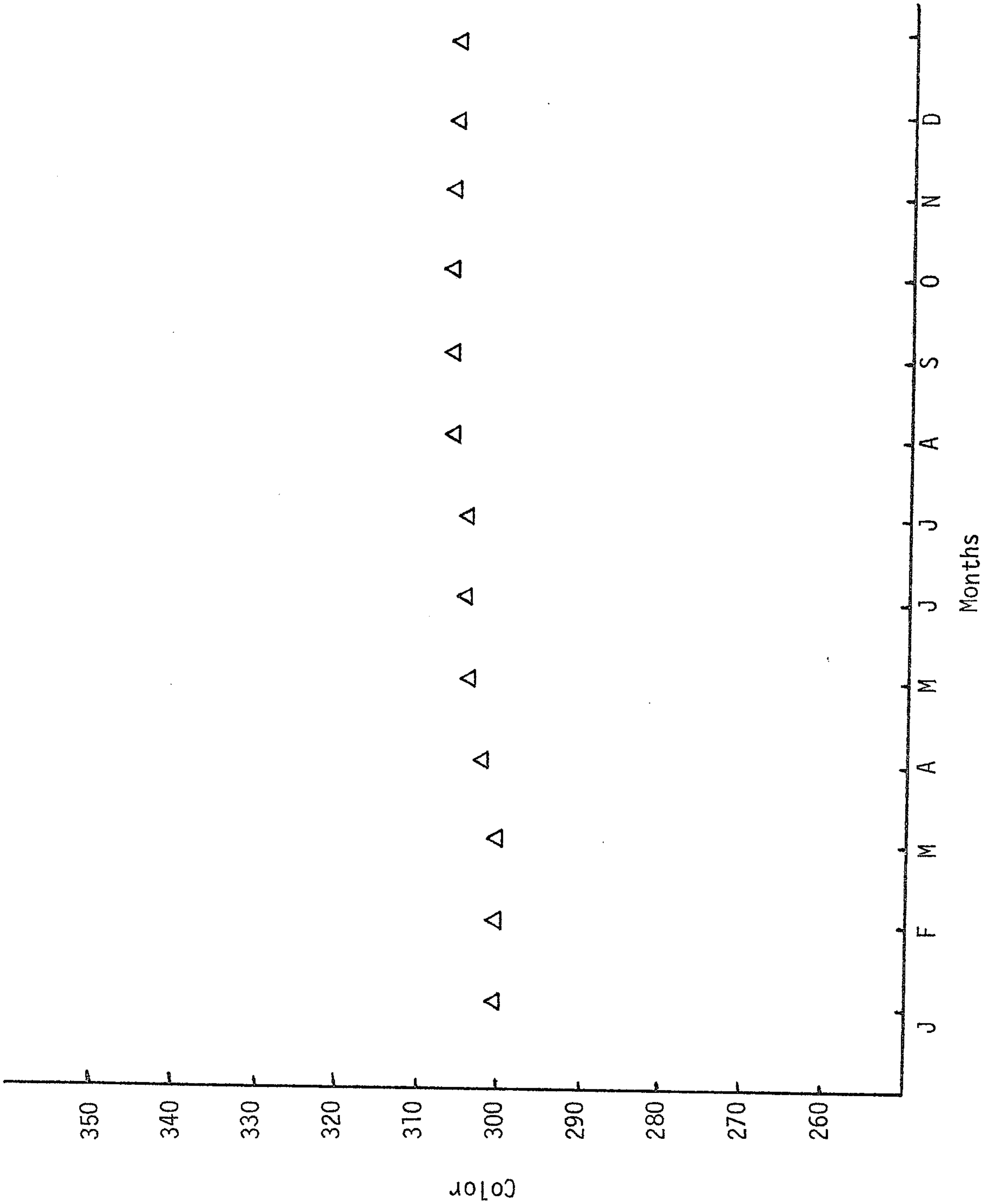

Color
260
270
280
290
300
310
320
330
340
350
Months
J
F
M
A
M
J
J
A
S
O
N
D

Figure 4

Color versus pH

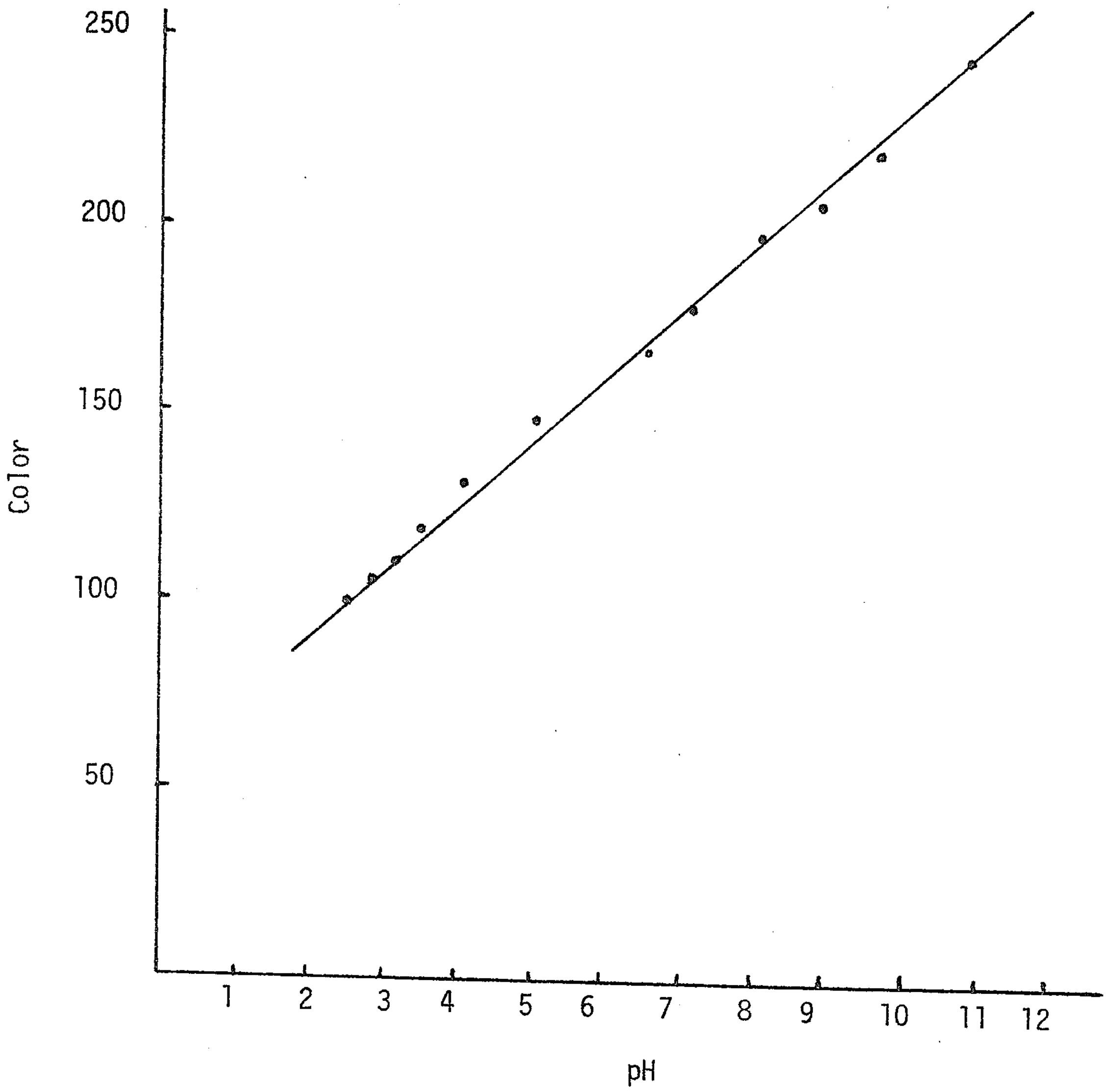

250
200
150
100
50
Color
1
2
3
4
5
6
7
8
9
10
11
12
pH

Figure 5

Titration curve to determine buffering capacity. pH versus ml NaOH at 245 units

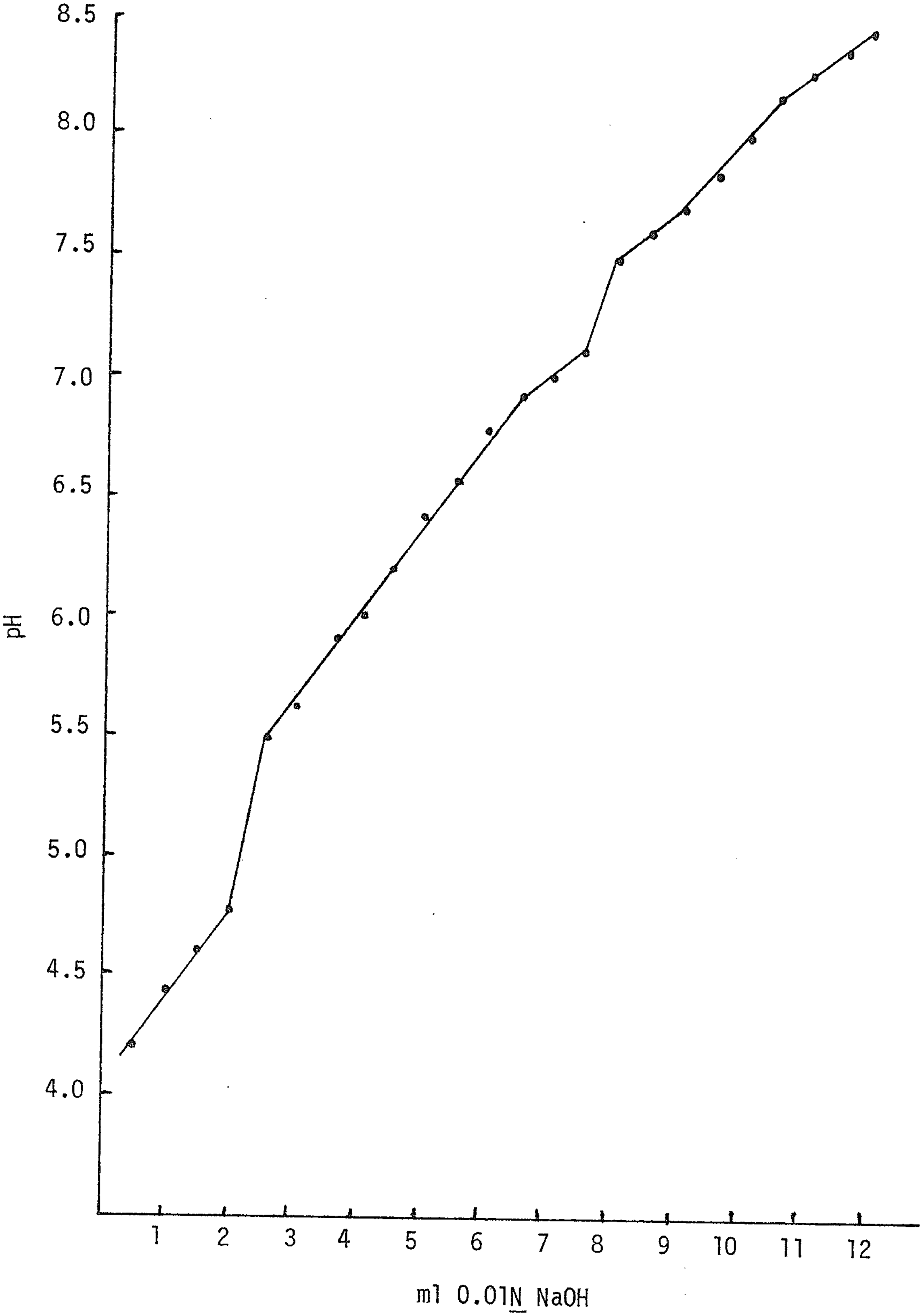

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
pH
1
2
3
4
5
6
7
8
9
10
11
12
ml 0.01N NaOH

Figure 6

Titration curve to determine buffering capacity. pH versus ml NaOH at 40 units

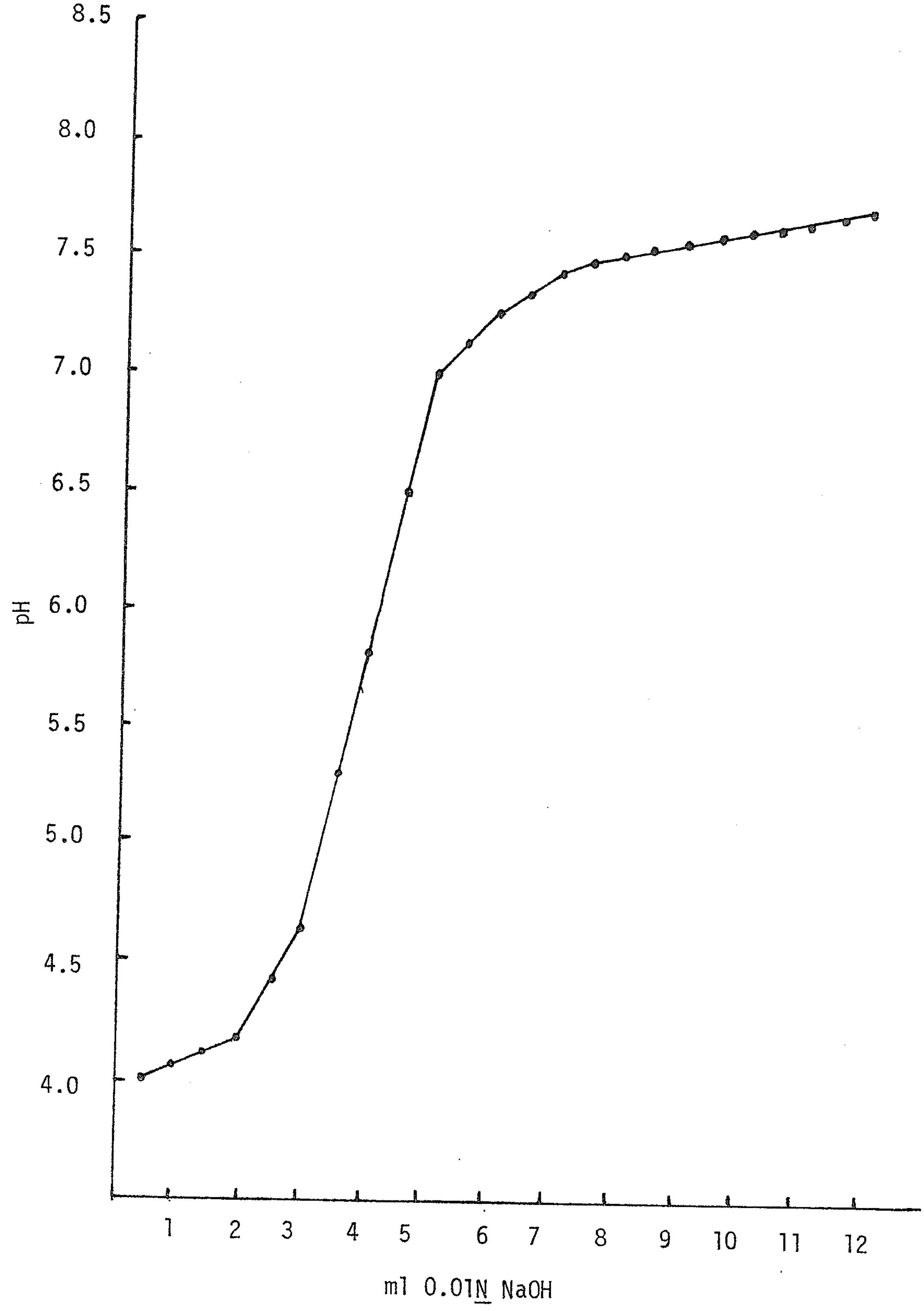

8.5
8.0
7.5
7.0
6.5
pH
6.0
5.5
5.0
4.5
4.0
1
2
3
4
5
6
7
8
9
10
11
12
ml 0.01N NaOH

Figure 7

pH versus percent ferric iron complexed with the coloring colloids

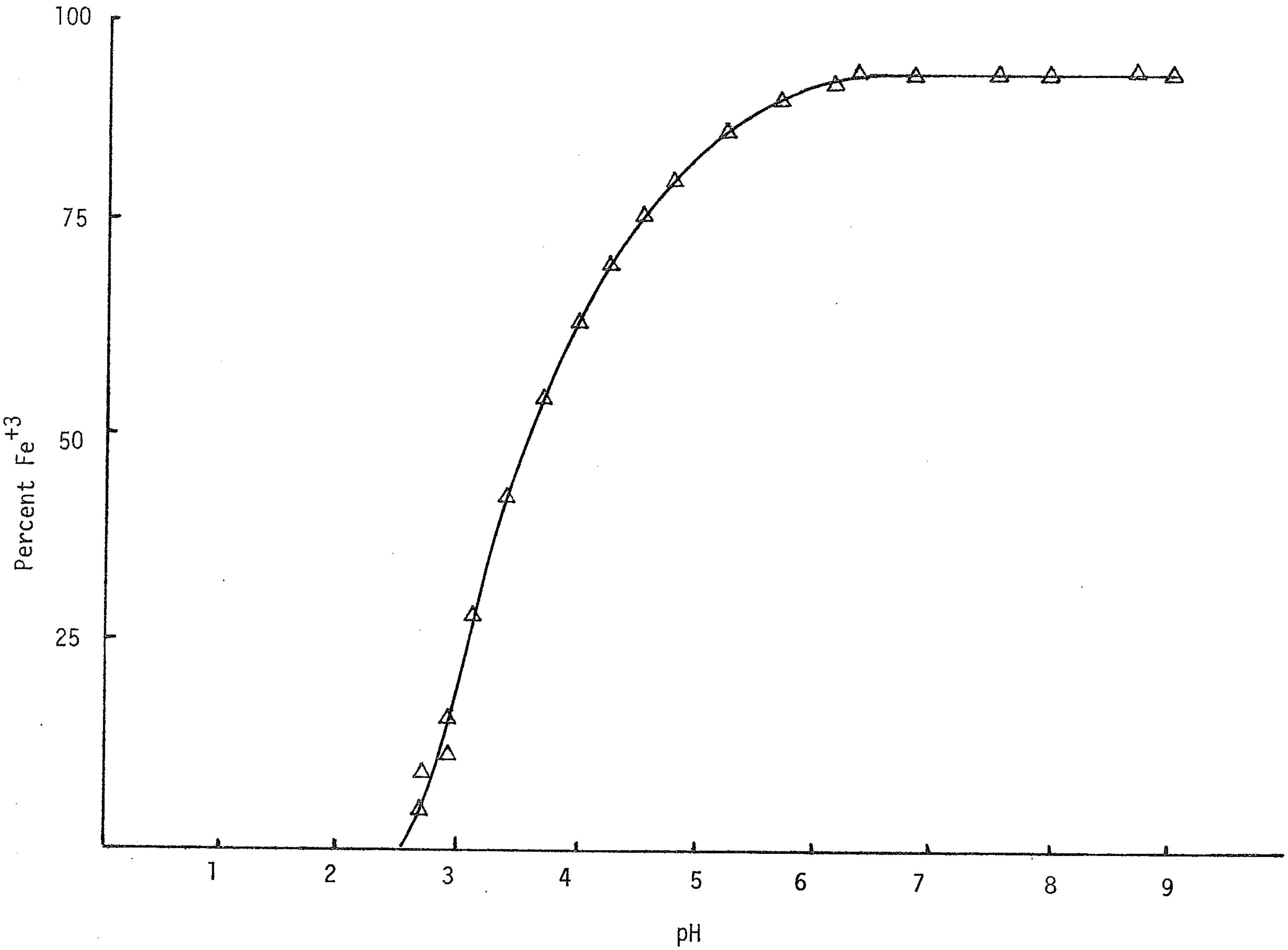

Percent Fe^{+3}
100
75
50
25
1
2
3
4
5
6
7
8
9
pH

Figure 8

Color versus percent ferric iron complexed with the coloring colloids

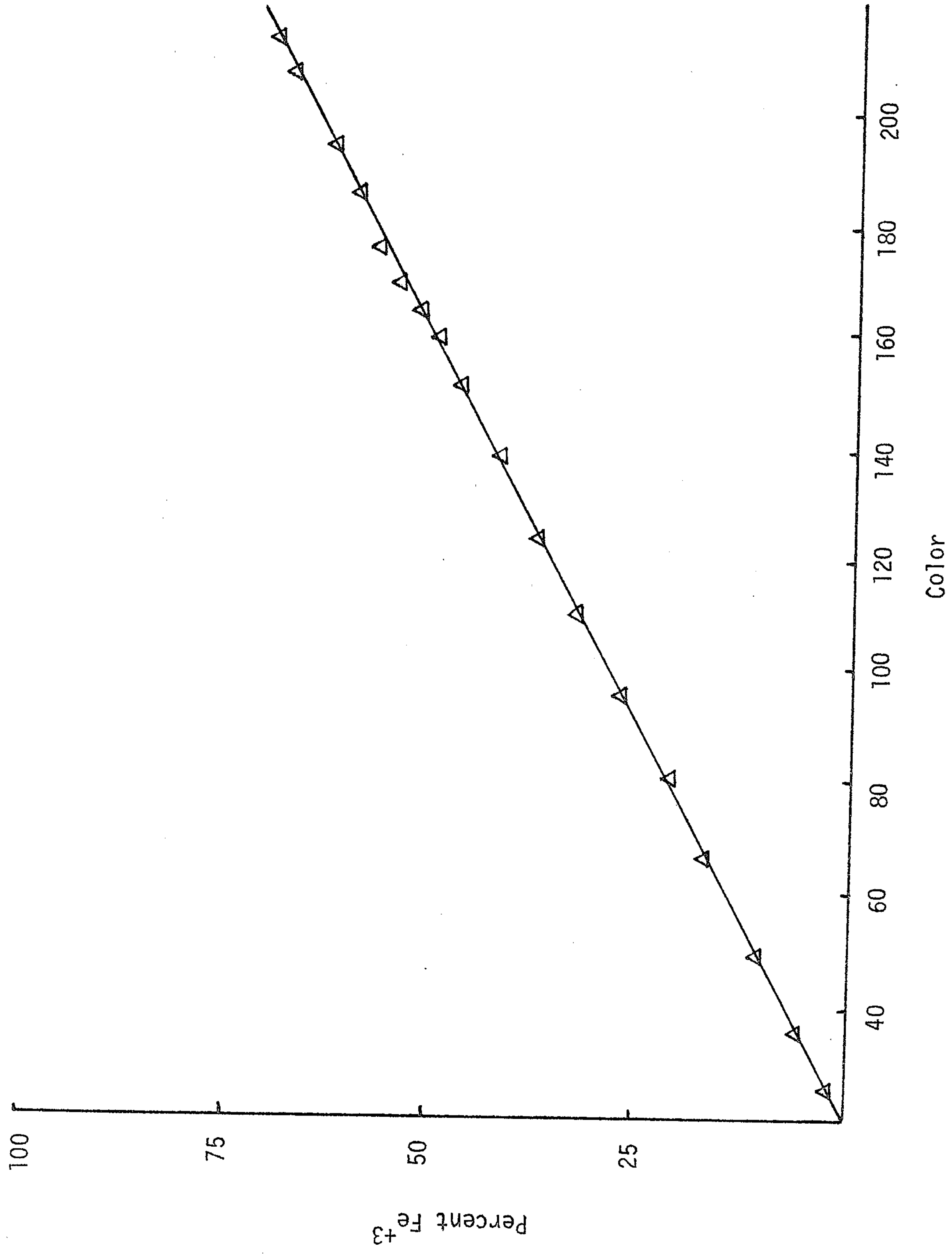

Percent Fe+3
100
75
50
25
Color
40
60
80
100
120
140
160
180
200

Figure 9

Percent well water versus percent ferric iron complexed with the coloring colloids

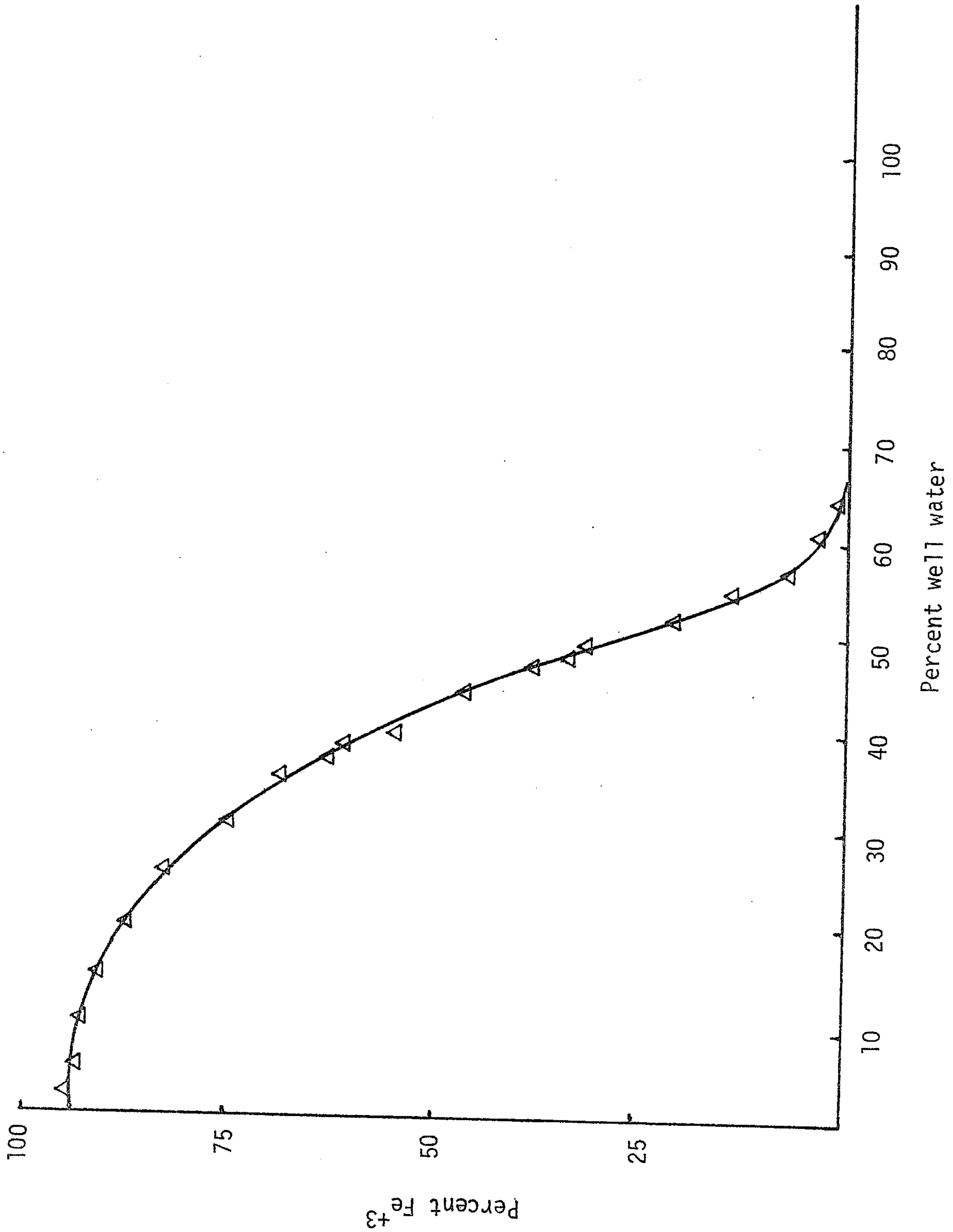

Percent Fe^{+3}
100
75
50
25
Percent well water
10
20
30
40
50
60
70
80
90
100

Figure 10

Ferric-ferrous iron relationship in Bayou Lacombe, St. Tammany Parish, Louisiana

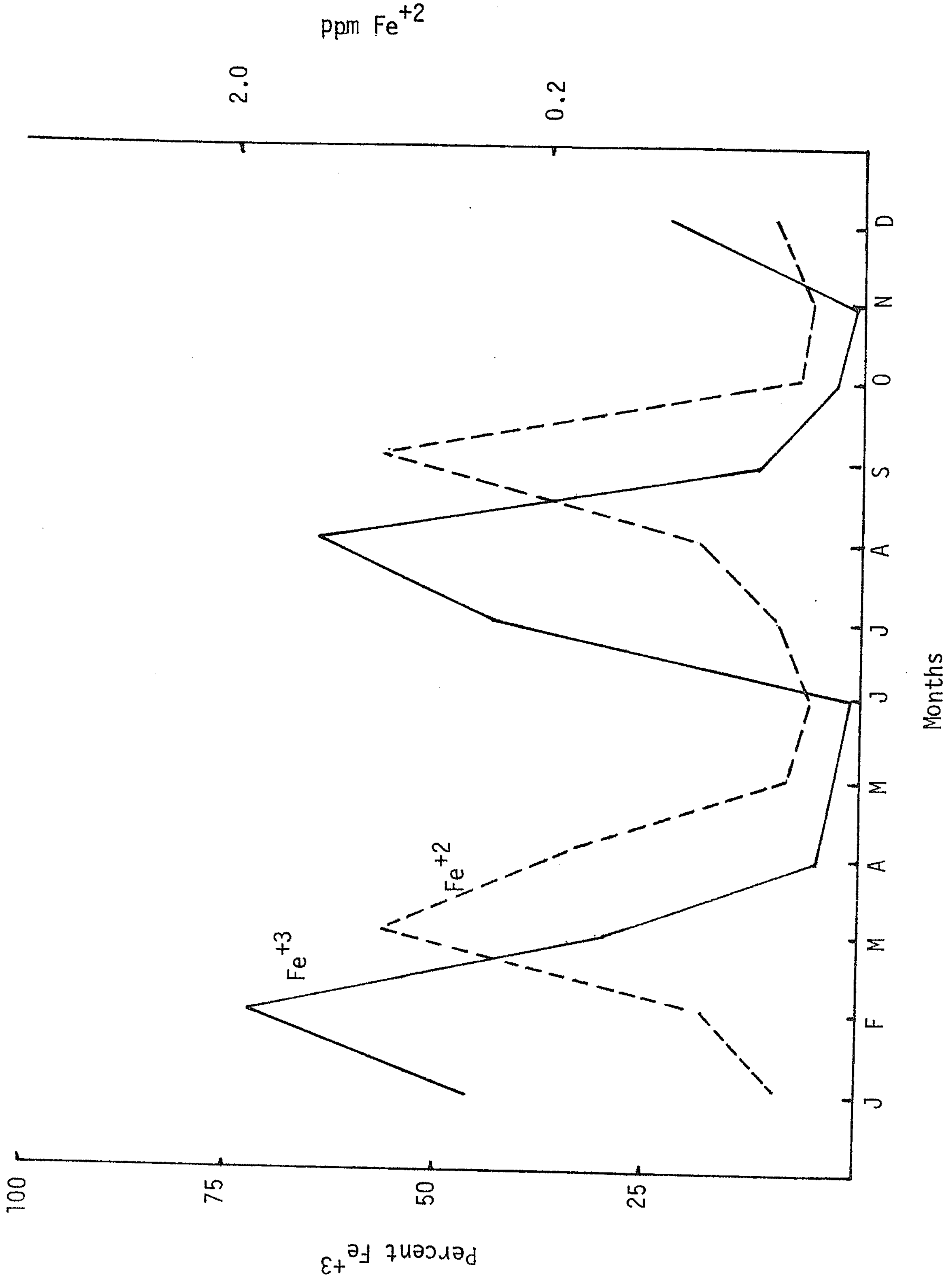

ppm Fe^{+2}
2.0
0.2
Percent Fe^{+3}
100
75
50
25
J
F
M
A
M
J
J
A
S
O
N
D
Months
Fe^{+3}
Fe^{+2}

Figure 11

Fulvic acid concentrations along Bayou Lacombe, St. Tammany Parish, Louisiana

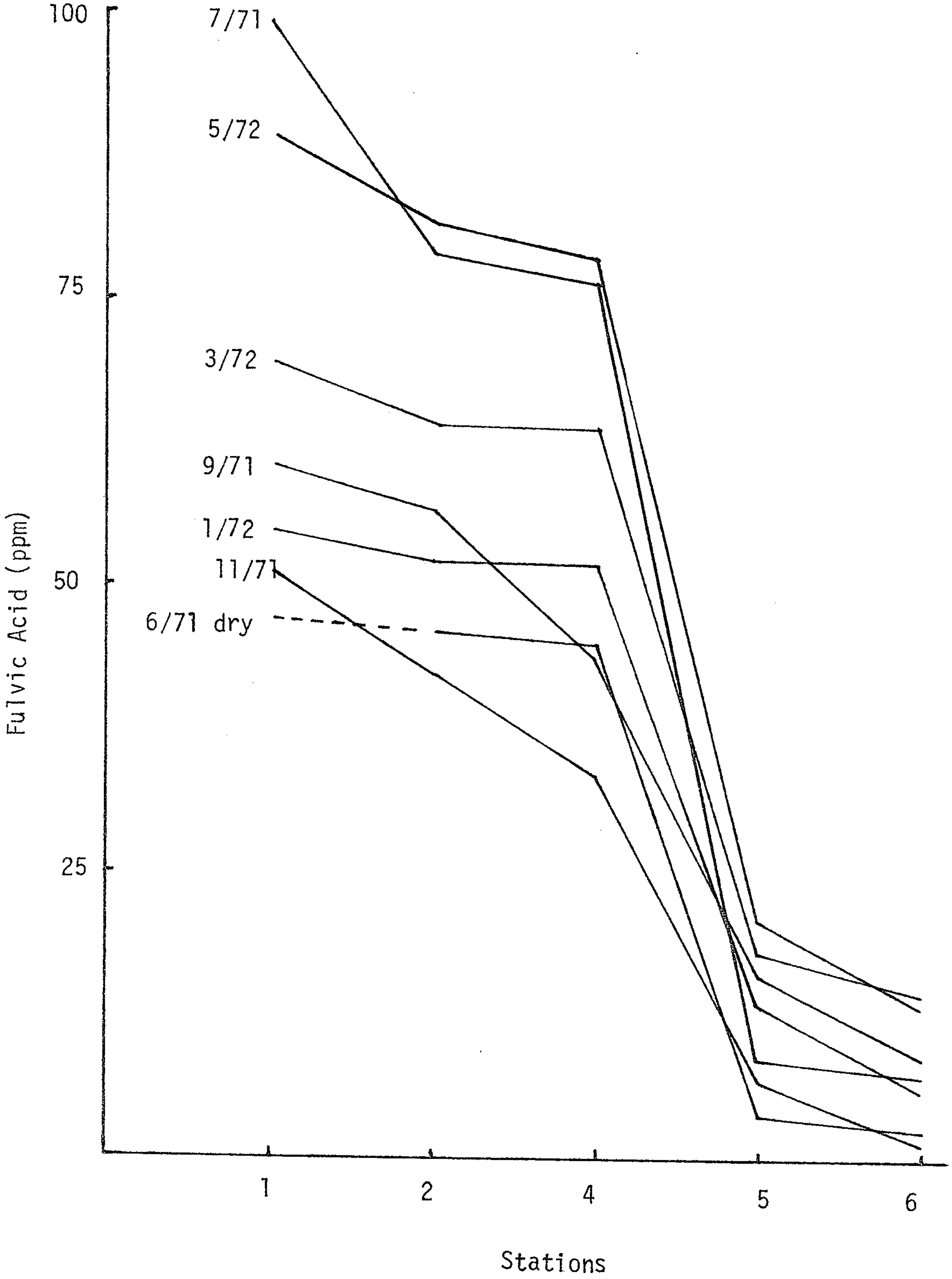

100
75
50
25
Fulvic Acid (ppm)
7/71
5/72
3/72
9/71
1/72
11/71
6/71 dry
1
2
4
5
6
Stations

Figure 12

Hymatomelanic acid concentrations along Bayou Lacombe, St. Tammany Parish, Louisiana

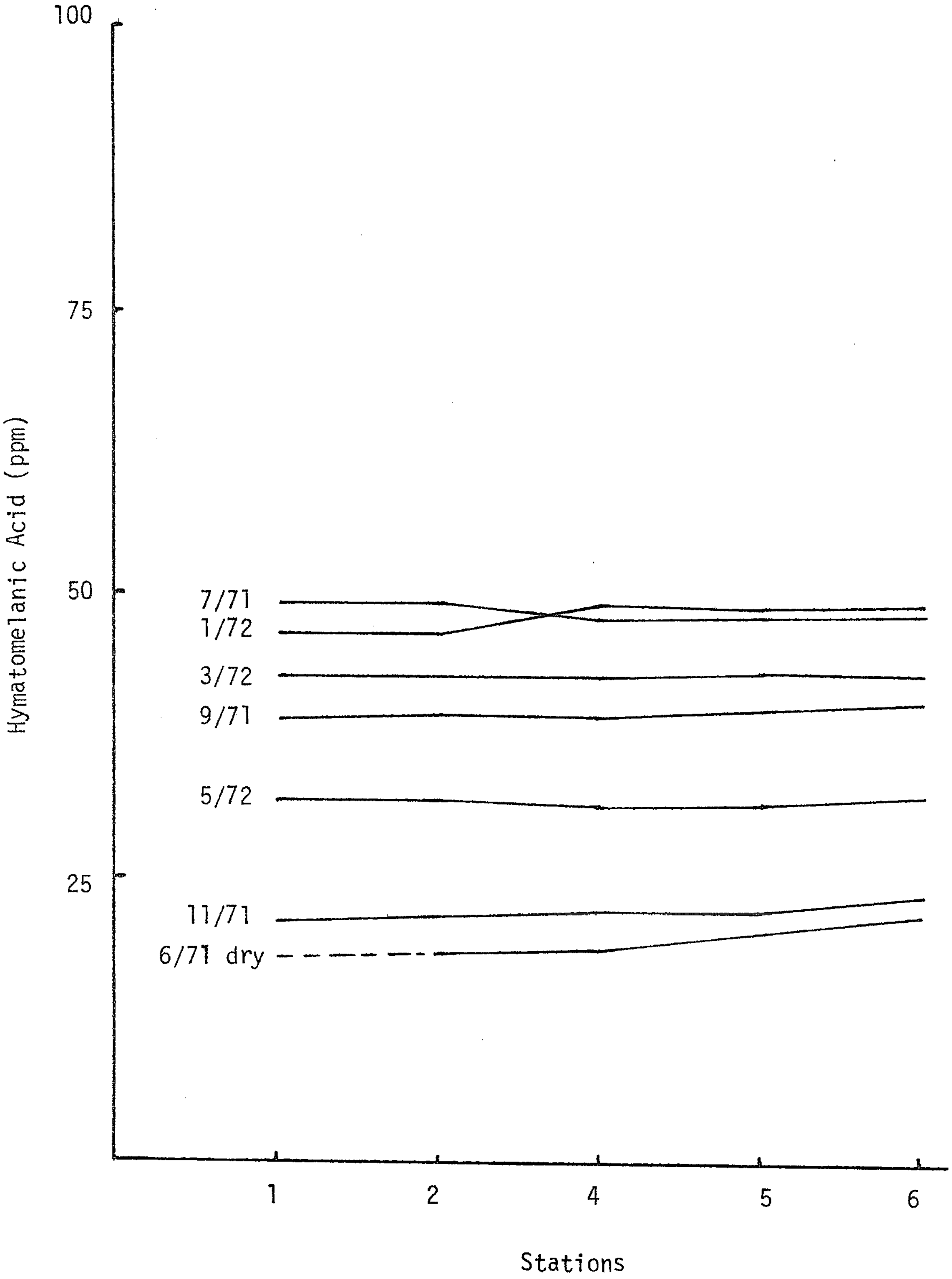

100
75
50
25
Hymatomelanic Acid (ppm)
7/71
1/72
3/72
9/71
5/72
11/71
6/71 dry
1
2
4
5
6
Stations

Figure 13

Humic acid concentrations along Bayou Lacombe, St. Tammany Parish, Louisiana

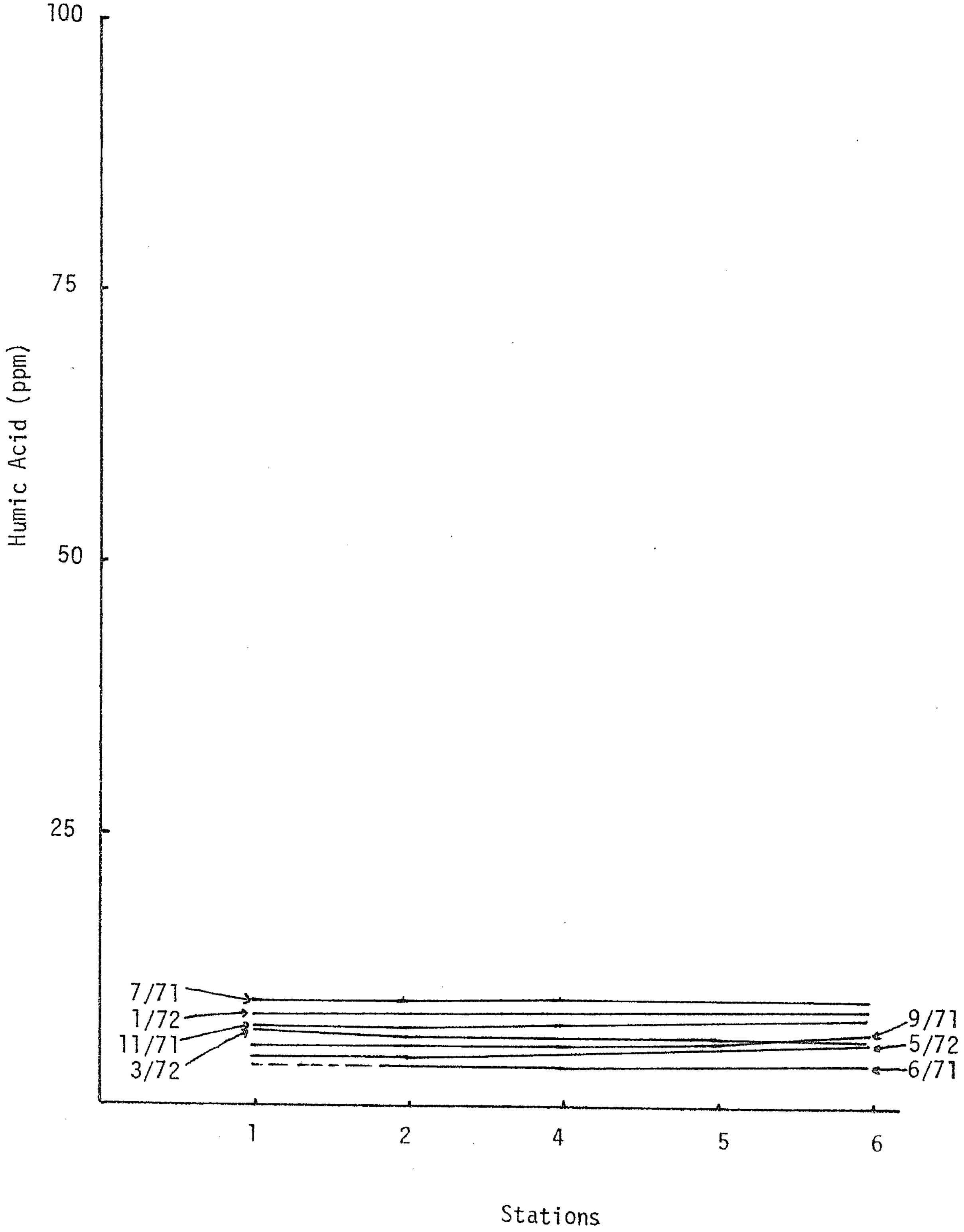

100
75
50
25
Humic Acid (ppm)
7/71
1/72
11/71
3/72
9/71
5/72
6/71
1
2
4
5
6
Stations

Figure 14

Conductivity versus concentrations of the three coloring acids

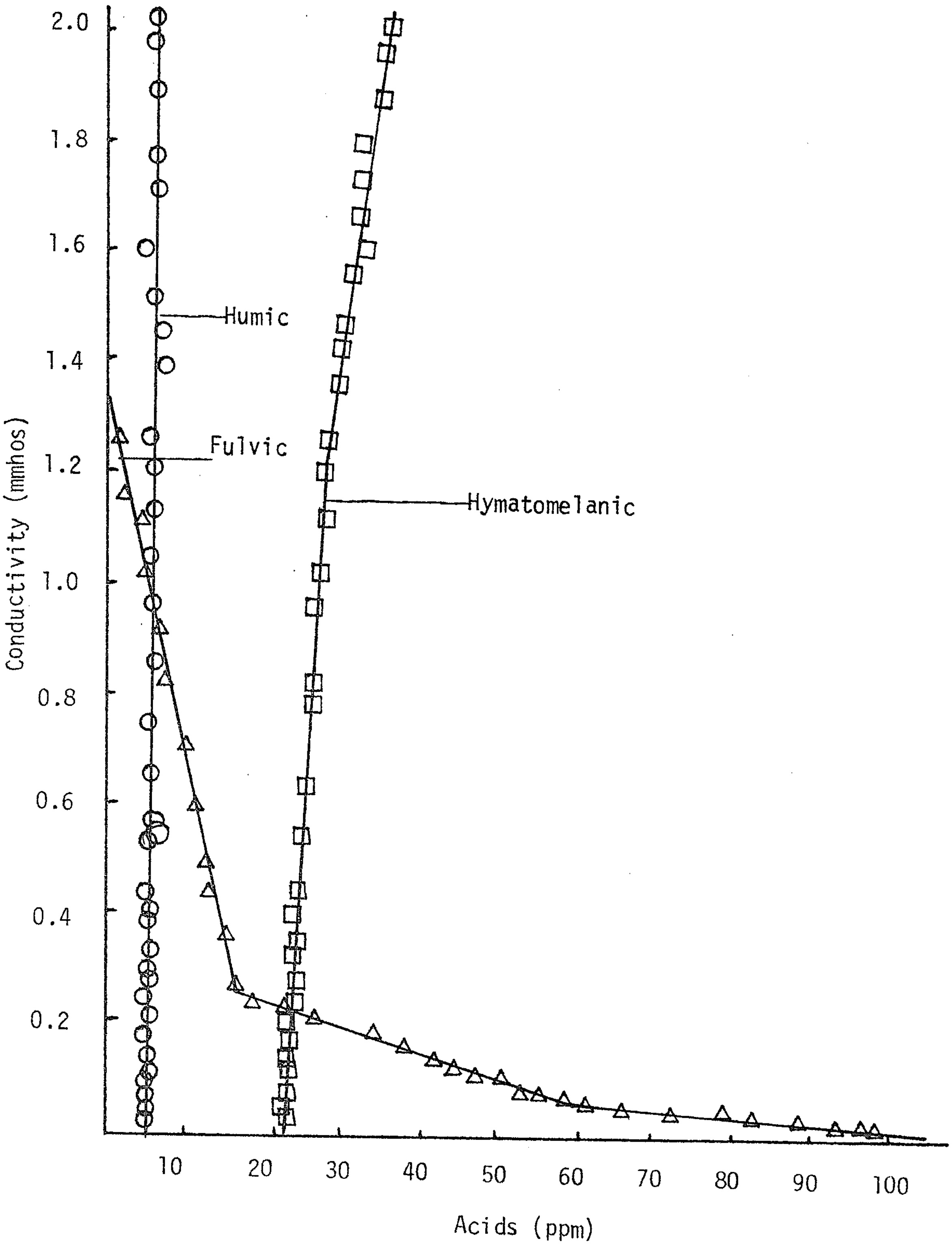

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Conductivity (mmhos)
Humic
Fulvic
Hymatomelanic
10
20
30
40
50
60
70
80
90
100
Acids (ppm)

Figure 15

Conductivity versus relative percentages of the three coloring acids

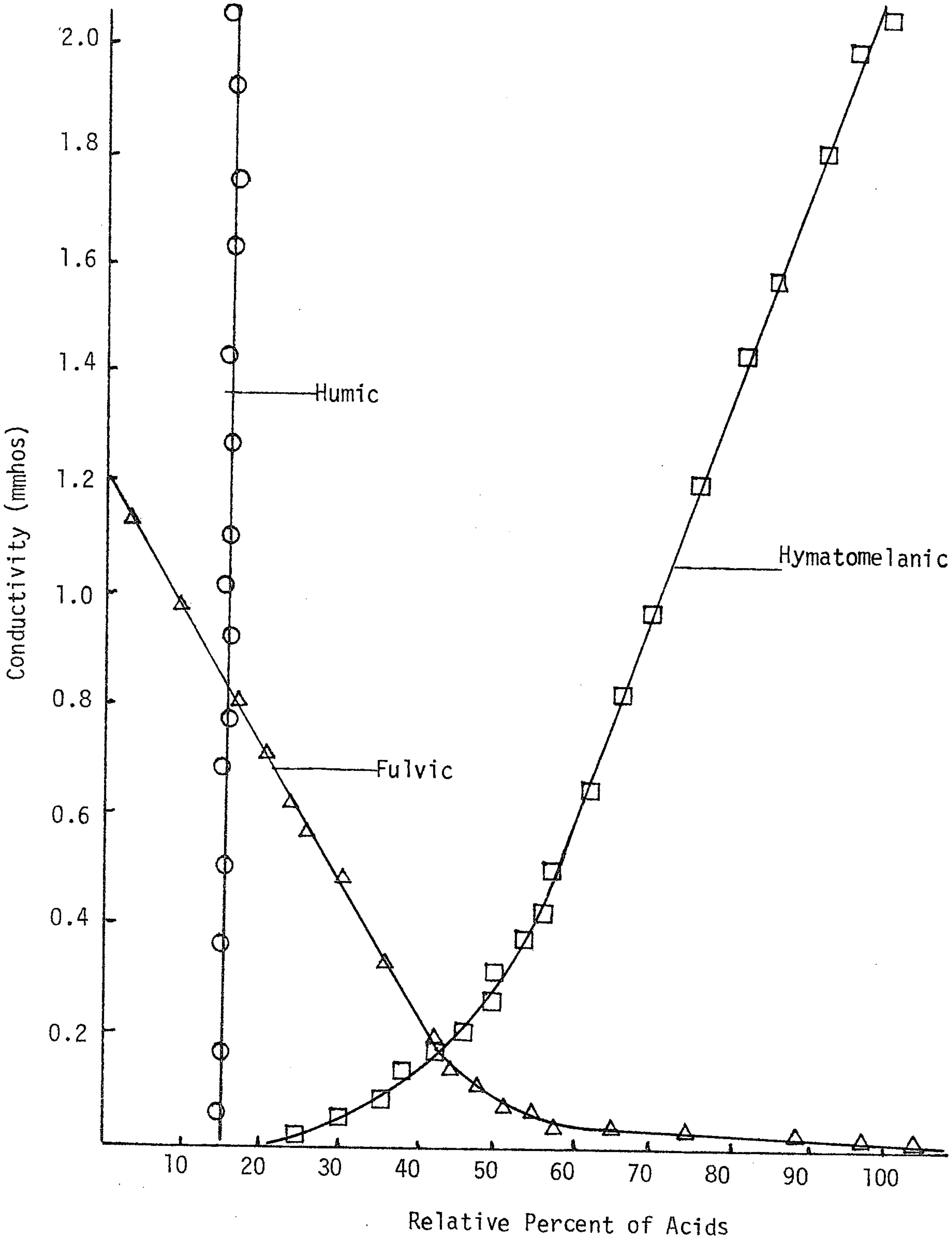

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
Conductivity (mmhos)
Humic
Fulvic
Hymatomelanic
10
20
30
40
50
60
70
80
90
100
Relative Percent of Acids

Figure 16

Particle size of coloring colloids versus pH

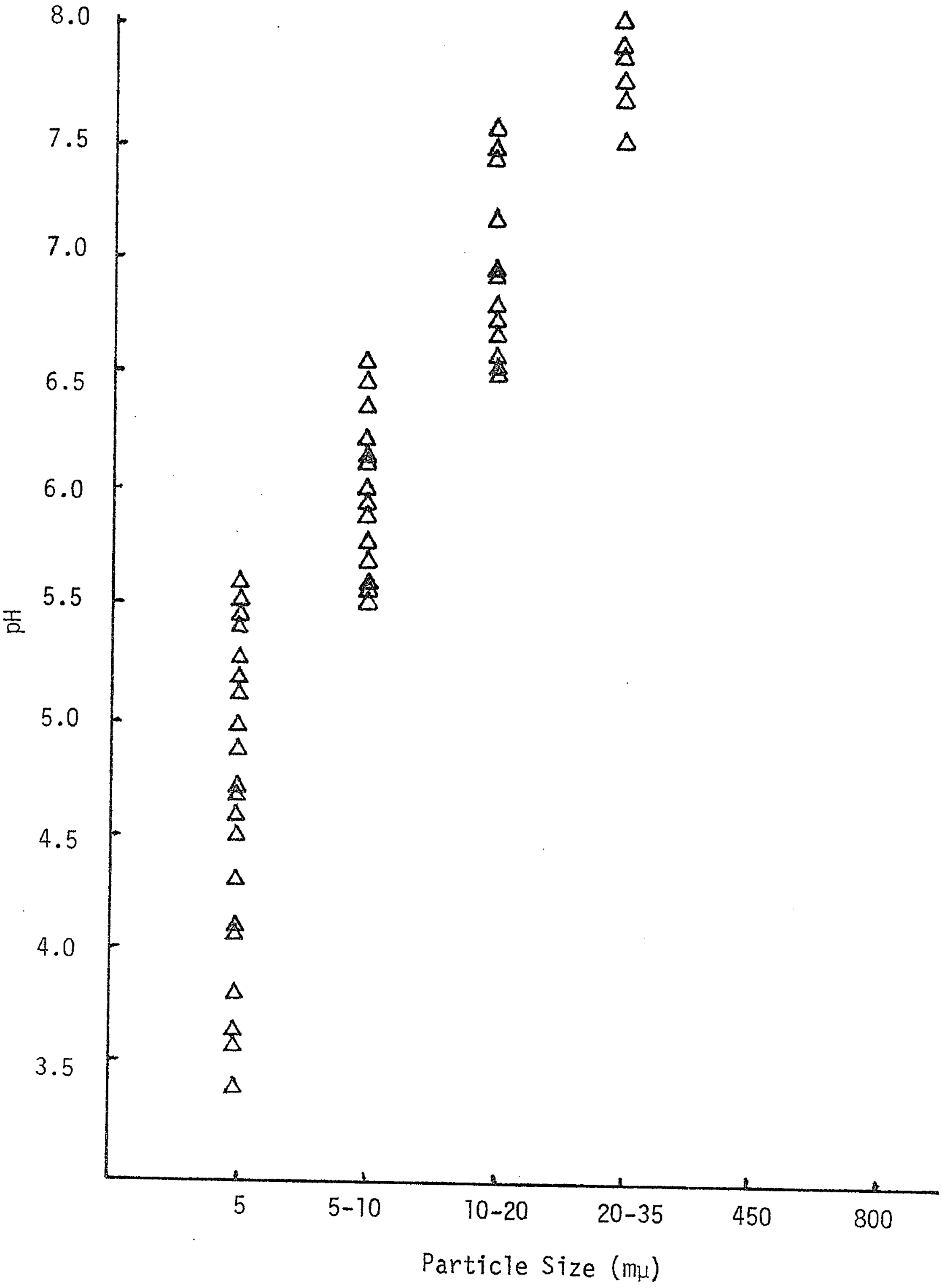
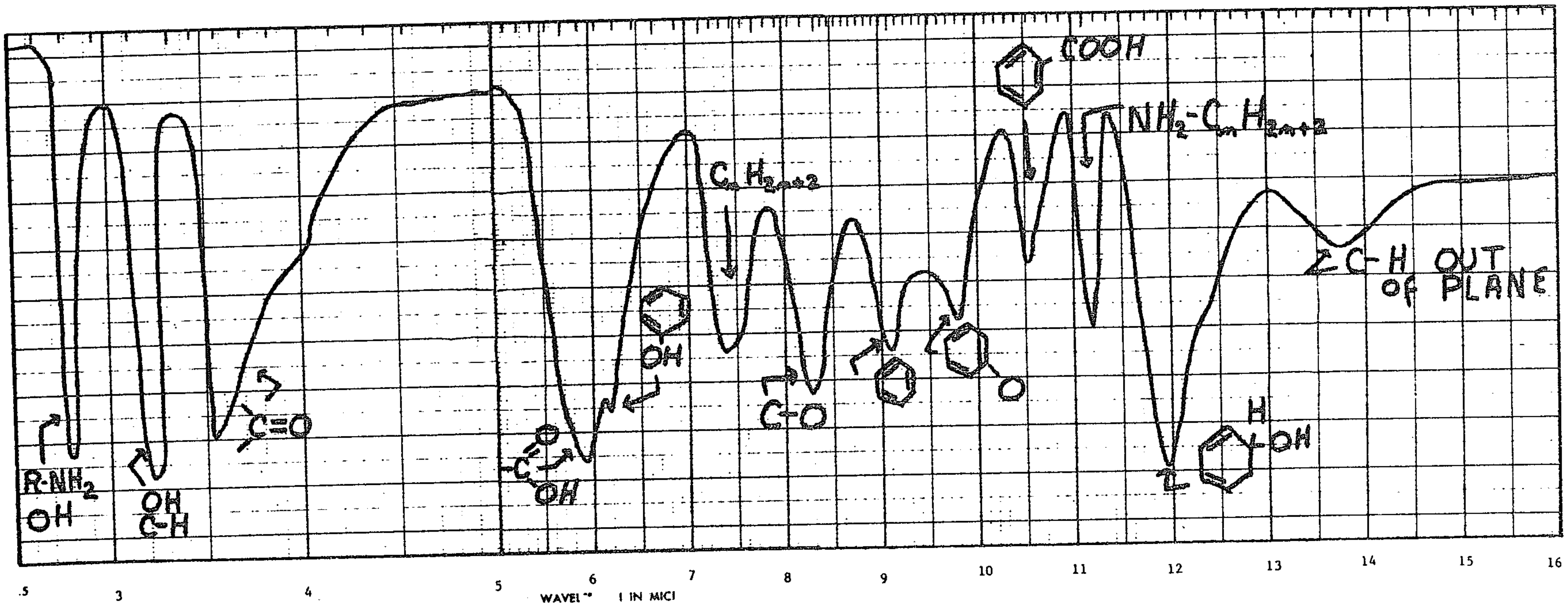

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
pH
5
5-10
10-20
20-35
450
800
Particle Size (mμ)

Figure 17

Infrared spectrograph of fulvic acid


R-NH2
OH
OH
C-H
C=O
-C-OH
OH
C$_n$H$_{2n+2}$
C-O
COOH
NH2-C$_n$H$_{2n+2}$
H
OH
C-H OUT OF PLANE
.5
3
4
5
6
7
8
9
10
11
12
13
14
15
16
WAVEL   I IN MICI

APPENDIX II. Tables

TABLE I

Filmore Pond Water Chemistries

pH	6.95
RpH	7.35
Eh	+345 mv
CO_3	0
HCO_3	50.0 ppm
CO_2	5.0 ppm
Color	200 units
Conductivity	177 μmhos
PO_4	0.72 ppm
NO_3	0.36 ppm
Humic Acid	4.7 ppm
Hymatomelanic Acid	16.2 ppm
Fulvic Acid	82.1 ppm
% Fe^{+++} complexed	6.41 %
Particle size	10-20 mμ

TABLE II

Contents of Jars for Reduction Experiment

A. 3 liters of brown water (control)

B. 3 liters of brown water + 4 <u>Rangia</u>

C. 3 liters of brown water + 4 crushed <u>Rangia</u>

D. 3 liters of brown water + H_2S*

E. 3 liters of brown water + CH_4*

F. 2.7 liters of brown water + 0.3 liters ground water (1600 ft. capped artesian well in Talisheek, La.)

G. 1.5 liters of brown water + 1.5 liters of ground water

H. 3 liters of brown water + 2 pH units acidic (HCl)

I. 3 liters of brown water + 10 ppm dextrose

J. 2.995 liters of brown water + 0.005 liter hydroxylamine HCl

K. 3 liters centrifuged brown water + 82.1 ppm fulvic acid

L. 3 liters (K) + H_2S

M. 3 liters centrifuged# brown water + 16.2 ppm hymatomelanic acid

N. 3 liters (M) + H_2S

O. 3 liters centrifuged brown water + 4.7 ppm humic acid

P. 3 liters (O) + H_2S

Q. 3 liters centrifuged brown water

R. 3 liters (Q) + H_2S

* - generated at 24 bubbles/min from laboratory cylinder through Tygon tubing (¼" i.d.)

\# - at 17,500 rpm for 30 min at 25°C

TABLE III

Effect of Reducing Substances on Colored Water

Solution	Eh (mv)	Color (units)	Fe (valence)
A (control)	+345	200	+3
B	+300	200	+3
C	-442	250	+2
D	-321	310	+2
E	-100	275	+2
F	+210	255	+2
G	+150	320	+2
H	+100	270	+2
I	-070	310	+2
J	+101	300	+2
K	+320	150	+3
L	-296	205	+2
M	+350	120	+3
N	-200	175	+2
O	+337	105	+3
P	-256	165	+2
Q	+304	115	+3
R	-294	115	+2

TABLE IV

Contents of Jars for Oxidation Experiments

A. 3 liters of brown water (control)

B. 3 liters brown water + compressed air*

C. 3 liters brown water + mechanical shaking

D. 3 liters of brown water + 2 pH unit increase (NaOH)

E. 3 liters of brown water + O_2*

F. 2.950 liters of brown water + 0.050 liter of 0.1 N $KMnO_4$

G. 2.950 liters of brown water + 0.050 liter of 3% H_2O_2

H. 3 liters of centrifuged# brown water + 82.1 ppm fulvic acid

I. 3 liters (H) + O_2

J. 3 liters of centrifuged brown water + 16.2 ppm hymatomelanic acid

K. 3 liters (J) + O_2

L. 3 liters of centrifuged brown water + 4.7 ppm humic acid

M. 3 liters (L) + O_2

N. 3 liters of centrifuged brown water

O. 3 liters (N) + O_2

* - generated at 24 bubbles/min from laboratory cylinder through Tygon tubing (¼" i.d.)

\# - at 17,500 rpm for 30 min at 25°C

TABLE V

Effect of Oxidizing Substances on Colored Water

Solution	Eh (mv)	Color (units)	Fe (valence)
A (control)	+345	200	+3
B	+355	210	+3
C	+368	200	+3
D	+481	205	+3
E	+525	218	+3
F	+518	225	+3
G	+619	240	+3
H	+320	150	+3
I	+513	205	+3
J	+350	120	+3
K	+418	195	+3
L	+337	105	+3
M	+391	200	+3
N	+304	115	+3
O	+610	0	+3

TABLE VI

Contents of Jars for Redox Shift

A. 3 liters of brown water (control)

B. 3 liters of brown water + H_2S* (then O_2*)

C. 3 liters of centrifuged# brown water + 82.1 ppm fulvic acid

D. 3 liters (C) + H_2S (then O_2)

E. 3 liters of centrifuged brown water + 16.2 ppm hymatomelanic acid

F. 3 liters (E) + H_2S (then O_2)

G. 3 liters of centrifuged brown water + 4.7 ppm humic acid

H. 3 liters (G) + H_2S (then O_2)

I. 3 liters of centrifuged brown water

J. 3 liters (I) + H_2S (then O_2)

* - generated at 24 bubbles/min from a laboratory cylinder through Tygon tubing (¼" i.d.)

- at 17,500 rpm for 30 min at 25°C

TABLE VII

Effect of Reduction then Oxidation on Colored Water

	Reduced				Oxidized							
					Supernate				Precipitate			
Soln	Eh	Color	UV	Fe	Eh	Color	UV	Fe	Eh	Color	UV	Fe
A (control)	+345	200	+	+3	+345	200	+	+3	N O N E			
B	-320	310	+	+2	+350	0	-	0	+350	150	+	+3
C	+320	150	+	+3	+320	150	+	+3	N O N E			
D	-295	205	+	+2	+400	0	-	0	+400	155	+	+3
E	+350	120	+	+3	+350	120	+	+3	N O N E			
F	-200	175	+	+2	+400	0	-	0	+395	125	+	+3
G	+337	105	+	+3	+337	105	+	+3	N O N E			
H	-255	165	+	+2	+400	0	-	0	+395	120	+	+3
I	+304	115	0	+3	+304	115	0	+3	N O N E			
J	-295	155	0	+2	+385	0	0	0	+385	70	0	+3

TABLE VIII

Contents of Jars for Salinity Experiment

A.	3 liters of brown water (control)
B.	3 liters of brown water at 5 ppt*
C.	3 liters of brown water at 10 ppt
D.	3 liters of brown water at 15 ppt
E.	3 liters of centrifuged# brown water + 82.1 ppm fulvic acid
F.	3 liters (E) at 5 ppt
G.	3 liters (E) at 15 ppt
H.	3 liters of centrifuged brown water + 16.2 ppm hymatomelanic acid
I.	3 liters (H) at 5 ppt
J.	3 liters (H) at 15 ppt
K.	3 liters of centrifuged brown water + 4.7 ppm humic acid
L.	3 liters (K) at 5 ppt
M.	3 liters (K) at 15 ppt
N.	3 liters centrifuged brown water
O.	3 liters (N) at 5 ppt
P.	3 liters (N) at 15 ppt

* - made saline by the addition of Instant Ocean Sea Salts

\# - at 17,500 rpm for 30 min at 25°C

TABLE IX

Effect of Increasing Salinity on Colored Water

Soln.	Sal.(ppt) 6/25	Sal.(ppt) 6/28	Color (units)	Acids*	(ppm)	Fulvic acid (ppm)
A (control)	0	0	200	Hu Hy Fu	4.7 16.2 82.1	0
B	5.05	4.55	105	Hu Hy Fu	4.6 16.8 42.1	38.0
C	10.10	8.31	35	Hu Hy Fu	4.7 16.8 4.3	78.3
D	14.93	11.44	10	Hu Hy Fu	4.5 16.5 0	80.8
E	0	0	150	Fu	82.3	0
F	5.32	4.80	72	Fu	40.5	40.4
G	15.11	12.11	0	Fu	0	80.1
H	0	0	120	Hy	16.2	-
I	5.10	5.07	120	Hy	16.2	-
J	14.90	14.95	120	Hy	16.2	-
K	0	0	105	Hu	4.7	-
L	5.05	5.00	105	Hu	4.9	-
M	15.14	15.12	105	Hu	4.9	-
N	0	0	115	-		-
O	5.21	5.22	115	-		-
P	15.06	15.10	115	-		-

* = Hu = humic acid
Hy = hymatomelanic acid
Fu = fulvic acid

TABLE X

Filter Papers or Membranes Used

	Filter	Model No.	Porosity (mμ)
A.	Reeve Angel	201	900
B.	Millipore	AAWG-047-00	800
C.	Sartorius	S-111 06-047	800
D.	Sartorius	S-117 30-047	450
E.	Sartorius	S-117 33-047	20-35
F.	Sartorius	S-117 36-047	5-10
G.	Sartorius	S-117 39-047	5
H.	Amicon	C-048-047	4.8
I.	Schleicher & Schuell	21-275	3.5

APPENDIX III

List of Stations and Their Water Chemistries

STATIONS

1. Bayou Lacombe at Fire Tower Road off Hwy 41; St. Tammany Parish.
2. East Branch of Bayou Lacombe at Hwy 36; St. Tammany Parish.
3. Bayou Lacombe at Hwy 434 in St. Tammany, La.; St. Tammany Parish.
4. Bayou Lacombe at Hwy 434, 1 mi. north of I-10; St. Tammany Parish.
5. Bayou Lacombe at Hwy 190; St. Tammany Parish.
6. Bayou Lacombe at Lake Pontchartrain off Hwy 434; St. Tammany Parish.
7. Kenta Drainage Canal at Crown Point, La., off Hwy 45; Jefferson Parish.
8. Bonne Carre Spillway at southeast section (riverside); St. Charles Parish.
9. Swamp, 4 mi. north Moisant Airport off Hwy 61; St. Charles Parish.
10. Pond off last exit of I-10 east before Lake Pontchartrain; Orleans Parish.
11. City Park pond system at Marconi Ave. and Robert E. Lee Ave.; Orleans Parish.
12. Filmore Pond (City Park); Orleans Parish.
13. North Shore of Lake Pontchartrain, 5 mi. west of Hwy 11; St. Tammany Parish.
14. Bayou Bonfouca at Lake Pontchartrain; St. Tammany Parish.
15. Michoud Canal at pumping station; Orleans Parish.
16. Michoud Canal off I-10; Orleans Parish.
17. Lake Pontchartrain at Mandeville harbor; St. Tammany Parish.
18. Lake Pontchartrain under Causeway bridge (north); St. Tammany Parish.
19. Bayou Lacombe, 1/2 mi. south of mouth; St. Tammany Parish.
20. Bayou Lacombe, 1/4 mi. south of mouth; St. Tammany Parish.

21. Bonnabel Canal at Veterans Hwy; Jefferson Parish.
22. Pond, 2 mi. north of Crown Point, La., off Hwy 45; Jefferson Parish.
23. Little Woods Drainage Canal, 1 1/2 mi. south of I-10 on Hwy 47; Orleans Parish.
24. Bayou Bienvenue at Hwy 47; St. Bernard Parish.
25. Violet Canal at Hwy 39; St. Bernard Parish.
26. Violet Canal at Tere Beau Bayou; St. Bernard Parish.
27. Bayou Dupre at Lake Borgne; St. Bernard Parish.
28. Magnolia Canal at Hwy 46; St. Bernard Parish.
29. Bayou Terre aux Boeufs at Reggio, La.; St. Bernard Parish.
30. Bayou Lery at Delacroix Island, La.; St. Bernard Parish.
31. Bayou Gentilly at Delacroix Island, La.; St. Bernard Parish.
32. Shell Beach at Lake Borgne; St. Bernard Parish.
33. Bayou Loutre at Hopedale, La.; St. Bernard Parish.
34. Cane Ridge at Hwy 39; Plaquemines Parish.
35. River aux Chenes at Belair, La.; Plaquemines Parish.
36. Lopez Canal at Phoenix, La.; Plaquemines Parish.
37. Adina Canal at Point a la Hache, La.; Plaquemines Parish.
38. Felicity Bay at Bohemia, La.; Plaquemines Parish.
39. Bay Pomme D'or at Buras, La.; Plaquemines Parish.
40. Porpoise Bayou at Venice, La.; Plaquemines Parish.
41. Bouge Chitto river at Hwy 437; Washington Parish.
42. Tchefuncte river at Hwy 16; Washington Parish.
43. Bouge Chitto river at 2 mi. east of Richardson, La.; Washington Parish.

44. Tangipahoa river at Hwy 16; Tangipahoa Parish.
45. Tangipahoa river at Hwy 442; Tangipahoa Parish.
46. Tickfaw river at Hwy 16; St. Helena Parish.
47. Tangipahoa river at Hwy 190; Tangipahoa Parish.
48. Tickfaw river at Hwy 10; St. Helena Parish.
49. Tickfaw river at Hwy 441; Livingston Parish.
50. Tickfaw river at Hwy 42; Livingston Parish.
51. Natalbany river at Hwy 22; Livingston Parish.
52. Amite river at Hwy 22; Livingston Parish.
53. Amite river at Hwy 190; East Baton Rouge Parish.
54. Amite river at I-12; Livingston Parish.
55. Amite river at Hwy 42; Ascension Parish.
56. Blind river at Hwy 61; St. James Parish.
57. Pond, 5 mi. south of Hwy 18 on Hwy 20; St. James Parish.
58. Slough at Hwy 90 and Hwy 1; Lafourche Parish.
59. Slough at Hwy 308 and Hwy 304; Lafourche Parish.
60. Lake Fields off Hwy 1; Lafourche Parish.
61. Long Lake off Hwy 1; Lafourche Parish.
62. Slough at Valentine, La., off Hwy 308; Lafourche Parish.
63. Lake des Almands at Hwy 90; St. Charles Parish.
64. Bonnabel Canal at Lake Pontchartrain; Jefferson Parish.
65. Industrial Canal off Morrison Road; Orleans Parish.
66. Industrial Canal off Hwy 39; St. Bernard Parish.
67. Industrial Canal off Hwy 47; Orleans Parish.
68. Pond, 2 mi. north of I-10 and Hwy 47; Orleans Parish.
69. Irish Bayou off I-10; Orleans Parish.

Water Chemistries

Station	1	1	1	1	1	1
Date	6/02/71	7/27/71	8/19/71	9/07/71	10/27/71	11/17/71
pH	5.0	-	3.9	4.8	5.2	5.6
RpH	5.2	-	4.5	5.2	5.5	6.0
Eh (mv)	+455	-	+260	+250	+750	+650
Temp. (°C)	31	-	27	24	18	20
Secchi (ft)	0.5	-	1.0	1.0	2.0	1.5
HCO_3 (ppm)	17.0	-	0	0	8.0	10.0
CO_3 (ppm)	0	-	0	0	0	0
CO_2 (ppm)	28.0	D	27.1	16.0	21.0	18.0
D.O. (ppm)	4.7	R	0.2	3.2	0.3	9.8
Color (units)	200	Y	200	275	130	130
Cl (ppm)	5.21	-	5.21	5.0	11.0	13.0
Conduc. (μmhos)	32	-	33	20	75	70
PO_4 (ppm)	2.0	-	0	0	0.12	0.63
TDS (ppm)	104	-	104	390	172	108
LOI (ppm)	96	-	75	111	60	30
Si (ppm)	0	-	5.2	32.0	52.0	18.0
NO_3 (ppm)	5.0	-	0.6	1.2	0.18	0.9
SO_4 (ppm)	0	-	0	0	10.0	11.0
Fe (ppm)	1.11	-	1.05	0.85	1.35	0.45
Humic (ppm)	9.6	-	-	4.8	-	4.0
Hymatomelanic (ppm)	17.1	-	-	14.9	-	12.2
Fulvic (ppm)	131.2	-	-	95.4	-	78.1
Particle size (mμ)	-	-	-	-	-	-

Station	1	1	1	1	1	1
Date	12/17/71	1/05/72	2/08/72	3/14/72	4/12/72	5/12/72
pH	5.0	5.3	5.0	4.4	4.8	5.0
RpH	5.5	5.9	5.6	4.7	5.6	5.6
Eh (mv)	+250	+325	+132	+104	+102	+104
Temp. (°C)	22	10	7	17	30	25
Secchi (ft)	1.0	1.5	1.5	1.0	0.5	0.5
HCO_3 (ppm)	2.0	8.0	2.0	1.0	3.0	7.0
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	18.0	10.0	18.0	9.0	21.0	24.0
D.O. (ppm)	2.6	10.0	7.2	9.6	3.2	4.2
Color (units)	200	180	260	400	380	360
Cl (ppm)	12.5	9.5	8.0	5.5	7.5	5.4
Conduc. (μmhos)	40	22	16	22	30	22
PO_4 (ppm)	0.12	1.14	3.2	2.0	2.0	0.3
TDS (ppm)	170	180	180	203	55	203
LOI (ppm)	65	144	137	77	10	77
Si (ppm)	25.0	18.0	17.0	32.0	32.0	32.0
NO_3 (ppm)	0.8	0.12	0.18	0.3	2.8	0.3
SO_4 (ppm)	0	2.0	3.0	2.0	4.0	2.0
Fe (ppm)	0.62	0.48	0.47	0.73	0.75	0.73
Humic (ppm)	-	4.6	-	5.1	-	9.1
Hymatomelanic (ppm)	-	15.3	-	15.5	-	15.1
Fulvic (ppm)	-	98.0	-	98.5	-	116.0
Particle size (mμ)	-	5	-	5	-	5

Station	1	2	2	2	2	2
Date	6/05/72	6/02/71	7/27/71	8/19/71	9/07/71	10/27/71
pH	7.2	6.3	5.5	5.5	4.5	5.9
RpH	7.3	6.9	6.0	6.2	4.9	6.2
Eh (mv)	+175	+615	+500	+230	+178	+620
Temp. (°C)	28	28	31	27	18	22
Secchi (ft)	1.0	1.5	1.5	1.0	1.0	2.0
HCO_3 (ppm)	6.0	19.0	10.0	5.0	0	15.0
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	1.3	31.0	32.0	15.0	11.0	23.0
D.O. (ppm)	4.5	10.0	4.7	6.0	4.2	4.4
Color (units)	400	60	130	120	180	55
Cl (ppm)	9.5	9.5	8.3	6.6	5.6	12.5
Conduc. (µmhos)	30	110	25	55	22	82
PO_4 (ppm)	0.38	1.10	2.81	0.30	1.22	1.20
TDS (ppm)	203	50	193	68	180	80
LOI (ppm)	14	5	100	44	71	5
Si (ppm)	28.0	18.0	21.1	32.0	32.6	20.0
NO_3 (ppm)	0.10	1.20	1.30	1.20	1.06	1.22
SO_4 (ppm)	18.5	60.0	2.8	1.8	0	30.0
Fe (ppm)	0.90	0.48	0.49	0.81	0.52	0.15
Humic (ppm)	-	3.2	8.4	-	4.2	-
Hymatomelanic (ppm)	-	10.0	15.6	-	13.8	-
Fulvic (ppm)	-	63.8	120.0	-	88.2	-
Particle size (mµ)	-	-	-	-	-	-

Station	2	2	2	2	2	2
Date	11/17/71	12/17/71	1/05/72	2/08/72	3/14/72	4/13/72
pH	5.9	4.6	4.5	5.4	5.1	5.6
RpH	6.5	4.9	4.6	5.6	5.4	6.3
Eh (mv)	+675	+172	+478	+155	+117	+112
Temp. (°C)	32	23	10	8	18	22
Secchi (ft)	1.0	1.5	1.5	1.5	1.5	0.5
HCO_3 (ppm)	15.0	2.0	5.3	3.9	4.8	10.7
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	10.0	18.2	9.3	5.5	10.5	22.8
D.O. (ppm)	8.4	4.0	4.7	8.8	9.5	4.8
Color (units)	40	190	180	270	390	210
Cl (ppm)	4.5	13.9	9.5	9.5	6.5	10.5
Conduc. (µmhos)	122	44	22	16	23	60
PO_4 (ppm)	0.71	1.29	2.89	1.65	0.69	1.26
TDS (ppm)	102	160	193	107	225	120
LOI (ppm)	12	51	112	27	81	42
Si (ppm)	21.2	36.1	28.6	19.0	30.2	23.8
NO_3 (ppm)	0.97	1.33	1.46	1.05	0.28	1.17
SO_4 (ppm)	100.0	0	2.0	2.0	2.0	3.8
Fe (ppm)	0.08	0.70	0.49	0.53	0.78	0.36
Humic (ppm)	0	-	6.9	-	3.3	-
Hymatomelanic (ppm)	0	-	14.1	-	13.6	-
Fulvic (ppm)	0	-	107.7	-	87.1	-
Particle size (mµ)	-	-	5	-	5	-

Station	2	2	3	3	3	3
Date	5/12/72	6/05/72	6/02/71	7/27/71	8/19/71	9/07/71
pH	6.1	5.0	6.6	5.6	6.0	6.3
RpH	6.7	5.8	7.0	5.8	6.2	6.7
Eh (mv)	+101	+176	+778	+250	+178	+350
Temp. (°C)	30	22	17	29	26	18
Secchi (ft)	1.75	2.5	3.0	2.7	2.6	1.5
HCO_3 (ppm)	16.8	12.4	18.7	5.1	5.1	11.8
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	28.6	23.1	10.9	5.8	4.8	4.1
D.O. (ppm)	4.5	4.7	15.3	10.1	4.2	8.1
Color (units)	360	80	60	120	120	120
Cl (ppm)	6.6	13.9	10.1	8.3	8.5	6.6
Conduc. (μmhos)	23	50	170	41	74	80
PO_4 (ppm)	0.58	0.74	2.31	2.18	1.19	0.85
TDS (ppm)	220	275	108	217	296	418
LOI (ppm)	78	41	15	114	78	112
Si (ppm)	24.8	18.4	18.2	14.9	21.9	17.8
NO_3 (ppm)	0.29	0.11	1.33	1.42	1.31	1.27
SO_4 (ppm)	2.8	6.9	80.6	1.7	21.8	1.0
Fe (ppm)	0.80	0.14	0.49	0.49	0.51	0.45
Humic (ppm)	7.9	-	-	-	-	-
Hymatomelanic (ppm)	14.1	-	-	-	-	-
Fulvic (ppm)	108.3	-	-	-	-	-
Particle size (mμ)	5-10	-	-	-	-	-

Station	3	3	3	3	3	3
Date	10/27/71	11/17/71	12/17/71	1/05/72	2/08/72	3/14/72
pH	6.3	5.6	4.6	4.6	5.1	5.6
RpH	6.6	6.3	4.9	4.8	5.3	5.9
Eh (mv)	+772	+755	+302	+307	+130	+101
Temp. (°C)	22	17	27	10	8	19
Secchi (ft)	2.0	2.9	1.5	2.5	1.75	1.0
HCO_3 (ppm)	5.1	10.3	2.1	3.1	3.9	4.8
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	3.3	2.8	15.0	5.2	8.6	11.5
D.O. (ppm)	4.8	6.7	5.2	4.5	10.6	9.2
Color (units)	50	50	190	200	290	355
Cl (ppm)	13.5	4.6	12.0	3.6	7.5	6.0
Conduc. (μmhos)	87	250	47	40	18	23
PO_4 (ppm)	1.22	0.76	2.35	1.29	1.77	1.13
TDS (ppm)	80	245	160	340	160	231
LOI (ppm)	0	78	44	110	43	86
Si (ppm)	32.6	32.9	16.4	32.7	21.0	25.1
NO_3 (ppm)	0.91	1.31	1.22	1.33	1.18	0
SO_4 (ppm)	85.1	120.6	0	1.0	1.9	3.1
Fe (ppm)	0.15	0.51	0.70	0.81	0.61	0.72
Humic (ppm)	-	-	-	-	-	-
Hymatomelanic (ppm)	-	-	-	-	-	-
Fulvic (ppm)	-	-	-	-	-	-
Particle size (mμ)	-	-	-	5	-	5-10

Station	3	3	3	4	4	4
Date	4/13/73	5/12/72	6/05/72	6/02/71	7/27/71	8/19/71
pH	6.0	6.4	5.8	6.8	6.4	7.4
RpH	6.2	6.7	6.1	7.0	6.8	7.6
Eh (mv)	+119	+100	+178	+221	+221	+250
Temp. (°C)	22	27	28	19	31	29
Secchi (ft)	1.0	0.5	3.5	1.4	1.0	2.0
HCO_3 (ppm)	15.8	18.4	2.8	40.7	8.7	8.6
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	2.6	16.4	4.6	5.9	7.2	3.0
D.O. (ppm)	8.3	6.7	8.3	8.3	4.4	8.5
Color (units)	140	100	30	50	105	140
Cl (ppm)	10.5	6.1	12.5	75.1	8.8	7.3
Conduc. (µmhos)	60	23	72	800	50	74
PO_4 (ppm)	0.47	1.15	0.87	1.65	1.411	0.02
TDS (ppm)	120	231	304	150	105	68
LOI (ppm)	61	96	45	19	25	44
Si (ppm)	22.8	25.9	18.9	32.0	20.8	13.1
NO_3 (ppm)	0	0	0.81	1.55	1.46	3.41
SO_4 (ppm)	8.3	3.8	12.3	4.7	1.2	8.2
Fe (ppm)	0.24	0.78	0.12	0.65	0.65	0.08
Humic (ppm)	-	-	-	9.4	5.3	-
Hymatomelanic (ppm)	-	-	-	53.6	16.7	-
Fulvic (ppm)	-	-	-	0	106.0	-
Particle size (mµ)	-	5-10	-	-	-	-

Station	4	4	4	4	4	4
Date	9/07/71	10/27/71	11/17/71	12/17/71	1/05/72	2/08/72
pH	6.3	7.1	6.1	4.5	4.6	5.1
RpH	6.4	7.2	6.5	4.8	4.8	5.3
Eh (mv)	+205	+720	+700	+253	+195	+133
Temp. (°C)	37	20	22	22	10	8
Secchi (ft)	2.3	1.5	1.5	1.5	1.0	1.0
HCO_3 (ppm)	12.8	11.7	11.9	5.1	4.7	5.9
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	4.5	2.2	2.6	15.7	10.1	7.2
D.O. (ppm)	6.4	9.8	9.8	5.6	4.7	10.2
Color (units)	150	25	25	240	200	295
Cl (ppm)	14.5	13.8	13.5	13.0	10.4	7.5
Conduc. (µmhos)	50	85	168	47	26	18
PO_4 (ppm)	0.08	0.63	0.64	1.45	1.41	1.77
TDS (ppm)	100	108	108	165	188	186
LOI (ppm)	48	0	5	56	105	115
Si (ppm)	27.9	18.4	18.2	26.8	24.5	20.3
NO_3 (ppm)	4.88	0.95	0.91	1.19	1.43	1.04
SO_4 (ppm)	2.8	110.7	110.3	0	1.8	3.6
Fe (ppm)	0.38	0.08	0.09	0.75	0.65	0.63
Humic (ppm)	3.7	-	0	-	3.6	-
Hymatomelanic (ppm)	11.7	-	0	-	13.4	-
Fulvic (ppm)	74.6	-	0	-	86.2	-
Particle size (mµ)	-	-	-	-	5	-

Station	4	4	4	4	5	5
Date	3/14/72	4/13/72	5/12/72	6/05/72	6/02/71	7/27/71
pH	5.7	6.6	6.7	6.4	6.8	6.4
RpH	6.0	6.8	6.9	6.5	7.0	6.8
Eh (mv)	+133	+111	+115	+185	+221	+221
Temp. (°C)	20	22	28	28	19	31
Secchi (ft)	1.5	2.1	1.0	3.6	1.0	1.0
HCO_3 (ppm)	6.6	7.7	10.5	6.3	40.7	30.1
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	9.1	2.6	12.9	2.3	5.1	10.5
D.O. (ppm)	9.2	7.5	6.7	8.9	8.3	8.3
Color (units)	340	130	90	30	50	210
Cl (ppm)	7.5	11.0	4.6	12.5	75.1	77.5
Conduc. (μmhos)	27	60	44	70	800	120
PO_4 (ppm)	0.33	0.43	0.21	0.75	1.65	1.64
TDS (ppm)	310	230	1047	350	150	490
LOI (ppm)	110	71	514	70	19	171
Si (ppm)	25.8	20.3	23.8	27.6	32.2	32.7
NO_3 (ppm)	0	0.38	0.83	0.92	1.53	1.59
SO_4 (ppm)	3.9	5.5	3.6	10.7	4.7	4.2
Fe (ppm)	0.73	0.20	0.59	0.06	0.65	0.65
Humic (ppm)	4.3	-	5.7	-	9.4	15.8
Hymatomelanic (ppm)	13.5	-	17.1	-	53.6	89.3
Fulvic (ppm)	86.9	-	109.2	-	0	0.9
Particle size (mμ)	5-10	-	10-20	-	-	-

Station	5	5	5	5	5	5
Date	8/19/71	9/07/71	10/27/71	11/27/71	12/17/71	1/05/72
pH	7.3	6.4	6.7	6.5	5.6	5.5
RpH	7.5	6.6	6.9	6.8	5.9	5.9
Eh (mv)	+200	+470	+253	+255	+302	+221
Temp. (°C)	34	17	26	26	23	12
Secchi (ft)	2.6	1.0	2.5	2.0	1.0	1.8
HCO_3 (ppm)	26.9	35.0	28.6	27.5	6.2	10.2
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	7.6	11.3	9.3	5.9	12.4	8.2
D.O. (ppm)	5.1	8.3	5.6	5.6	3.8	8.0
Color (units)	120	180	115	200	210	210
Cl (ppm)	526.5	76.1	590.3	590.3	95.1	75.2
Conduc. (μmhos)	950	5000	1700	1700	160	80
PO_4 (ppm)	0.02	1.38	1.28	1.24	1.43	1.75
TDS (ppm)	544	200	1140	1195	1150	496
LOI (ppm)	96	101	164	147	181	176
Si (ppm)	9.5	32.7	18.2	1.83	24.9	32.7
NO_3 (ppm)	0.62	2.68	1.65	1.62	28.5	1.54
SO_4 (ppm)	31.9	30.5	83.7	82.9	1.7	4.7
Fe (ppm)	0.29	0.12	0.18	0.17	0.48	0.65
Humic (ppm)	-	14.6	-	13.9	-	14.3
Hymatomelanic (ppm)	-	82.0	-	78.8	-	80.4
Fulvic (ppm)	-	0.4	-	0.3	-	0.3
Paricle size (mμ)	-	-	-	-	-	5

Station	5	5	5	5	5	6
Date	2/08/72	3/14/72	4/13/72	5/12/72	6/05/72	6/02/71
pH	5.8	6.1	6.6	6.8	6.8	7.7
RpH	6.1	6.2	6.8	7.2	6.8	7.9
Eh (mv)	+143	+113	+113	+107	+150	+220
Temp. (°C)	11	21	25	30	29	20
Secchi (ft)	1.5	1.8	2.0	3.0	2.5	1.2
HCO_3 (ppm)	7.4	15.9	15.9	32.6	15.8	50.2
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	6.3	3.1	7.4	12.1	3.6	2.5
D.O. (ppm)	9.0	6.1	7.2	7.3	6.2	4.3
Color (units)	290	320	250	120	120	55
Cl (ppm)	45.9	40.6	105.2	51.8	42.9	800.2
Conduc. (μmhos)	26	44	220	59	156	1900
PO_4 (ppm)	1.83	0.26	0.84	0.37	0.15	0.15
TDS (ppm)	496	1047	750	1214	760	4003
LOI (ppm)	172	514	113	717	95	527
Si (ppm)	21.0	32.8	20.7	25.8	17.3	21.5
NO_3 (ppm)	1.18	0.85	0	0.85	0.12	0.13
SO_4 (ppm)	3.7	3.8	3.9	3.5	9.9	102.3
Fe (ppm)	0.63	0.63	0.33	0.72	0.19	0.43
Humic (ppm)	-	18.4	-	17.4	-	9.3
Hymatomelanic (ppm)	-	104.0	-	116.3	-	52.6
Fulvic (ppm)	-	1.6	-	4.6	-	61.9
Particle size (mμ)	-	5-10	-	10-20	-	-

Station	6	6	6	6	6	6
Date	7/27/71	8/19/71	9/07/71	10/27/71	11/17/71	12/17/71
pH	7.5	8.0	7.0	7.3	7.0	6.8
RpH	7.9	8.6	7.1	7.6	7.3	6.9
Eh (mv)	+220	+415	+128	+302	+302	+300
Temp. (°C)	27	34	28	26	26	23
Secchi (ft)	1.0	2.0	1.0	2.5	2.5	3.0
HCO_3 (ppm)	40.2	34.8	40.1	38.6	25.8	26.9
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	13.7	2.5	3.7	4.9	4.2	5.5
D.O. (ppm)	4.3	7.2	13.7	6.6	6.4	6.2
Color (units)	105	105	80	95	120	150
Cl (ppm)	875.4	1772.3	5982.3	2705.1	2814.5	1200
Conduc. (μmhos)	1880	5400	8100	6000	6023	3700
PO_4 (ppm)	0.14	0	0.03	0.10	0.11	0.12
TDS (ppm)	4577	312	5048	4116	4132	4200
LOI (ppm)	861	112	832	740	738	811
Si (ppm)	21.7	5.5	15.2	9.2	8.4	12.7
NO_3 (ppm)	0.13	0.53	3.8	0.13	0.12	0.12
SO_4 (ppm)	102.5	203.7	290.9	260.4	237.1	160.7
Fe (ppm)	0.43	0.08	0.02	0.11	0.17	0.12
Humic (ppm)	14.6	-	18.1	-	9.2	-
Hymatomelanic (ppm)	82.6	-	103.7	-	52.1	-
Fulvic (ppm)	0.3	-	0.9	-	0.4	-
Particle size (mμ)	-	-	-	-	-	-

Station	6	6	6	6	6	6
Date	1/05/72	2/08/72	3/14/72	4/13/72	5/12/72	6/05/72
pH	6.6	6.5	7.0	7.2	7.5	6.8
RpH	6.9	6.8	7.1	7.4	7.6	7.0
Eh (mv)	+220	+130	+115	+110	+105	+117
Temp. (°C)	13	10	25	27	30	30
Secchi (ft)	1.0	1.5	1.7	3.0	2.7	2.5
HCO_3 (ppm)	18.3	6.8	23.1	45.2	48.2	32.2
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	4.7	6.1	2.1	3.9	2.8	6.9
D.O. (ppm)	4.0	10.4	6.0	7.5	8.3	6.7
Color (units)	180	340	300	95	70	90
Cl (ppm)	800	75.4	125.8	1375.4	125.9	1855.8
Conduc. (µmhos)	1900	100	280	4200	280	5300
PO_4 (ppm)	0.15	1.97	0.53	0.95	0.54	0.81
TDS (ppm)	4468	4561	4182	1422	4721	1153
LOI (ppm)	852	811	782	612	726	204
Si (ppm)	21.5	24.9	18.3	2.3	18.2	5.2
NO_3 (ppm)	0.13	1.93	0	0.20	0	0.12
SO_4 (ppm)	103.7	5.2	8.2	203.2	8.1	220.1
Fe (ppm)	0.43	0.62	0.52	0.08	0.55	0.10
Humic (ppm)	14.1	-	18.2	-	17.9	-
Hymatomelanic (ppm)	79.2	-	105.5	0	101.3	-
Fulvic (ppm)	0.9	-	0.8	-	0.8	-
Particle Size (mµ)	5-10	-	10-20	-	10-20	-

Station	7	8	9	10	11	12
Date	8/12/71	9/21/71	9/21/71	10/05/71	10/05/71	10/05/71
pH	6.9	7.5	6.6	7.6	6.7	6.6
RpH	7.3	7.8	6.8	7.6	6.9	6.7
Eh (mv)	+200	+130	-240	+132	+237	+113
Temp. (°C)	29	25	25	28	29	29
Secchi (ft)	1.0	1.4	0.5	0.5	1.5	1.8
HCO_3 (ppm)	85.2	102.7	92.1	201.1	36.9	40.9
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	24.9	10.2	34.9	10.2	3.3	7.2
D.O. (ppm)	0.51	1.7	0.1	5.7	6.0	4.1
Color (units)	200	130	150	180	110	130
Cl (ppm)	479.5	14.0	129.5	290.9	1330.6	37.5
Conduc. (µmhos)	1550	210	570	1480	4104	3600
PO_4 (ppm)	0.44	2.96	6.53	0.44	0.98	0.10
TDS (ppm)	952	176	364	872	2276	296
LOI (ppm)	236	88	136	172	364	136
Si (ppm)	7.5	21.9	28.3	0.9	10.9	22.8
NO_3 (ppm)	0.51	0.13	7.22	0.92	0.11	0.15
SO_4 (ppm)	32.7	8.3	0	92.4	190.0	78.4
Fe (ppm)	0.43	0.17	0	0.28	0.12	0.23
Humic (ppm)	12.4	0.5	31.4	16.7	16.2	14.2
Hymatomelanic (ppm)	69.6	10.1	177.1	94.3	91.4	80.5
Fulvic (ppm)	1.0	56.9	1.9	1.0	0.4	0.3
Particle size (mµ)	10-20	10-20	10-20	20-35	10-20	10-20

Station	13	14	15	16	17	18
Date	11/20/71	12/02/72	1/27/72	2/13/72	2/08/72	2/08/72
pH	7.5	7.2	7.4	7.2	8.2	8.3
RpH	7.6	7.2	7.6	7.4	8.2	8.4
Eh (mv)	+172	+237	+130	+150	+133	+135
Temp. (°C)	17	12	17	13	11	15
Secchi (ft)	3.0	1.5	1.5	1.9	3.0	3.0
HCO_3 (ppm)	18.2	105.2	184.2	107.3	31.1	35.9
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	17.3	8.6	18.0	8.3	2.7	1.6
D.O. (ppm)	7.8	2.6	8.0	7.2	12.5	14.5
Color (units)	100	80	390	280	70	70
Cl (ppm)	4180.7	1400.7	1700.3	1360.9	1500.4	1710.5
Conduc. (μmhos)	8400	3800	4300	3700	3470	3300
PO_4 (ppm)	2.87	1.00	0.20	2.17	1.36	0.84
TDS (ppm)	5048	2275	5041	1540	88	100
LOI (ppm)	942	364	1160	970	12	19
Si (ppm)	5.8	14.4	41.9	21.8	7.0	7.0
NO_3 (ppm)	1.66	0.11	0.15	0.99	0.11	0.17
SO_4 (ppm)	320.9	204.7	350.6	210.0	200.1	217.2
Fe (ppm)	0.03	0.20	0.42	0.38	0.07	0.81
Humic (ppm)	20.6	14.2	14.8	25.8	12.0	16.5
Hymatomelanic (ppm)	118.2	80.1	84.0	142.2	67.6	93.6
Fulvic (ppm)	1.2	0.8	0.2	6.2	0.7	0.9
Particle size (mμ)	10-20	10-20	10-20	10-20	20-35	20-35

Station	19	20	21	22	23	24
Date	2/22/72	2/22/72	2/19/72	3/07/72	6/05/72	6/12/72
pH	7.8	7.0	7.3	7.6	3.2	7.5
RpH	8.3	7.4	7.4	7.7	3.4	7.7
Eh (mv)	+195	+100	+233	+185	+102	+113
Temp. (°C)	16	16	17	30	22	24
Secchi (ft)	1.5	1.0	2.0	1.3	0.5	3
HCO_3 (ppm)	34.0	26.3	22.5	17.5	2.0	32.8
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	1.3	6.8	15.8	1.1	42.5	43.1
D.O. (ppm)	10.8	9.0	7.0	8.1	0.4	6.5
Color (units)	110	370	40	250	5155	310
Cl (ppm)	1760.5	300.1	230.8	1.7	43.4	521.5
Conduc. (μmhos)	4900	800	970	55	165	1400
PO_4 (ppm)	1.03	1.66	4.42	0.25	0.54	0.21
TDS (ppm)	4615	5613	1477	750	2068	3342
LOI (ppm)	580	720	565	81	413	410
Si (ppm)	5.5	19.9	29.1	0.5	1.02	2.5
NO_3 (ppm)	0.93	0.83	0.25	0	0.12	1.19
SO_4 (ppm)	221.6	30.5	21.9	4.0	21.6	31.7
Fe (ppm)	0.07	0.49	0.09	0.82	3.13	0.37
Humic (ppm)	11.2	11.3	21.0	7.9	0	16.7
Hymatomelanic (ppm)	64.2	63.7	114.1	25.1	18.3	95.1
Fulvic (ppm)	0.6	1.0	0	160.0	104.1	1.7
Particle size (mμ)	10-20	10-20	10-20	10-20	5	10-20

Station	25	26	27	28	29	30
Date	6/12/72	6/12/72	6/12/72	6/12/72	6/12/72	6/12/72
pH	7.3	7.2	6.8	6.1	7.2	7.2
RpH	7.6	7.2	7.2	6.6	7.2	7.2
Eh (mv)	+103	+111	+105	+110	+101	+116
Temp. (°C)	28	28	28	20	28	28
Secchi (ft)	2.6	1.0	2.0	0.5	2.8	1.0
HCO_3 (ppm)	41.8	42.8	11.5	16.9	31.9	28.5
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	6.8	0.2	12.3	20.1	0.3	3.5
D.O. (ppm)	6.5	7.7	4.5	5.1	6.7	6.5
Color (units)	280	290	300	410	390	410
Cl (ppm)	32.0	54.6	4000.2	13.2	5045.1	5150.0
Conduc. (μmhos)	1050	1475	6500	450	11160	10550
PO_4 (ppm)	0.36	0.33	4.31	0.22	0.82	0.33
TDS (ppm)	987	1600	6130	483	6120	6155
LOI (ppm)	75	313	414	101	313	319
Si (ppm)	3.9	6.3	11.3	32.8	28.3	19.2
NO_3 (ppm)	0.14	0.22	21.32	0.21	1.11	0.16
SO_4 (ppm)	210.2	252.7	230.5	20.6	210.8	230.4
Fe (ppm)	0.55	0.79	0.48	1.99	0.77	1.24
Humic (ppm)	21.6	14.6	17.9	9.4	15.4	17.4
Hymatomelanic (ppm)	122.0	82.7	102.1	53.2	84.6	99.0
Fulvic (ppm)	1.4	0.7	1.0	0.4	0	0.6
Particle size (mμ)	10-20	10-20	10-20	10-20	10-20	10-20

Station	31	32	33	34	35	36
Date	6/12/72	6/12/72	6/12/72	6/15/72	6/15/72	6/15/72
pH	7.2	7.2	7.3	7.1	7.2	7.4
RpH	7.5	7.5	7.5	7.3	7.3	7.5
Eh (mv)	+117	+101	+107	+117	+100	+099
Temp. (°C)	29	28	32	26	30	30
Secchi (ft)	1.5	3.0	1.5	1.4	2.3	1.3
HCO_3 (ppm)	29.1	27.5	28.3	15.5	20.4	19.2
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	3.5	4.5	5.2	10.5	6.2	0.5
D.O. (ppm)	7.1	7.1	8.3	4.4	5.2	6.5
Color (units)	400	380	350	450	450	390
Cl (ppm)	5213.8	4088.1	5065.4	17.1	42.3	47.5
Conduc. (μmhos)	12950	7428	11150	250	1300	1750
PO_4 (ppm)	0.87	0.16	0.21	0.31	0	0.05
TDS (ppm)	6123	4021	6396	553	613	613
LOI (ppm)	404	321	414	71	105	115
Si (ppm)	19.0	33.5	20.3	10.5	2.3	7.2
NO_3 (ppm)	0.15	0.21	0	0	0.25	0.11
SO_4 (ppm)	210.5	211.7	212.9	55.2	100.2	152.5
Fe (ppm)	1.36	1.55	1.82	1.77	2.39	0.74
Humic (ppm)	27.0	17.7	19.7	8.3	17.8	22.2
Hymatomelanic (ppm)	152.0	101.0	112.0	23.7	102.1	126.0
Fulvic (ppm)	1.0	0.3	0.3	152.0	0.2	1.8
Particle size (mμ)	10-20	10-20	10-20	10-20	10-20	10-20

Station	37	38	39	40	41	42
Date	6/15/72	6/15/72	6/15/72	6/15/72	7/25/72	7/25/72
pH	7.0	7.2	7.3	7.6	6.2	6.9
RpH	7.4	7.2	7.6	7.6	6.5	7.3
Eh (mv)	+112	+112	+102	+101	+319	+195
Temp. (°C)	28	27	28	29	32	27
Secchi (ft)	1.3	2.0	2.8	1.0	1.5	1.5
HCO_3 (ppm)	21.2	28.9	19.7	35.6	66.3	78.3
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	14.5	0.3	4.3	0.8	0.9	0.6
D.O. (ppm)	7.3	8.3	8.5	8.0	7.4	5.2
Color (units)	400	410	280	400	490	828
Cl (ppm)	251.3	503.2	877.2	955.6	2.3	2.1
Conduc. (μmhos)	3400	6120	12606	18570	178	119
PO_4 (ppm)	0	0.25	0	0.28	1.81	0.08
TDS (ppm)	1733	844	6213	6310	654	459
LOI (ppm)	212	94	402	212	13	23
Si (ppm)	16.5	28.3	31.1	23.2	31.9	33.3
NO_3 (ppm)	0.18	0.38	0.18	0.07	0.31	0.34
SO_4 (ppm)	230.4	300.2	205.6	210.2	8.4	23.5
Fe (ppm)	0.72	1.57	0.77	0.72	0.31	0.42
Humic (ppm)	27.4	18.5	25.2	19.1	13.2	5.2
Humatomelanic (ppm)	154.0	106.2	142.1	109.1	22.7	34.6
Fulvic (ppm)	2.6	0.53	1.8	0.8	174.1	192.2
Particle size (mμ)	10-20	10-20	10-20	10-20	5-10	10-20

Station	43	44	45	46	47	48
Date	7/25/72	7/24/72	7/24/72	7/24/72	7/24/72	7/24/72
pH	7.3	4.5	7.3	4.5	6.1	7.3
RpH	8.1	5.1	7.7	5.3	6.3	7.5
Eh (mv)	+132	+456	+235	+452	+650	+369
Temp. (°C)	27	24	28	31	29	32
Secchi (ft)	1.0	1.5	2.0	1.3	1.5	1.5
HCO_3 (ppm)	83.0	7.35	7.5	85.3	29.3	78.3
CO_3 (ppm)	1.1	0	0	0	0	0
CO_2 (ppm)	0.2	1.1	0.6	16.3	0.9	0.9
D.O. (ppm)	4.1	8.3	4.5	8.2	7.4	6.5
Color (units)	560	650	475	250	731	453
Cl (ppm)	1.5	2.3	4.3	8.3	1.1	2.3
Conduc. (μmhos)	117	175	183	153	78	135
PO_4 (ppm)	0.82	0.41	0.72	0.02	0.16	0.65
TDS (ppm)	651	432	653	453	342	253
LOI (ppm)	49	19	101	18	19	19
Si (ppm)	23.9	12.3	33.5	32.3	8.3	19.3
NO_3 (ppm)	0.33	0.15	0.09	0.15	0.56	0.32
SO_4 (ppm)	16.5	6.5	11.9	16.2	2.5	8.5
Fe (ppm)	0.55	0.11	0.53	0.31	0.37	0.41
Humic (ppm)	6.8	4.3	4.9	6.8	4.2	2.6
Hymatomelanic (ppm)	24.1	14.2	14.9	22.1	15.7	22.2
Fulvic (ppm)	154.1	90.5	95.2	141.2	100.1	117.2
Particle size (mμ)	10-20	5	20-35	5	5-10	10-20

Station	49	50	51	52	53	54
Date	7/24/72	7/24/72	7/24/72	7/28/72	7/28/72	7/28/72
pH	7.3	3.1	5.6	6.9	7.3	6.1
RpH	7.3	5.3	6.2	7.0	7.3	6.9
Eh (mv)	+242	+452	+193	+089	+101	+195
Temp. (°C)	29	33	26	34	33	26
Secchi (ft)	1.0	0.5	1.7	1.0	1.5	1.5
HCO_3 (ppm)	17.5	3.2	11.3	16.3	55.3	43.0
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	0	45.3	10.3	5.7	1.1	4.3
D.O. (ppm)	8.2	2.8	7.1	8.0	8.6	7.8
Color (units)	731	4887	875	445	750	552
Cl (ppm)	3.2	1.7	2.3	5.3	2.1	3.4
Conduc. (μmhos)	117	78	111	117	95	114
PO_4 (ppm)	0.01	0.31	1.10	0.82	0.04	0.83
TDS (ppm)	453	1046	345	439	732	325
LOI (ppm)	17	783	17	35	11	63
Si (ppm)	8.5	20.3	11.3	17.2	32.4	16.3
NO_3 (ppm)	0.86	0.33	0.21	0.41	0.41	0.05
SO_4 (ppm)	11.2	7.8	14.3	3.2	16.0	2.8
Fe (ppm)	0.41	1.15	0.21	0.73	0.51	0.44
Humic (ppm)	7.6	4.8	3.6	5.4	6.5	6.6
Hymatomelanic (ppm)	27.3	14.9	11.3	18.7	23.6	22.0
Fulvic (ppm)	174.1	95.3	72.1	119.9	150.9	140.4
Particle size (mμ)	10-20	5	5	10-20	20-35	5-10

Station	55	56	57	58	59	60
Date	7/28/72	7/30/72	8/11/72	8/11/72	8/11/72	8/21/72
pH	6.5	5.8	7.4	4.3	4.2	6.3
RpH	6.7	6.3	7.5	5.0	4.8	6.5
Eh (mv)	+155	+143	+603	+517	+570	+450
Temp. (°C)	27	34	29	30	30	30
Secchi (ft)	1.5	1.8	2.0	2.0	1.8	1.3
HCO_3 (ppm)	16.3	15.4	21.3	7.3	5.5	44.7
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	7.8	6.0	2.1	8.4	7.1	8.3
D.O. (ppm)	5.2	4.5	7.3	4.5	4.1	7.0
Color (units)	500	350	325	850	950	750
Conduc. (μmhos)	155	94	635	95	102	200
PO_4 (ppm)	0.93	1.17	0.38	0.01	0.04	0.03
TDS (ppm)	857	455	403	495	935	430
LOI (ppm)	113	70	85	112	119	250
Si (ppm)	32.9	28.3	16.3	14.9	17.2	0
NO_3 (ppm)	0.32	0.11	1.10	0.05	0.01	0.02
SO_4 (ppm)	16.6	10.3	20.3	26.6	24.6	5.5
Fe (ppm)	0.32	0.86	0.35	3.54	4.37	0.52
Humic (ppm)	3.7	4.7	4.1	5.3	6.1	4.5
Hymatomelanic (ppm)	12.2	14.2	13.8	17.9	19.7	14.4
Fulvic (ppm)	78.1	91.1	88.1	114.8	126.2	92.1
Particle size (mμ)	10-20	5-10	10-20	5	5	5-10

Station	61	62	63	64	65	66
Date	8/21/72	8/21/72	9/11/72	9/11/72	9/11/72	9/11/72
pH	5.8	6.3	6.3	7.4	6.3	7.3
RpH	6.2	6.4	7.0	7.6	6.4	7.6
Eh (mv)	+401	+350	+250	+103	+273	+450
Temp. (°C)	30	34	30	25	25	23
Secchi (ft)	1.5	1.3	2.0	2.0	2.1	2.5
HCO_3 (ppm)	16.9	24.3	24.1	111.3	78.2	135.2
CO_3 (ppm)	0	0	0	0	0	0
CO_2 (ppm)	8.1	3.1	2.1	6.3	3.1	3.4
D.O. (ppm)	6.3	4.5	6.8	6.7	4.3	6.8
Color (units)	550	450	299	275	250	255
Cl (ppm)	8.3	8.1	10.1	271.2	480.2	21.8
Conduc. (μmhos)	231	201	230	1507	2200	440
PO_4 (ppm)	0.04	0.04	0.33	0.48	0.32	0.41
TDS (ppm)	735	693	635	1731	838	939
LOI (ppm)	216	298	144	653	251	211
Si (ppm)	1.4	2.1	2.3	32.8	10.2	36.2
NO_3 (ppm)	0.12	0.10	0.02	0.81	0.23	0.08
SO_4 (ppm)	8.3	16.3	10.4	231.9	350.1	181.2
Fe (ppm)	0.52	0.33	0.35	0.02	0.07	0.32
Humic (ppm)	4.8	3.9	29.8	15.6	21.6	26.1
Hymatomelanic (ppm)	16.0	12.7	169.1	88.4	115.1	148.2
Fulvic (ppm)	102.2	81.4	1.1	1.0	0	2.1
Particle size (mμ)	5-10	5-10	5-10	10-20	5-10	10-20

Station	67	68	69
Date	9/17/72	9/17/72	9/21/72
pH	7.4	3.5	7.3
RpH	7.6	3.7	7.5
Eh (mv)	+136	+102	+613
Temp. (°C)	17	22	31
Secchi (ft)	1.5	0.5	2.2
HCO_3 (ppm)	184.2	2.1	41.2
CO_3 (ppm)	0	0	0
CO_2 (ppm)	18.3	7.3	7.1
D.O. (ppm)	8.0	0.4	7.5
Color (units)	390	850	325
Cl (ppm)	1700.3	81.2	5930.1
Conduc. (μmhos)	4300	450	22000
PO_4 (ppm)	0.20	0.53	0.03
TDS (ppm)	5042	2071	943
LOI (ppm)	1160	319	101
Si (ppm)	41.8	0.84	0.3
NO_3 (ppm)	0.15	0.13	0
SO_4 (ppm)	356.1	75.4	45.7
Fe (ppm)	0.32	0.03	0.41
Humic (ppm)	27.4	16.8	12.8
Hymatomelanic (ppm)	155.2	95.4	72.5
Fulvic (ppm)	2.3	1.1	0
Particle size (mμ)	20-35	5	10-20

LITERATURE CITED

American Public Health Association. 1971. Standard methods for the examination of water and wastewater. American Public Health Association, New York. 874 p.

American Water Works Associaition. 1966. Research committee on color problems report for 1966. Jour. Amer. Water Works Assoc. 59(8): 1023-1035.

Aschan, O. 1909. Water soluble humus materials in the northern fresh waters. Jour. Prac. Chem. 77: 172-188.

Bick, G. H., L. E. Hornuff, and E. N. Lambremont. 1953. An ecological reconnaisance of a naturally acid stream in southern Louisiana. Jour. Tenn. Acad. Sci. 28: 221-231.

Black, A. P., and D. G. Willems. 1961. Electrophoretic studies of coagulation for removal of organic color. Jour. Amer. Water Works Assoc. 53: 589-604.

____________, and R. F. Christman. 1963a. Characteristics of colored surface waters. Jour. Amer. Water Works Assoc. 55: 753-770.

____________, and R. F. Christman. 1963b. Chemical characteristics of fulvic acid. Jour. Amer. Water Works Assoc. 55: 897-912.

Collier, A. 1958. Some biochemical aspects of red tides and related oceanographic problems. Limnol. Oceanogr. 3(1): 33-39.

Datski, V. G. 1940. Photometric investigation of color reactions of sulfuric acid with organic sbustances in natural water. Jour. Appl. Chem. (USSR) 13: 384-396.

Federal Water Pollution Control Administration. 1968. Water quality criteria. Report to the Secretary of the Interior. U. S. Government Printing Office, Washington, D. C. 234 p.

Gegan, D. W. 1959. An ecological survey of a disturbed, naturally acid stream. M.S. Thesis. Loyola University of the South. 113 p.

____________. 1963. An ecological survey of a disturbed, naturally acid stream. Southwest. Natur. 8(3): 127-141.

Ghassemi, M., and R. F. Christman. 1967. Properties of yellow organic acids of natural waters. Limnol. Oceanogr. 13: 583-597.

Giddings, J. C., and M. B. Monroe. 1972. Our chemical environment. Carfield Press, San Francisco. 367 p.

Gjessing, E. T. 1964. Ferrous iron in water. Limnol. Oceanogr. 56: 272-274.

Hach Chemical Company. 1969. Water and wastewater analysis procedures. Catalog number 10. Hach Chemical Company, Ames, Iowa. 104 p.

Hopkins, T. L. 1961. Natural coloring matter as an indication of inshore water masses. Limnol. Oceanogr. 6(4): 484-486.

Kaufmann, G. 1969. Color of water in Florida streams and canals. Bur. Geol. Fla. Dept. Natur. Resourc. Map Ser. No. 35.

Kononova, M. M. 1961. Soil organic matter. Pergamon Press, Oxford. 451 p.

Lamar, W. L. 1968. Evaluation of organic color and iron in natural surfaces waters. U.S. Geol. Sur. Prof. Paper 600D. D24-D29.

Langelier, W. F., and H. F. Ludwig. 1949. Mechanism of flocculation in the clarification of turbid waters. Jour. Amer. Water Works Assoc. 41: 163-181.

Masri, M. S., and M. Friedman. 1972. Mercury uptake by polyamine carbohydrates. Environ. Sci. Tech. 6(8): 745-746.

Matijevic, E. 1961. Defection of metal ion hydrolysis by coagulation. III. Aluminum. Jour. Phys. Chem. 65: 826-829.

National Technical Advisory Committee. 1969. Raw water quality criteria for public supplies. Jour. Amer. Water Works Assoc. 61(3): 133-138.

Oldham, W. K., and E. F. Gloyna. 1969. Effect of colored organics on iron removal. Jour. Amer. Water Works Assoc. 61(11): 610-614.

Overbeck, J. 1952. Irreversible systems. In H. R. Kruyt [ed.] Colloid science. Elsevier Pub. Co., Huston. 352 p.

Packham, R. F. 1964. Studies of organic colour in natural water. Proc. Soc. Water Treat. Exam. 13: 316-334.

Pilipovich, J. A., A. P. Black, A. Eidsness, and T. W. Stearns. 1958. Electrophoretic studies of water coagulation. Jour. Amer. Water Works Assoc. 50: 1467-1482.

Poirrier, M. A., B. R. Bordelon, and J. L. Laseter. 1972. Adsorption and concentration of dissolved carbon-14 DDT by coloring colloids in surface waters. Environ. Sci. Tech. 6(12): 1033-1035.

Postma, H. 1967. Sediment transport and sedimentation in the estuarine environment. p. 158 to 179. In G. H. Lauff [ed.] Estuaries. Amer. Assoc. Adv. Sci., Washington, D. C.

Prakash, A., and M. A. Rashid. 1968. Influence of humic substances on the growth of marine phytoplankton: dinoflagellates. Limnol. Oceanogr. 13: 598-606.

Rainwater, F. H., and L. L. Thatcher. 1960. Methods for collection and analysis of water samples. U. S. Geol. Surv. Water Supply Paper 1454. 301 p.

Shapiro, J. 1957. Chemical and biological studies on the yellow organic acids of lake water. Limnol. Oceanogr. 3: 161-179.

__________. 1964. Effect of yellow organic acids on iron and other metals in water. Jour. Amer. Water Works Assoc. 56: 1062-1082.

Shriver, R. L., R. C. Fuson, and D. Y. Curtin. 1965. The systematic identification of organic compounds. John Wiley and Sons, Inc., New York. 458 p.

Sienko, M., and R. Plane. 1966. Chemistry: principle and properties. McGraw - Hill Co., New York. 623 p.

Stevenson, F. J. 1972. Structural chemistry of soil humic substances. No. 4.0106 (Abstr.). In E.P.A. [ed.] Research catalog for 1972, Part I. E.P.A., Washington, D. C.

Stumm, W., and J. Morgan. 1970. Aquatic chemistry. Wiley- Interscience, New York. 583 p.

Swain, F. 1963. Geochemistry of humus, p. 81 to 147. In I. Breger [ed.] Organic geochemistry. Macmillan Co., New York. 658 p.

Symons, J. M., S. R. Weibel, and G. G. Roberts. 1969. Water quality behavior in reservoirs. Public Health Service Pub. No. 1930: 322-326.

U, S. Geological Survey. 1965. Water resources data for Louisiana. Part 2. Water quality records. U. S. Dept. Int., Baton Rouge, La. 46 p.

Welch, P. S. 1948. Limnological methods. McGraw-Hill Co., New York. 381 p.

Yellow Springs Instrument Company. 1970. Instructions for Y.S.I. model 51A oxygen meter. Y.S.I. Co., Yellow Springs, Ohio. 27 p.

VITA

Billy Ray Bordelon was born on March 3, 1948 in New Orleans, Louisiana. He attended elementary school in St. Bernard Parish and graduated from Chalmette Senior High School in 1966. He attended Louisiana State University in New Orleans and received a Bachelor of Science Degree in Biology Education in May of 1970. In September, 1970 he entered the Graduate School of Louisiana State University in New Orleans and is presently a candidate for the degree of Master of Science in Biological Sciences.