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C.2THE pH OF WATER IN FLORIDA STREAMS
AND CANALSby
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UNITED STATES GEOLOGICAL SURVEY
in cooperation with the
BUREAU OF GEOLOGY
FLORIDA DEPARTMENT OF NATURAL RESOURCES
TALLAHASSEE, FLORIDA
1970

INTRODUCTION

A knowledge of the distribution and range of the fluctuation of pH in surface waters, from natural as well as man-influenced sources, is important to the understanding and management of the quality aspects of Florida's surface-water resources.

According to the Florida Statutes, 1969 (28-5.05 through 28-5.11), for those waters categorized under classes I-V, the pH shall not vary more than one unit above or below normal; and the lower value shall not be less than 6.0, and the upper value not more than 8.5. For those waters categorized under class V, the pH shall not be lower than 5.0 nor greater than 9.5 except certain swamp waters which may be as low as 4.5. Recognizing that certain waters of the State, due to natural causes, may not fall within desired or prescribed limitations, the Statutes provide for authorized exceptions upon presentation of good and sufficient evidence.

This report presents in a succinct and usable form information on the pH of streams and canals throughout Florida as an aid to water managers, users, and planners. The variations in pH are related to environmental causes.

The minimum pH of water and the range through which the pH of stream waters fluctuates in the various geographic areas (large map) is significant with respect to industrial, municipal, and recreational uses, aquatic productivity, the State of Florida's water quality standards, corrosivity, and selection of materials with regard to waterway structures such as culverts, in addition to governing the toxicity, mobility, and solubility of many compounds.

Florida's surface waters exhibit distinct regional variations in pH extremes, especially in regard to minimum values. Depending on environmental conditions, pH values in Florida waters range from less than 4.0 to greater than 8.5. Environmental controls such as surficial geology, the hydrologic flow system, soil types and vegetation, proximity to natural swamplands that are flushed by overland runoff, and industrial and agricultural effluents, among others, govern the pH. The map shows areas within which the minimum pH values of surface waters are about the same. The distribution pattern of these values provides insight into the hydrologic flow system and suggests certain environmental controls on water quality. This map is one step toward the portrayal of water quality data for Florida on a regional basis.

DEFINITION OF pH, SIGNIFICANCE, AND RECOMMENDED LIMITS

The pH of a solution is a measure of the hydrogen-ion activity and is expressed as the negative logarithm (base 10) of the effective hydrogen-ion concentration. The range of pH values from strong acids to strong bases is from 0 to 14. The pH of a neutral aqueous solution is 7. A change of one pH unit indicates a 10-fold change in the hydrogen-ion activity.

As noted by Mason (1952, p. 158-159), pH exerts a major influence on the mobility of many elements in the hydrosphere. Such factors as solubility, hydroxide precipitation, degree of complexation, and sorption of solutes by particulate matter may depend highly on pH (Lee and Hoadley, 1967). For example, the solubility of ferrous iron (Fe^{2+}) at pH 6 is about 10^5 times greater than at pH 8.5. In addition, as discussed by McKee and Wolf (1963, p. 235), the concentration of H^+ ions controls the degree of dissociation of many substances, and as the undissociated compounds are frequently more toxic than the ionic forms, pH may be a significant factor in determining limiting or threshold concentrations. For example, reduction of about 1.5 pH units can cause a thousand-fold increase in the acute toxicity of a metalocyanide complex, whereas the addition of strong alkalis may cause the formation of undissociated NH_4OH or unionized NH_3 in quantities that may be toxic (FWPCA, 1968, p. 41). Industrial wastes may be strongly acidic or basic and their effect upon the pH of the receiving waters depends largely on the buffering capacity of the receiving waters.

Waters with a pH below 6.0 can cause excessive corrosion in plumbing systems. Extremes in pH cannot usually be tolerated by industry; recommended values for industrial uses (process waters) normally range from 6.0 to 8.3. Recommended pH values for boiler feedwater range from 8.0 to 9.6, depending on pressure (McKee and Wolf, 1963, p. 235-236; Rainwater and Thatcher, 1960, p. 237). The pH of primary contact recreation waters should be within the range of 6.5 to 8.3 except when due to natural causes, and in no case should be less than 5 or more than 9 (FWPCA, 1968, p. 4). The hydrogen-ion concentration with co-dependence upon the buffer capacity of the water is of importance in relation to eye irritation among swimmers.

The availability of many nutrient substances varies markedly with pH, and the tolerance of fish to low concentrations of dissolved oxygen is greater with higher pH. The nonlethal limits of pH are narrower for some fish-food organisms than for fish. From the standpoint of aquatic productivity it is best to maintain the pH in the range of about 6.5 to 8.2 (McKee and Wolf, 1963, p. 236; FWPCA, 1968, p. 41).

NATURAL RANGES OF pH, AND ENVIRONMENTAL CONTROLS

The pH of a water results from (1) the balance of a series of chemical reactions, and (2) equilibria among the ions in solution, the most important of which involves the hydrolysis of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions (Hem, 1959, p. 44-46). Natural waters commonly contain dissolved carbon dioxide (CO_2) and HCO_3^- ions, which form a buffered system with carbonic acid (Davis and DeWiest, 1966, p. 76). The pH of a solution with high buffer capacity tends to remain relatively constant when small amounts of acid or base are added, whereas the pH of a solution of low buffer capacity may be subject to pronounced changes. Carbonate rocks abound in nature and therefore are a source of bicarbonate in many terrestrial waters. The resulting buffering system tends to neutralize acids and bases and thus reduces the range in fluctuations of pH.

In natural environments, pH ranges mostly from 4 to 9. The carbonic system (CO_2 , HCO_3^- , CO_3^{2-}) is the principal control of the pH of most natural waters and is effective at pH above about 5. "A saturated solution of CO_2 at its partial pressure in the atmosphere has a pH of 5.2, and a solution of calcite in air-saturated water has a pH near 8" (Mason, 1952, p. 158). The pH of an organic-rich environment, under aerobic conditions, would be that of a carbonic acid solution in equilibrium with CO_2 at one atmosphere, or about 4. In the presence of decaying vegetation, the pH could be a little lower because of CO_2 and organic acids produced during decomposition (Krauskopf, 1967, p. 314).

Lee and Hoadley (1967) note that large populations of aquatic organisms may markedly influence the pH as well as the buffer capacity of waters as a result of respiration and photosynthesis (i.e., diurnal variations caused by addition and removal of CO_2 from solution).

REGIONAL pH DISTRIBUTIONS, CHEMICAL ASSOCIATIONS, AND VARIATIONS WITH STREAMFLOW AND TIME

The large map shows the minimum pH of water and the range through which the pH of stream waters fluctuates in different areas of Florida. The color patterns show the lower limits of pH that prevail, and delineate areas in which stream waters exhibit similar ranges in pH. In general, the pH of the principal streams within the area of a given color fluctuates within the extremes indicated by that color.

Within each area the range of fluctuation in pH may be related to one or more environmental controls such as (1) geology (for example, carbonate versus non-carbonate terrane), (2) significant alkaline ground-water inflow, (3) drainage from natural swamplands, and (4) industrial and agricultural effluents. These relations are discussed in more detail below.

The pH values represent laboratory data for 10-day composite samples, plus daily and intermittent instantaneous samples (early 1940's through 1966, plus selected 1967 data). Laboratory values may, and probably in some cases do, differ from field values. Regional distribution patterns and placement of the boundaries between colored areas are of necessity generalized, and local variations may be expected to exist. Detailed data pertaining to pH values in each of the delineated areas are on file in the U. S. Geological Survey Water Quality Laboratory, Ocala, Florida.

Most natural waters with minimum pH of 4 to 5 (orange and yellow areas on the large map) are (1) upstream from the influences of significant alkaline (HCO_3^- -rich) ground-water inflow, (2) drain non-carbonate terranes, or (3) are affected by drainage from swamps, especially during periods of high flow. In general, low-pH waters have low specific conductance, low HCO_3^- ion concentration, are soft, highly colored (except in western Florida), and contain appreciable iron. They are sodium chloride in type, weakly buffered, potentially corrosive, and tend to be relatively unstable, exhibiting wide fluctuations in pH. The low pH is related to the low buffer capacity of these waters, which allows CO_2 and organic acids produced during decomposition of organic matter to have a large influence.

The tendency of some waters to fluctuate chemically in response to changes in discharge is exemplified by data for three north Florida rivers (figs. 1-3). In general, decreased pH values occur in conjunction with increased discharge. Figure 4 further illustrates this pH-discharge association. During periods of low flow, stream pH approaches that of the artesian Floridan Aquifer (median pH 7.7, with 90 percent of measured values falling between 7.4 and 8.0, for 17 Floridan Aquifer springs). During periods of high flow, the pH approaches that of a CO_2 - and organic-acid-rich environment (pH 4) where influence of alkaline ground-water inflow is negligible. Where alkaline ground-water inflow occurs in conjunction with high flow, the minimum pH usually stabilizes between 5 and 7.

Natural waters with pH ranging from 6 or 7 to 8.5 or above (blue and green areas on the large map) reflect the presence of areas where limestone crops out or are influenced by significant alkaline ground-water inflow. These waters have moderate to high specific conductance, hardness, and bicarbonate concentration, and are calcium bicarbonate in type. They are well buffered and tend to be relatively stable, with only minor fluctuations in pH. Diurnal variations in pH based on field measurements in several southeast Florida canals ranged from 7.3 to 7.8, attesting to the relative stability and high buffer capacity of these waters (C. B. Sherwood, U. S. Geological Survey, oral commun., 1969).

The significance of the carbonic system as the principal control of pH in many natural waters is illustrated (in part) in figure 5. A direct relation between pH and HCO_3^- over a wide range is indicated for three weakly buffered streams. The dense grouping of values for the Miami Canal indicates the relative stability of both pH and HCO_3^- in well-buffered high- HCO_3^- waters. For comparative purposes, the median pH vs. the median HCO_3^- concentration for 17 Floridan Aquifer springs is also plotted.

Downstream variations in pH and associated chemical characteristics (from orange to yellow to blue areas on the large map) for the Santa Fe River in north-central peninsular Florida are given in table 1. The downstream increase in pH, specific conductance and HCO_3^- ion concentration accompanied by decreased color illustrate the effect of proximity to swamps and of alkaline ground-water inflow, as discussed earlier.

Waters within the red areas on the large map are affected by acidic industrial or agricultural effluents. Depending on source, the waters of low pH are characterized by high specific conductance, sulfate (SO_4), phosphate (PO_4), iron (Fe), fluoride (F), or nitrate (NO_3). Many are calcium sulfate in type. Representative chemical characteristics of waters of differing pH are given in table 2, along with remarks concerning environmental influences such as streamflow, swamp drainage, alkaline ground-water inflow, and discharge of waste.

Curves showing the percentage of time that the pH has remained at or below a specific value in selected Florida surface waters are portrayed in figure 6. The St. Marys River typifies waters affected by acidic overland runoff and flushing of swamps. Analysis of four streams within the orange areas for the period of record indicates the pH ranged below 5.0 during 33 to 55 percent of the time, and below 4.5 during 7 to 27 percent of the time. The Alafia River, which receives acidic wastes, was below 5.0 during 27 percent of the time in 1965-66, but only 2 percent of the time in 1964-65. The relatively unstable Suwannee River reflects the mixture of acidic overland runoff or swamp drainage during high-flow periods and influent alkaline ground water during low-flow periods. The Yellow and Escambia Rivers do not receive a significant amount of such input, and thus their pH values are somewhat more stable. The St. Johns River illustrates the relatively well-buffered stability of large streams influenced by significant alkaline ground-water inflow, and the Miami Canal reflects the predominance of well-buffered alkaline ground water in southeast Florida.

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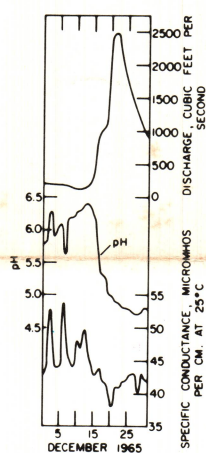


Figure 1. Relation of pH to specific conductance and streamflow, St. Marys River near Macclenny.

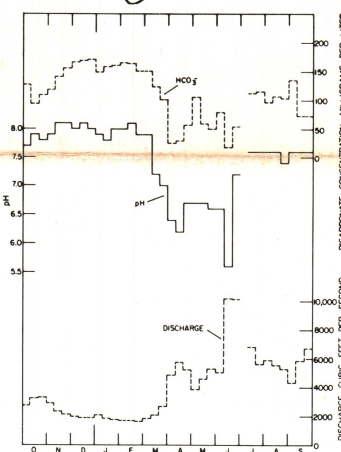


Figure 2. Variations of pH and HCO_3^- with discharge, Suwannee River near Branford.

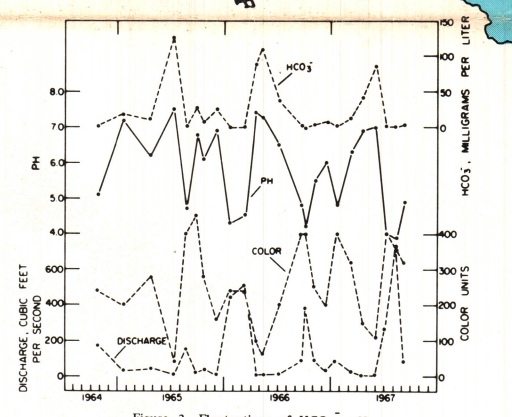


Figure 3. Fluctuations of HCO_3^- , pH, color and discharge, Sopchoppy River near Sopchoppy, 1964-67.

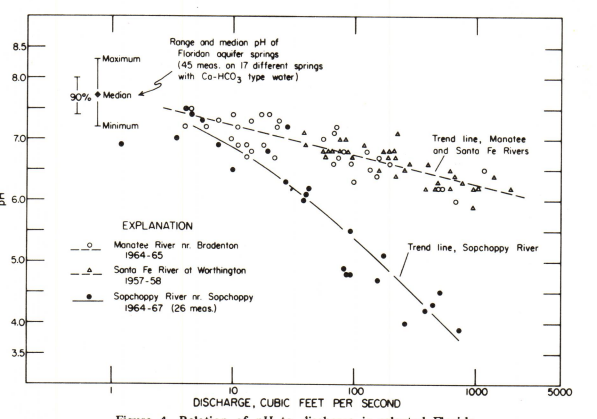


Figure 4. Relation of pH to discharge in selected Florida streams.

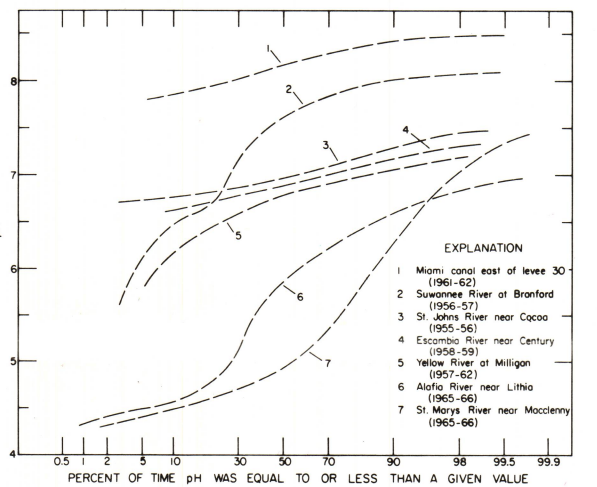


Figure 6. Frequency curves of pH in selected Florida streams and canals.

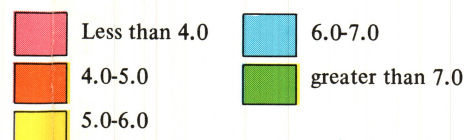
Table 2. Representative chemical characteristics of waters of differing pH

Stream or Canal	Date	Discharge (cfs)	pH	Bicarbonate (mg/l)	Sulfate (mg/l)	Spec. Cond. (microhm/cm at 25°C)	Color (Pt-Co units)	Chemical type	Remarks
North Prong Alafia R. at Mulberry	4-26-65	56	4.3	0	432	1,150	15	CaSO_4	Acidic industrial waste, high in SO_4 , PO_4 and Fe .
Indian Prairie Canal	11-28-56	---	3.7	0	316	777	100	CaSO_4	Agricultural drainage high in SO_4 , NO_3 and Fe .
Sopchoppy R. near Sopchoppy	8-14-67 6-8-65	734 4.1	3.9 7.5	0 127	1.6 2.4	43 215	360 40	NaCl CaHCO_3	Swamp drainage, high flow. Base flow, influenced by alkaline ground water.
St. Mary's R. near Macclenny	8-17-65 5-9-67	4,210 46.1	4.6 7.0	0 36	5.6 0.4	30 80	200 85	NaCl , SO_4 CaHCO_3	Swamp drainage, high flow. Base flow, influenced by alkaline ground water.
Suwannee R. near Branford	6/11/20/57 2/11/20/57	11,960 1,690	5.6 8.1	17 164	3.2 18	47 301	210 7	CaHCO_3 CaHCO_3	High flow. Base flow, influenced by alkaline ground water.
Silver Springs	2-3-64	681	7.7	200	51	428	5	CaHCO_3	Floridan Aquifer spring, high SO_4 .
Withlacoochee R. near Holder	5-29-62	150	7.7	148	34	328	10	CaHCO_3	Base flow, influenced by alkaline ground water.
West Palm Beach Canal at Canal Pt.	9-19-56	824	8.2	369	153	1,320	340	CaHCO_3	Agricultural drainage high in sodium (Na), SO_4 , Cl , and NO_3 .
Miami Canal East of Levee 30	11/1-10/64	331	8.4	232	0	492	60	CaHCO_3	Influenced by alkaline ground water.
Fenholloway R. at Foley	5-16-66	138	8.2	514	104	2,400	1,400	NaCl , HCO_3	Alkaline industrial waste high in Na , HCO_3 , Cl and SO_4 .

^a Reverse flow

EXPLANATION

Generalized areal distribution of minimum pH values of water in Florida streams and canals.



Maximum pH values in all areas are generally 8.0 to 8.5.

- Minimum of 4 yrs. Bimonthly, or at least 20 complete analyses, all flow conditions.
- Minimum of 2 yrs. Semiannual, or at least 5 complete analyses, all flow conditions.
- Annual, 1-4 complete analyses, generally represents low flow conditions.
- △ Daily specific conductance station, minimum record 1 yr.

Water Quality Data Stations, Florida streams and canals, U. S. Geological Survey, 1940-1966.

0 10 20 30 40 50 MILES

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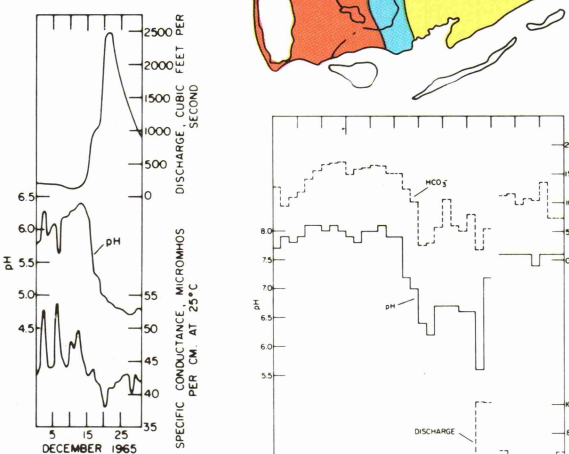


Figure 1. Relation of pH to specific conductance and streamflow, St. Marys River near Macclenny.

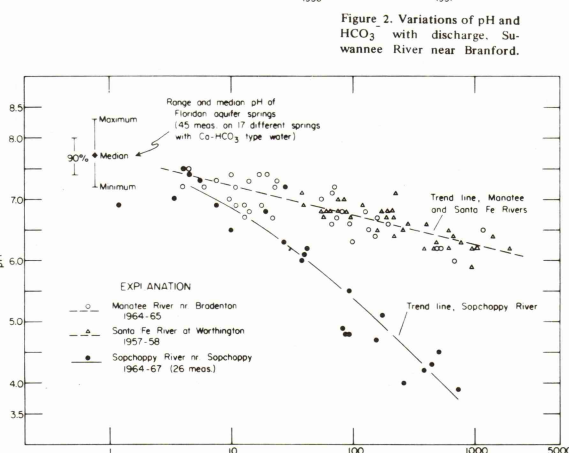


Figure 2. Variations of pH and HCO_3^- with discharge, Suwannee River near Branford.

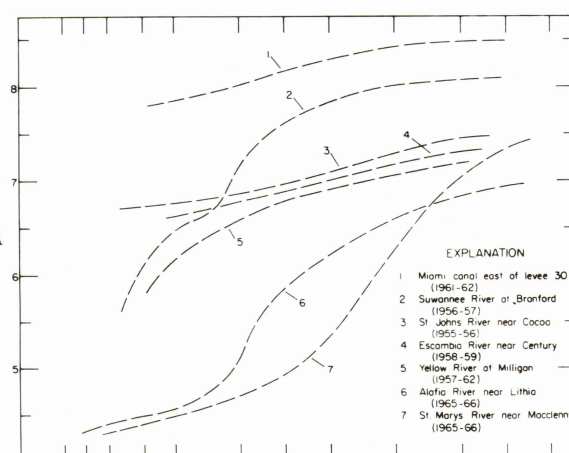


Figure 3. Fluctuations of HCO_3^- , pH, color and discharge, Sopchoppy River near Sopchoppy, 1964-67.

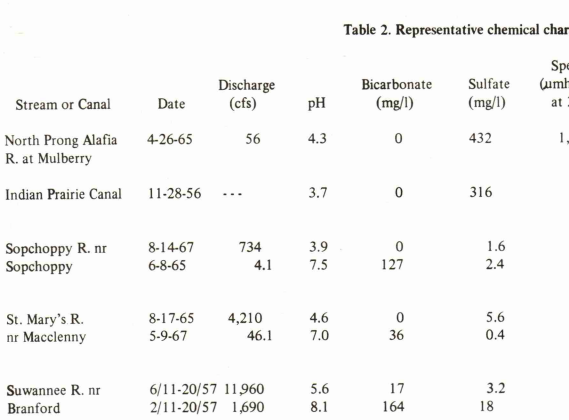


Figure 4. Relation of pH to discharge in selected Florida streams.

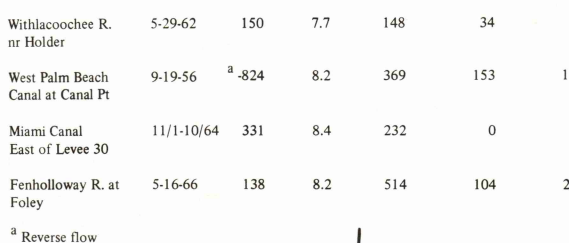


Figure 5. Frequency curves of pH in selected Florida streams and canals.

Table 2. Representative chemical characteristics of waters of differing pH

Stream or Canal	Date	Discharge (cfs)	pH	Bicarbonate (mg/l)	Sulfate (mg/l)	Spec. Cond. (micromhos per cm. at 25°C)	Color (Pt-Co units)	Chemical type	Remarks
North Prong Alafia R. at Mulberry	4-26-65	56	4.3	0	432	1,150	15	Ca-SO_4	Acidic industrial waste, high in SO_4 , PO_4 and F.
Indian Prairie Canal	11-28-56	---	3.7	0	316	777	100	Ca-SO_4	Agricultural drainage high in SO_4 , NO_3 and Fe.
Sopchoppy R. nr Sopchoppy	8-14-67 6-8-65	734 4.1	3.9 7.5	0 127	1.6 2.4	43 215	360 40	Na-Cl Ca-HCO_3	Swamp drainage, high flow. Base flow, influenced by alkaline ground water.
St. Mary's R. nr Macclenny	8-17-65 5-9-67	4,210 46.1	4.6 7.0	0 36	5.6 0.4	30 80	200 85	Na-Cl, SO_4 Ca-HCO_3	Swamp drainage, high flow. Base flow, influenced by alkaline ground water.
Suwannee R. nr Branford	6/11-20/57 2/11-20/57	11,960 1,690	5.6 8.1	17 164	3.2 18	47 301	210 7	Ca-HCO_3 Ca-HCO_3	High flow. Base flow, influenced by alkaline ground water.
Silver Springs	2-3-64	681	7.7	200	51	428	5	Ca-HCO_3	Floridan Aquifer spring, high SO_4
Withlacoochee R. nr Holder	5-29-62	150	7.7	148	34	328	10	Ca-HCO_3	Base flow, influenced by alkaline ground water.
West Palm Beach Canal at Canal Pt	9-19-56	824	8.2	369	153	1,320	340	Ca-HCO_3	Agricultural drainage high in sodium (Na), SO_4 , Cl, and NO_3 .
Miami Canal East of Levee 30	11/1-10/64	331	8.4	232	0	492	60	Ca-HCO_3	Influenced by alkaline ground water.
Fenholloway R. at Foley	5-16-66	138	8.2	514	104	2,400	1,400	Na-Cl, HCO_3	Alkaline industrial waste high in Na, HCO_3 , Cl and SO_4 .

^a Reverse flow

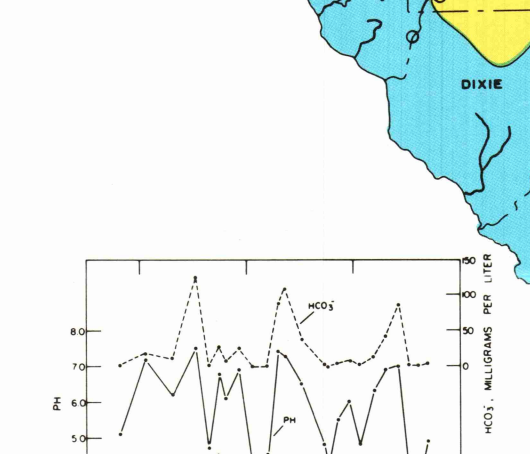


Figure 6. Frequency curves of pH in selected Florida streams and canals.

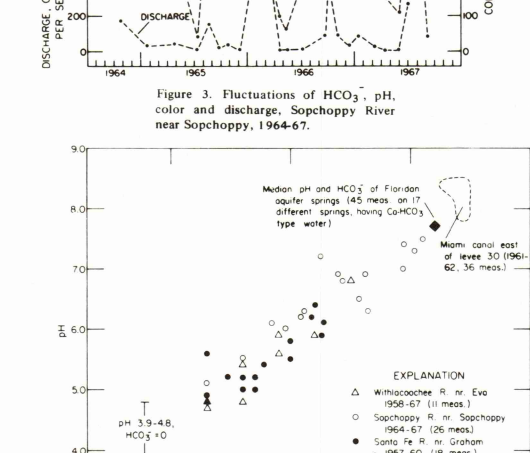


Figure 7. Relation of pH to HCO_3^- ion concentration in selected Florida streams and canals.

Station	Period of record used	Median pH	Range	HCO_3^- (mg/l)	HCO_3^- (micromhos per cm. at 25°C)	Color (Pt-Co units)	Remarks
Near Graham	1957-60	5.3	4.4-6.4	5 ^a	57	265	Swamp drainage, upper reach of river.
At Worthington	1959-60	6.4	5.9-7.4	20	77	160	Mostly swamp drainage during high flow, alkaline ground-water inflow during low-flow.
Near High Springs	1959-60	7.4	6.4-8.3	100	247	100	Lower reach of river, influenced by alkaline ground-water inflow from artesian springs.

^a Median

[†] Time-Weighted Average

EXPLANATION

Generalized areal distribution of minimum pH values of water in Florida streams and canals.

- Less than 4.0
- 4.0-5.0
- 5.0-6.0
- 6.0-7.0
- greater than 7.0

Maximum pH values in all areas are generally 8.0 to 8.5.

- Minimum of 4 yrs. Bimonthly, or at least 20 complete analyses, all flow conditions.
- Minimum of 2 yrs. Semiannual, or at least 5 complete analyses, all flow conditions.
- Annual, 1-4 complete analyses, generally represents low flow conditions.
- Daily specific conductance station, minimum record 1 yr.

Water Quality Data Stations, Florida streams and canals, U. S. Geological Survey, 1940-1966.

0 10 20 30 40 50 MILES