STATE OF FLORIDA
STATE BOARD OF CONSERVATION
DIVISION OF GEOLOGY

FLORIDA GEOLOGICAL SURVEY
Robert O. Vernon, *Director*

REPORT OF INVESTIGATIONS NO. 46

FLUORIDE IN WATER IN THE ALAFIA AND PEACE RIVER BASINS, FLORIDA

By
L. G. Toler

Prepared by the
UNITED STATES GEOLOGICAL SURVEY
in cooperation with the
SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT
and the
FLORIDA GEOLOGICAL SURVEY

TALLAHASSEE, FLORIDA
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LETTER OF TRANSMITTAL

Florida Geological Survey

TALLAHASSEE

April 27, 1967

Honorable Claude R. Kirk, Jr., *Chairman*
Florida State Board of Conservation
Tallahassee, Florida

Dear Governor Kirk:

The Division of Geology of the Florida Board of Conservation is publishing, as Report of Investigations No. 46, a study of the quality of water as found in the Alafia and Peace River Basins, Florida. The report, entitled "Fluoride in Water in the Alafia and Peace River Basins, Florida," was prepared by L. G. Toler, of the U.S. Geological Survey, in cooperation with the Southwest Florida Water Management District and the Division of Geology.

You will recognize that waste water from phosphate chemical plants in the tributary headquarters of these two basins contribute waste products, including fluorides, to the river water. Fluoride concentrations range from 3.2 to 30 parts per million in the Alafia River, and .6 to 2.2 parts per million in the Peace River. While the concentration in the Peace River is probably beneficial, that contained in the Alafia River is excessive for human consumption.

It is hoped that a detailed investigation of some of the plant operations and settling lagoons will establish the geologic and hydrologic conditions necessary to control these wastes more effectively.

Respectfully yours,
Robert O. Vernon
Director and State Geologist

Completed manuscript received
April 27, 1967
Published for the Florida Geological Survey
By St. Petersburg Printing Company
St. Petersburg, Florida

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FLUORIDE IN WATER IN THE ALAFIA AND PEACE RIVER BASINS, FLORIDA

By
L. G. Toler

ABSTRACT

Waste water from phosphate chemical plants in the tributary headwater areas contributes fluoride and other waste products to the Alafia and Peace rivers.

The fluoride concentration of the Alafia River at Lithia, Florida, ranged from 3.2 to 30 ppm (parts per million) and the Peace River at Arcadia, Florida, ranged from 0.6 to 2.2 ppm in samples of water collected daily from October 1964 to September 1965. The natural fluoride concentration in streams in the Alafia and Peace River basins generally ranged from 0.2 to 0.4 ppm as determined from analysis of water from streams away from the active areas of mining and processing of fluoride-bearing phosphatic minerals.

Most of the waste water from the phosphate chemical plants is routed to lagoons (gypsum ponds) where the solids settle out and the water circulates for reuse. High concentrations of fluoride and phosphate in samples of surface water at sites downstream from the phosphate chemical plants indicate that some waste water enters the streams continuously. Analysis of the relation between concentration of fluoride, dissolved fluoride load, and discharge of the streams suggests that much more waste water is released to the streams during periods of high discharge than during periods of low discharge. Overflow of the settling lagoons, flushing of naturally ponded water from flat headwater areas or controlled release of water of high fluoride content during periods of high discharge could account for the observed relations.

Fluoride in waste water has apparently not entered the ground in sufficient quantity to cause widespread increases in the concentration of fluoride in ground water. Fluoride does occur naturally in ground water and ranges from 0.0 to about 4.0 ppm. The concentration of fluoride in ground water is highest in water from the Hawthorn Formation and Tampa Formation of Miocene age. The fluoride apparently dissolves from the fluoride-bearing phosphatic minerals in the rocks.

The areal approach used in this investigation did not resolve whether contamination of ground water by fluoride occurs locally. The greatest potential hazard to ground water appears to be the chemical plant settling lagoons.

Predictions of the zonal pattern of a fluoride contaminant in the ground requires a knowledge of the ground-water flow patterns and the effects of any chemical reactions between the fluoride and the water and rocks in the ground. A detailed investigation of one or more of the chemical plant settling lagoons is desirable to establish the geologic-hydrologic conditions and ground-water flow patterns in the vicinity of the lagoons. The chemical reactions between water of high fluoride content and water in a limestone aquifer need investigation.

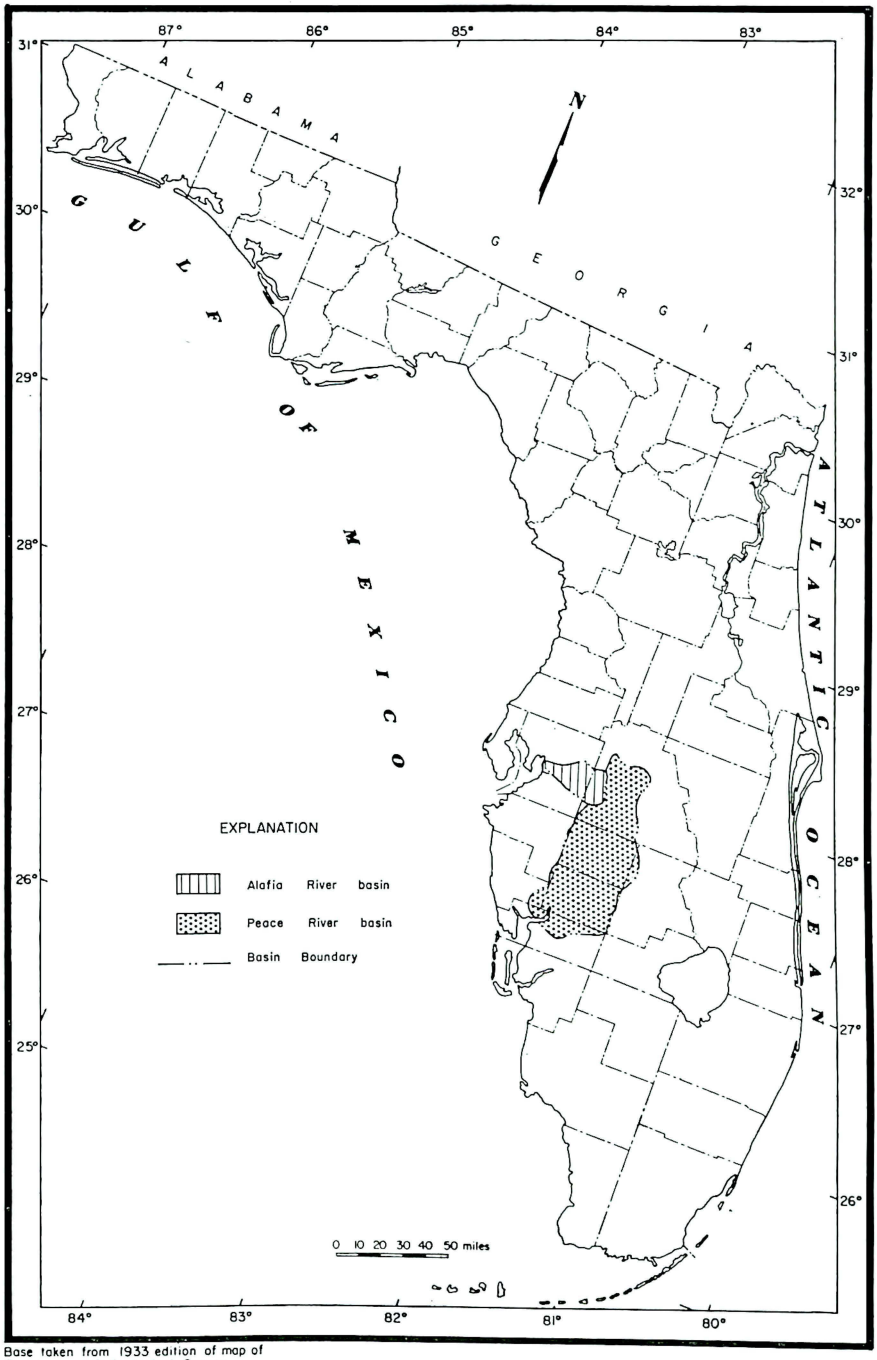
INTRODUCTION

PURPOSE AND SCOPE

The use of the Peace and Alafia rivers to dispose of phosphate and other wastes has caused local and statewide concern about contamination of the river water. Recently, this concern has been expanded to include the possible effects on ground-water supplies, should the contaminants enter the ground and mix with the fresh water. This report is a product of an investigation with the general objectives of appraising the problem of contamination and evaluating the need for additional investigations. The specific objectives of this report are to determine to what degree, if any, ground-water contamination has occurred; evaluate the effects of fluoride from phosphate mining and processing on ground water; determine the quantity of selected constituents being wasted to the streams; examine the effect of these constituents on the quality of water in the streams; and determine some system of monitoring wastes in streams and ground-water supplies.

DESCRIPTION OF THE AREA

The Alafia and Peace rivers both have their headwaters in Polk County, Florida. They have a combined drainage area of 2,820 square miles and discharge an average total of about 1,500 million gallons of water per day to the Gulf of Mexico. The locations of the basins within the state are shown in figure 1. Figure 2 shows the drainage patterns of the streams and the political boundaries of the Peace and Alafia River Basins Boards. The political boundary of the Alafia Basin Board (fig. 2) encompasses the drainage area of the Alafia River and part of the Little Manatee River. Drainage areas and a summary of flow statistics are included in table 1. For the Peace River the political boundary closely approximates the natural drainage divide. In the headwater area, the drainage divide is not always well defined but may be in flat swampy areas where the direction of flow is governed



Base taken from 1933 edition of map of Florida by U S Geological Survey

Figure 1.—Location of the Alafia and Peace River basins.

by the amount of rainfall on different parts of the area. South of Bartow, the main stem of the Peace River has a well-defined channel. Drainage is dendritic except where altered by strip mining for phosphate. The river flows southward from Polk County through Hardee and DeSoto counties and into Charlotte Harbor in Charlotte County.

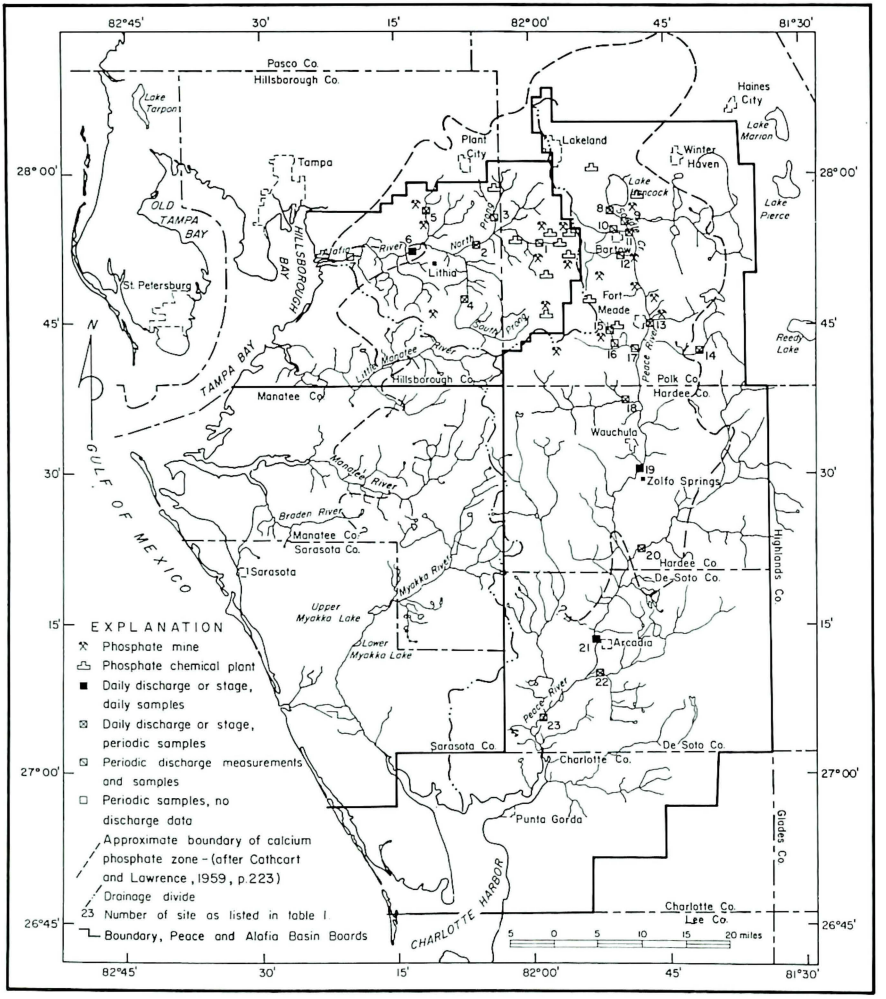


Figure 2.—Location of sampling sites on streams and area of phosphate mining and processing.

The U.S. Geological Survey has maintained gaging stations on the main stem of the Peace River at Bartow for 26 years, at Zolfo Springs for 32 years, and at Arcadia for 34 years prior to September 1965.

TABLE 1.—Sampling sites, drainage areas, and discharge data for streams.
I — discharge measurements made at time sample collected.
P — periodic, about 8 times per year.
D —daily.
Dates refer to water year ending September 30

Number	Station name	Drainage area square miles	Discharge record began	Average Discharge cfs	Frequency of sampling 1964-1966
	ALAFIA RIVER BASIN				
1.	North Prong Alafia River at Mulberry		1964 I		P
2.	North Prong Alafia River at Keysville	135	1950	185	P
3.	English Creek near Mulberry		1964 I		P
4.	South Prong Alafia River near Lithia	107	1962	109	P
5.	Turkey Creek near Durant	15	1964		P
6.	Alafia River at Lithia	335	1933	385	D
7.	Alafia River at Riverview		None		P
	PEACE RIVER BASIN				
8.	Saddle Creek at Structure P-11	135	1964		P
9.	Saddle Creek near Bartow		None		P
10.	McKinney Branch near Bartow		1964 I		P
11.	Peace River at Bartow	390	1939	313	P 1965 D 1966
12.	Sixmile Creek near Bartow		1964 I		P
13.	Peace River at Fort Meade	465	1964	Stage only	P 1965 D 1966
14.	Bowlegs Creek near Fort Meade	47	1964		P
15.	Mill Branch tributary		1964 I		P
16.	Mill Branch near Fort Meade		1964 I		P
17.	Whidden Creek near Fort Meade		1964 I		P
18.	Paynes Creek near Bowling Green	121	1964	111	P
19.	Peace River at Zolfo Springs	826	1933	772	D
20.	Charlie Creek near Gardner	330	1950	335	P
21.	Peace River at Arcadia	1,367	1931	1,280	D
22.	Joshua Creek at Nocatee	132	1950	121	P
23.	Peace River at Fort Ogden	1,790	1964	Stage only	P

Table 1 summarizes the streamflow data for the basin. Total drainage area of the basin is about 2,400 square miles.

The Alafia River has the headwaters of its major tributaries, the North and South Prongs, in the phosphate mining area of western Polk County. These tributaries merge in eastern Hillsborough County to form the Alafia River which flows westward into Hillsborough Bay.

Phosphate mining began in southwest Florida with the dredging of river pebble deposits along the Peace River in the late 1800's. Several periods of prosperity and depression have governed the rate of development of the phosphate deposits. In the years following World War II, the demand for phosphate and phosphate products has continually been on the upswing and the industry has flourished accordingly. The Alafia and Peace rivers are the only streams that drain the area of phosphate mining and they have received waste from the industry.

Most of the waste products from the mining and processing of phosphate rock do not reach the streams. The solid waste is retained in settling lagoons and the clear water circulated for reuse. Nevertheless, a significant amount of waste water enters the streams, either

directly or from overflow of the settling lagoons. The character of the water in the settling lagoons depends on the source of the waste water. Water from the mining operations is essentially sediment-laden waste water and is not of bad chemical quality. Water from the phosphate processing plants, however, may be of poor chemical quality. These waste waters, which contain high concentrations of inorganic chemicals acquired during the processing, have entered the streams in sufficient quantities to cause water in some of the streams to be unfit for some uses. In recent years, the increase in mining activity and the increase in the number of chemical plants have increased the volume of waste products dissipated to the streams.

The investigation was conducted by the U.S. Geological Survey in cooperation with the Alafia and Peace River Basin Boards of the Southwest Florida Water Management District as a part of the cooperative program to evaluate the water resources of Florida with the Florida Geological Survey, Division of Geology, Florida Board of Conservation. The investigation was performed under the general direction of C. S. Conover, District Chief, Water Resources Division, U.S. Geological Survey.

PREVIOUS WORK

The Florida State Board of Health (1955a) reported the first complaint about turbidity in the Alafia River from a resident at Riverview in 1946. Subsequent investigations by various organizations, generally sponsored by the phosphate companies, have resulted in a number of reports on pollution of the rivers and recommendations for minimizing pollution of the water.

Specht (1950) concluded the clear effluent from phosphate processing was not deleterious to fish life. His work included experiments with electrolytes to flocculate the colloidal phosphate slimes and reduce the turbidity of effluent to the streams.

The Florida State Board of Health (1955a, 1955b) reported on the results of investigations of the Peace and Alafia rivers during the period 1950 to 1953. They recognize three major sources of pollution in the Peace River; municipal and domestic sewage, the citrus processing industry, and the phosphate mining and processing industry. They divide the Peace River into two segments based on type and intensity of pollution. The segment north of Homeland (about 5 miles south of Bartow) was considered excessively polluted by organic and chemical pollutants and the segment south of Homeland suffered only from intermittent excessive inorganic turbidity and slime.

Two major sources of pollution considered by the Florida State Board of Health (1955b) for the Alafia River were domestic sewage from cities and towns and the waste products from the phosphate operations.

From 1953 to 1955 the major concern of the State Board of Health about waste products from the phosphate industry was the turbidity and slime from mining and washing operations of the phosphate ore. The waste products from the phosphate processing plants were only beginning to be a major source of pollution, especially in the Alafia River basin. They recommended waste disposal be controlled so that the pH of the rivers not be reduced below 5.0 and the concentration of fluoride not exceed 5.0 ppm.

Lanquist (1955), as a part of the investigation by the State Board of Health, made a biological survey of the Peace River. His conclusion number 4 (p. 67) states that, "at times the effects of acid water from the phosphatic fertilizer plant at Bartow produced near-sterile conditions in Bear Branch, adversely affected the water-hyacinths and fauna in the Peace River at Bartow and possibly affected the Crustacea at P-11."

Specht (1960) described the mining of phosphate ore and processing of the phosphate minerals to superphosphate, triple superphosphate and elemental phosphorous. He also describes the methods employed by the industry to reduce the turbidity, acidity, and fluoride content of waste water discharged to the streams.

In preparing a basic plan for development of the water resources of the Peace and Alafia rivers, Johnson (1960, 1963) recognized the need for control of pollution of the rivers. He (1963. p.ii.) noted an increase in the number of major phosphate chemical plants since the survey by the State Board of Health in 1953 and presented data collected by the State Board of Health (1963, p. I-16, I-18) to show an increase in acidity and fluoride content of the Alafia River during the ten-year interval.

Menke, Meredith, and Wetterhall, (1961) conducted an investigation of the water resources of Hillsborough County from 1956 to 1958. Graphical presentations of fluoride and pH of the Alafia River at Lithia for the period October 1957 to September 1958 show the fluoride concentration as high as 17 ppm but below the 5.0 ppm maximum set by the State Board of Health about 65 percent of the time. The pH during this period ranged from 5.5 to 6.7. They did not report on fluoride in ground water but warned that: "Extensive use of Alafia River

waters for irrigation could result in contamination of ground-water supplies hydraulically connected downgradient from the irrigated land."

Woodard (1964) in a preliminary report on the geology and ground-water resources of Hardee and DeSoto counties reported on the occurrence of fluoride in ground water in south peninsular Florida and suggests that the geographic spread is controlled by the hydrology of the area. The possibility is presented that the source of fluoride is the phosphatic sediments of Miocene age and that the high fluorides are confined to the upper part of the Floridan aquifer. In referring to the piezometric surface of the Floridan aquifer, Woodard stated: "The high pressure areas north and east of the phosphate deposits would cause the fluorides entering the aquifer to move to the south and west." He found no evidence which pointed to contamination of ground water by the phosphate processing industry.

Shattles (1965) mapped with distribution of dissolved solids and selected constituents in the Floridan aquifer in Hillsborough County. He shows an increase in all constituents from the interior toward the coast. Fluoride was not mapped though the fluoride content of water from 25 of 28 wells sampled was below 0.8 ppm.

PHOSPHATE MINING AND PROCESSING

In the early days of phosphate mining on the Peace River only the coarse phosphate pebbles were recovered by screening and the fine material was wasted back to the stream. Later the discovery of "land pebble" phosphate deposits that could be removed by strip-mining methods moved the mining operations away from the river.

The "land pebble" phosphate deposits are located in a shield-shaped area that covers large parts of Polk, Hillsborough, Hardee, and Manatee counties and extends into Sarasota and DeSoto counties as shown in figure 2. Most of the large mining operations are currently in Polk and Hillsborough counties.

Advances in technology, which made it possible to remove thick over-burdened deposits and to mine the phosphate ore below the water table, and greater demand for phosphate opened large areas as economic phosphate deposits. Improved methods of recovery, especially the introduction of the flotation process to recover fine-grained phosphate, greatly aided the growth of the phosphate industry.

The phosphate is mined by first removing the overburden, which is as much as 60 feet thick, with large capacity draglines. The underlying phosphate ore may be from 5 to 50 feet thick and consists of a mixture of phosphate pebbles and granules, cobbles and boulders of phosphatized limestone, quartz sand and silt, and clay.

The phosphate ore is then deposited, by the dragline, into a shallow pit from where it is sluiced to a pump through a four-inch grizzly. The slurry formed by the sluicing operation is then pumped to the washer which may be several miles from the mine. This pumping operation requires large quantities of water which help to disaggregate the ore but which must be separated during the washer operation and disposed of or recycled.

The slurry from the mine goes through two processes to separate the phosphate from the matrix. A combination of washing, scrubbing, and screening separates the pebble phosphate larger than about one millimeter from the fine grained matrix. The pebble phosphate is then ready for shipment or chemical processing. The smaller material is then separated by flotation. In the flotation cells the fine material is treated to cause the phosphate particles to float off in an oily froth. Reagents used are caustic soda, fuel oil, and a mixture of fatty and resin acids. Some quartz sand is floated in this process and in a second flotation cell the phosphate is selectively depressed by use of an amine.

From the washing and flotation plants the water which still carries the waste material from each stage of the process is pumped to large settling areas. After the solids have settled the water may be reused in the mining operation. Some of this water may be wasted to streams, especially during the rainy season (Specht 1960). Because most of the reagents used in the flotation process adhere to the minerals (State Board of Health, 1955a, 1955b), the reagents probably are not a serious source of stream pollutants.

From the screening and flotation plants, the phosphate minerals may be marketed directly or transported to the chemical plants for further processing. The details of chemical processing of phosphate rock and the products obtained vary according to the plant and the nature of the product obtained. Some generalization about the process may be made which is pertinent to water pollution by chemical plant effluent.

The processes of converting the phosphate minerals into a form more readily available as plant nutrients require acidification of the phosphate mineral. Subsequently, some of the fluorides are released. For making superphosphate, phosphate rock is treated with sulfuric acid to form a monocalcium phosphate fertilizer. Silicon tetrafluoride, carbon dioxide, and fluorosilisic acid are other products of the reaction.

Triple superphosphate is produced by allowing the above reaction

to go to completion to form phosphoric acid which is used to treat more phosphate rock to form the triple superphosphate.

The two part reaction may be generalized as follows:

(1) $Ca_5(PO_4)_3F + 5H_2SO_4 = 3H_3PO_4 + 5CaSO_4 + HF$

Phosphate rock; Sulfuric acid; Phosphoric acid; Gypsum; Acid fluoride

(2) $Ca_5(PO_4)_3F + 7H_3PO_4 = 5Ca(H_2PO_4)_2 + HF$

Phosphate rock; Phosphoric acid; Monocalcium phosphate; Acid fluoride

The gypsum, precipitated in the first reaction, is separated from the phosphoric acid by vacuum filtration, washed and wasted to a settling lagoon where it may settle. The water is returned to the plant for reuse. Owing to silica and carbonate impurities, carbon dioxide and silicon tetrafluoride are evolved as gases. A complex system of multiple scrubbing, washing and evaporating removes and concentrates the fluorides as fluorosilisic acid which is recovered.

Water waste from the scrubbing process may go to the settling lagoons or to the streams. During rainy seasons some water may overflow from the settling lagoons and thus enter the streams. Considerable water containing high fluoride and phosphate enters the streams as evidenced by analyses of water from many locations downstream from the processing plants.

SIGNIFICANCE OF FLUORIDE AND ASSOCIATED WASTE PRODUCTS IN WATER

FLUORIDE

The effect of fluoride in drinking water has been the subject of intense investigations since 1931 when endemic mottled enamel in teeth was recognized as being associated with drinking water containing fluoride. Later investigations showed that small amounts of fluoride could prevent dental caries without the mottled enamel effect.

The U.S. Public Health Service (1962a) compiled 142 papers written by Public Health personnel prior to 1962 into one volume which describe dental fluorosis and dental caries and the physiological effects, analysis, and chemistry of fluoride. The results of many investigations by the Public Health Service have resulted in the adoption of standards of optimum concentrations of fluoride in drinking water on interstate carriers and which serve as a guide for others interested in maintaining

good, safe water supplies. According to the U.S. Public Health Service (1962b) the optimum fluoride level in drinking water in a given community depends on climatic conditions because the amount of water consumed by an individual is primarily influenced by air temperatures. The following table is taken from the U.S. Public Health Service (1962b, p. 8).

Annual average of maximum daily air temperatures °F	Recommended control limits—Fluoride concentrations in mg/l		
	Lower	Optimum	Upper
50.0 - 53.7	0.9	1.2	1.7
53.8 - 58.3	0.8	1.1	1.5
58.4 - 63.8	0.8	1.0	1.3
63.9 - 70.6	0.7	0.9	1.2
70.7 - 79.2	0.7	0.8	1.0
79.3 - 90.5	0.6	0.7	0.8

Water supplies subject to Federal quarantine regulations are subject to rejection when the fluoride concentration is greater than two times the optimum concentration.

These optimum concentrations of fluoride in drinking water are considered effective in preventing mottled enamel and caries in the teeth of children during the period of tooth development. McKee and Wolf (1963) report that concentrations of fluoride of 3 or 4 ppm are not likely to cause endemic cumulative fluorosis and skeletal effects in adults. Concentrations of 8 to 20 ppm, when consumed over a long period of time may cause some skeletal effects in adults.

McKee and Wolf (1963) have also summarized the reported effects of fluoride in water on stock and wildlife, fish and other aquatic life, and industrial uses. They report (p. 191) that the effects of fluoride in drinking water for animals are analogous to those for humans, but that fluoride ions appear to have direct toxic properties towards aquatic life. They summarize the available information with the following table of concentrations of fluoride that will not interfere with specified beneficial uses:

a. Domestic water supply	0.7 to 1.2 ppm
b. Industrial water supply	1.0 ppm
c. Irrigation water	10.0 ppm
d. Stock watering	1.0 ppm
e. Aquatic life	1.5 ppm

PHOSPHATE

Phosphates may occur in water from leaching of phosphatic minerals, agricultural drainage, decomposition of organic matter, sewage,

industrial wastes or cooling waters that have undergone phosphate treatment (McKee and Wolf, 1963, p. 240).

Usually, these sources contribute only minor amounts of phosphate to natural waters and probably have little physiological significance; however, they serve as a nutrient for growth of algae which is undesirable.

McKee and Wolf (1963, p. 240-241) summarize the work of other investigators on the effects of phosphate in water. Their summary includes effects on:

a. Domestic water supplies. Polyphosphates are used to prevent scale formation and corrosion. In raw water sources, polyphosphates interfere with coagulation, flocculation, and the lime soda treatment of water.

b. Irrigation. Phosphate in irrigation water may help increase the fertility of soil moisture; however, experiments with blueberry plants showed that 60 ppm may reduce the availability of inorganic iron and be detrimental.

c. Fish and aquatic life. Phosphates in streams and lakes may result in overabundant growth of algae with concomitant odors and detriment to fish. Phosphates are usually not toxic and may be beneficial to fish by increasing algae and zooplankton.

d. Industrial water. Phosphates may be beneficial by preventing scale formation and corrosion; however, they may encourage biological growth and be detrimental.

Phosphate in ground water is relatively rare. Small amounts may be present from the above sources; however, most phosphate is probably redeposited from ground water in the form of calcium, iron, and aluminum phosphate.

pH

The pH of water is a measure of the acidity of water. A pH of 7 is considered neutral, below 7 is acid and above 7 is basic. Waters that have a low pH tend to be corrosive to metal and concrete and are usually undesirable for domestic supplies. Water with a pH of about 4.0 may taste sour.

McKee and Wolf (1963, p. 236) summarize numerous investigations on the effect of pH on fish. Ranges of several pH units can be tolerated by most species; however, the range may depend on other factors, such as temperature, dissolved oxygen, prior acclimatization, and the content of other dissolved material.

TURBIDITY

Turbidity is an optical property of water that contains suspended and colloidal matter. This suspended material reduces light penetration into the water as a function of both the concentration and particle size of the material. Turbidity is reported as parts per million and is equivalent to the turbidity of standard solutions of silica.

Turbidity in streams may be caused by micro-organisms, organic detritus, silica, clay, or silt or any suspended material and may result from natural processes or domestic and industrial effluent.

The U.S. Public Health Service (1962b, p. 6) recommends that turbidity in drinking water should not exceed 5 ppm. McKee and Wolf (1963, p. 290) state that turbidity is generally undesirable for most industrial uses of water. They give recommended limiting values of turbidity for many industrial uses ranging from 1.0 to 100 ppm.

Turbidity in water may affect fish by reducing photosynthetic action and decreasing the productivity of fish-food organisms or by modifying the temperature structure of bodies of water. Turbid water is considered less productive for fish than is clear water; however, several hundred ppm turbidity have not been found lethal to fish (McKee and Wolf, 1963, p. 291).

GEOCHEMISTRY OF FLUORINE

Fluorine is a minor constituent in the rocks forming the earth's crust. Many minerals contain fluorine in minor amounts in complex mineral systems. The most important of these relative to the Alafia and Peace River Basin areas are the apatite group of minerals that are primarily calcium phosphate and vary according to the amount of fluoride, chloride, hydroxyl, and carbonate they contain. Fluorapatite has the general formula $Ca_5(PO_4)_3F$ and contains 3.8 percent fluoride. Chloride or the hydroxyl ion commonly substitutes for fluoride.

In Florida, the only rocks on or near the surface are sedimentary rocks. Barraclough (1962, p. 24) reported glauconite, phosphate, and muscovite (mica) in the sedimentary rocks in west Florida. Mica was reported to be especially abundant. The author has found minor amounts of fluoride in insoluble residues of limestone well cuttings from Sumter County in peninsular Florida.

The apatite group of minerals (phosphate rock) occur in the rocks in many areas in Florida. Where found, the amount varies from a few scattered grains to large minable deposits. The phosphate rock mined in the Alafia and Peace River basins is primarily fluorapatite.

Fluoride is usually one of the minor constituents of dissolved mate-

rial in natural water. Hem (1959) reported concentrations of fluoride in natural water may be 50 parts per million or more, but that concentrations of over 10 ppm are rare and surface waters rarely contain more than 1.0 ppm.

SURFACE WATER

The Peace and Alafia rivers have been described with respect to inorganic chemical contaminants by previous investigators. The conditions causing excessive inorganic pollution have been established (Florida State Board of Health, 1955a, 1955b) and recommendations made which give limits in terms of concentrations that certain constituents in river water should not exceed.

The Florida State Board of Health (1955b, p. 9) recommended that the waters of the Peace River basin should be maintained so that the following limits are not exceeded:

Dissolved Oxygen—not less than 3.5 ppm at all points.

Turbidity—not more than 100-200 ppm provided the duration is short. For continuing waste discharge, the resultant turbidity should not exceed 50 ppm.

Settleable solids—not more than .05 milliliters per liter.

pH—over 5.0 and under 8.5

Fluoride—not more than 5.0 ppm

Their recommendations for the Alafia River are the same (Florida State Board of Health, 1955a, p. 8) except for turbidity for which a recommended limit of 100 ppm is given.

A program of sampling and analysis of stream water was established as a part of the present investigation to define the ranges in concentration of chemical constituents, to define the sources and character of the chemical constituents, and to evaluate changes in concentrations from those conditions described by previous investigators. Particular attention was given to the fluoride and phosphate content of the streams.

Three sites were selected at the start of the investigation for sampling on a daily basis. Daily samples from each of the sites were analyzed for specific conductance, pH, turbidity, phosphate and fluoride.

A reconnaissance of the basin was made early in the investigation during which water samples were collected at 48 stream sites and analyses made for specific conductance, phosphate and fluoride. From these analyses, 23 sites were selected for periodic sampling and analysis. Of this number 14 were at gaging stations and 7 were at sites where discharge measurements were made at the time of sampling. Samples were collected at approximately six-week intervals. Figure 2 shows

the location of all stream sampling sites and the sites are identified in table 1.

Seven sites were selected on the Alafia River and its tributaries for periodic sampling for chemical analysis. Four of the sites are at gaging stations. The chemical analyses from all these sites are published in annual reports by the U.S. Geological Survey.

The stream-gaging site on the Alafia River at Lithia was selected for daily sampling because it is downstream from most of the phosphate mining operations, records of discharge for the river are available at this site, and earlier records of chemical analyses are available (Menke, Meredith, and Wetterhall, 1961).

Menke, Meredith and Wetterhall (1961) reported on a 2-year sampling program of the Alafia River at Lithia from October 1956 to September 1958. Their frequency curves for chemical constituents for one year, October 1957 to September 1958, are replotted with frequency curves for October 1964 to September 1965 in figures 3 and 4. The frequency curves for specific conductance (fig. 3) for both periods were prepared from measurements of daily samples and equally indicate conditions during each of these periods. The frequency curves for pH and concentrations of fluoride and phosphate were prepared from measurements made on daily samples for the 1965-66 period but for the 1957-58 period, they were prepared from measurements made on composite samples from 10 daily samples. The measurements represented an average for the 10-day period.

Frequency curves constructed by each of the two methods should give similar values at the 50 percent frequency; however, the greater number of measurements when daily samples are analyzed individually will give a wider range of values than will the measurements of the average composite sample by ten-day periods. The two curves should cross at about the 50 percent frequency and the curve prepared from the measurements of composite samples should be flatter than the one constructed from the daily measurements. Comparing the two curves for each constituent gives an indication of the changes in water quality since 1957-58.

The specific conductance of a water is a measure of the capacity of the water to conduct electricity. Pure water is a poor conductor of electricity; however, if water contains materials that ionize in solution, the capacity of the water to conduct electricity increases proportional to the ionization of material in solution. The proportionality factor will vary according to the type of material that is dissolved in the water. Menke, Meredith and Wetterhall (1961, p. 53) reported

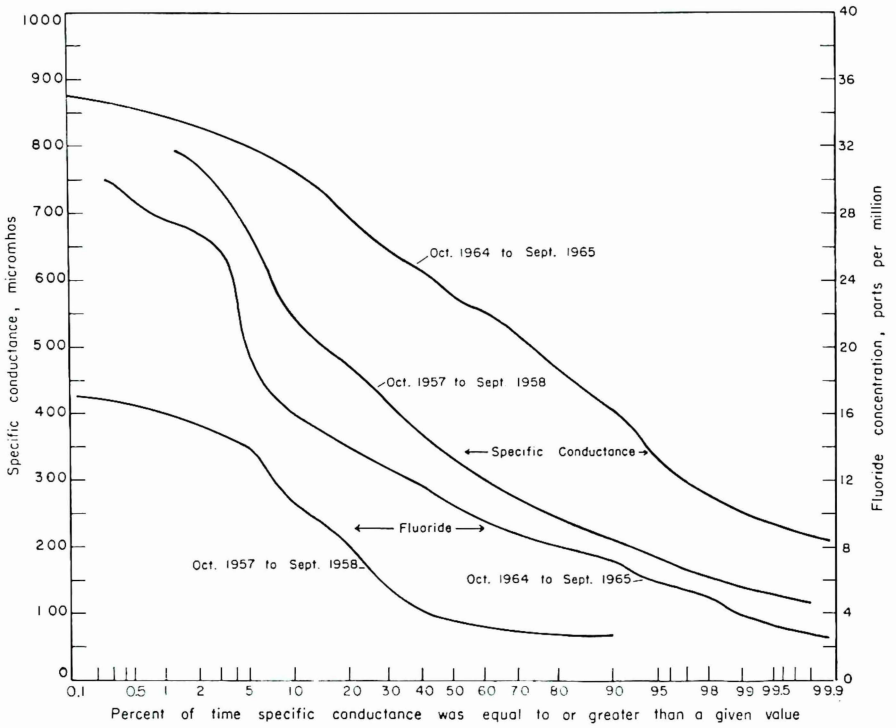


Figure 3.—Frequency curves of specific conductance and concentration of fluoride for the Alafia River at Lithia.

that, for the Alafia River at Lithia, the mineral content of the water, in parts per million, was about 77 percent of the specific conductance in micromhos.

The two frequency curves for specific conductance in figure 3 show that the specific conductance, and hence the mineral content, of water in the Alafia River at Lithia during 1964-65 was generally higher than during 1957-58. The median value (50 percent frequency) was about 340 micromhos in 1957-58 compared to 580 micromhos in 1964-65. These values correspond to about 262 and 447 ppm mineral content, respectively.

The frequency curves for concentrations of fluoride and phosphate (figs. 3 and 4) show that both these constituents also were generally higher in 1964-65 than in 1957-58. The concentration of fluoride in water in the Alafia River at Lithia (fig. 3) exceeded the 5.0 ppm recommended by the Florida State Board of Health about 98 percent of the time during 1964-65 compared to about 30 percent of the time during 1957-58.

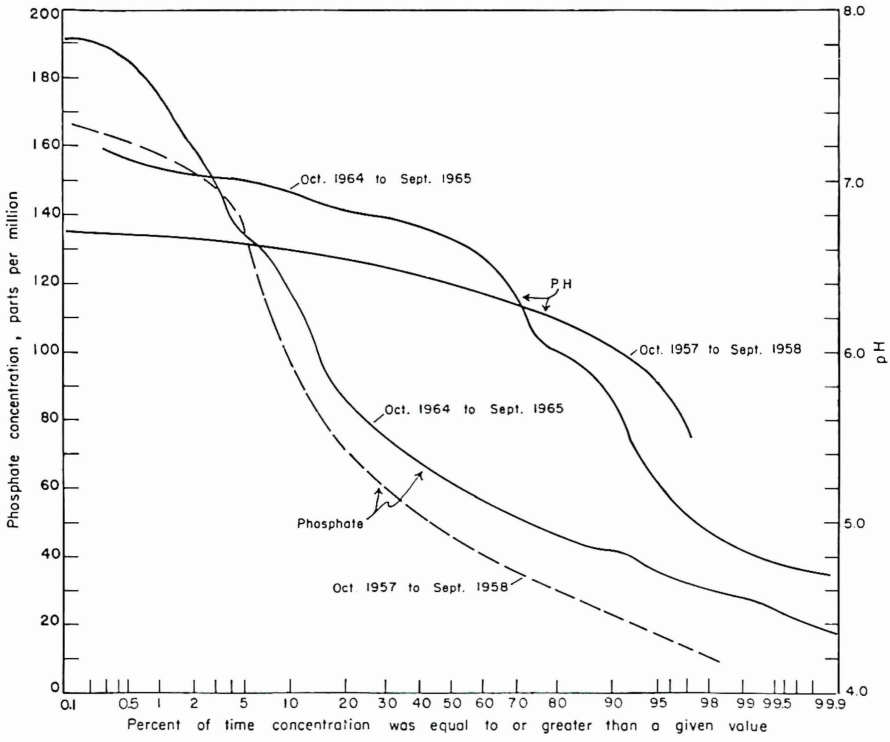


Figure 4.—Frequency curves of pH and concentration of phosphate for the Alafia River at Lithia.

Figure 5 shows hydrographs of discharge and concentrations of fluoride and phosphate for the Alafia River at Lithia from October 1964 to September 1965. The maximum concentrations of fluoride and phosphate during the year were 30 and 192 ppm, respectively. The concentration of phosphate was generally 5 to 7 times greater than that for fluoride.

Frequency curves for pH of water in the Alafia River at Lithia (fig. 4) show a wider range in pH during 1964-65 than during 1957-58. The differences between the two curves is probably, in large part, caused by the different sampling and analytical techniques. The pH was below the 5.0 lower limit recommended by the Florida State Board of Health for two percent of the time during 1964-65.

Turbidity was generally low in the Alafia River at Lithia but exceeded the 100 ppm, recommended as maximum, during a six-day period in February 1965 when a retaining dam for phosphate slime failed on one of the headwater tributaries.

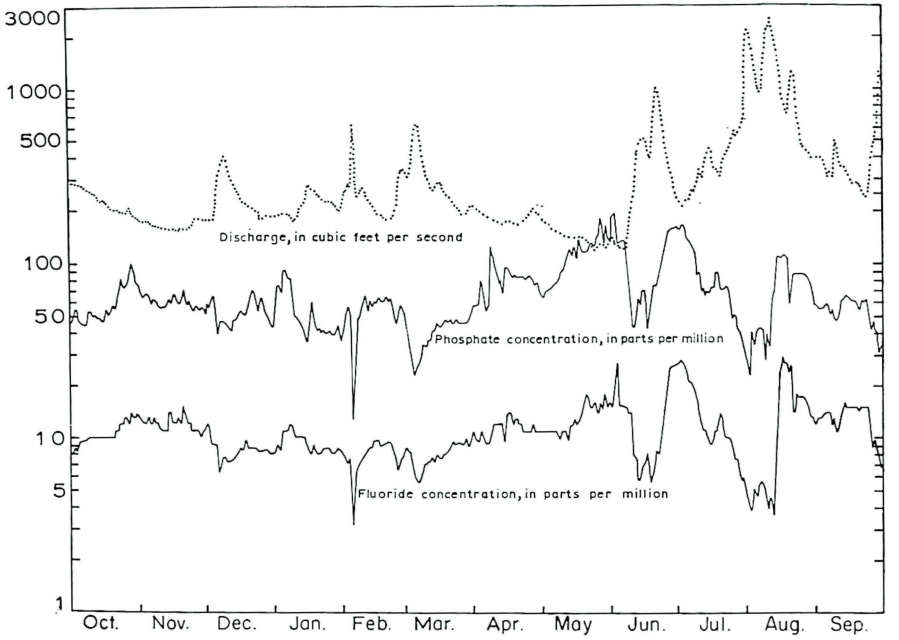


Figure 5.—Discharge and concentrations of fluoride and phosphate for the Alafia River at Lithia from October 1964 to September 1965.

The program of stream sampling in the Peace River basin was similar to that in the Alafia River basin. Of 15 sites selected for periodic sampling, 9 were at gaging stations.

The concentrations of fluoride and phosphate in the Peace River at Arcadia are shown in figure 6 and are not as high as those in the Alafia River at Lithia. From October 1964 to September 1965, the pH and fluoride concentrations of the Peace River at the daily sampling stations at Zolfo Springs and Arcadia remained within the limits set by the Florida State Board of Health. The turbidity of the Peace River at Zolfo Springs and Arcadia was above the 50 ppm limit (continuing waste turbidity) for 22 percent of the time at both stations from October 1964 to September 1965.

Several factors affect the amount of dissolved material carried by a stream. Some material dissolves from the atmosphere when water falls as rain. Additional material dissolves from the material on the land surface and from the soil zone as water flows to the streams. Some of the water that falls on the land surface enters the ground, moves downward to the water table and may eventually reach the streams. This water has a longer period of contact with the earth

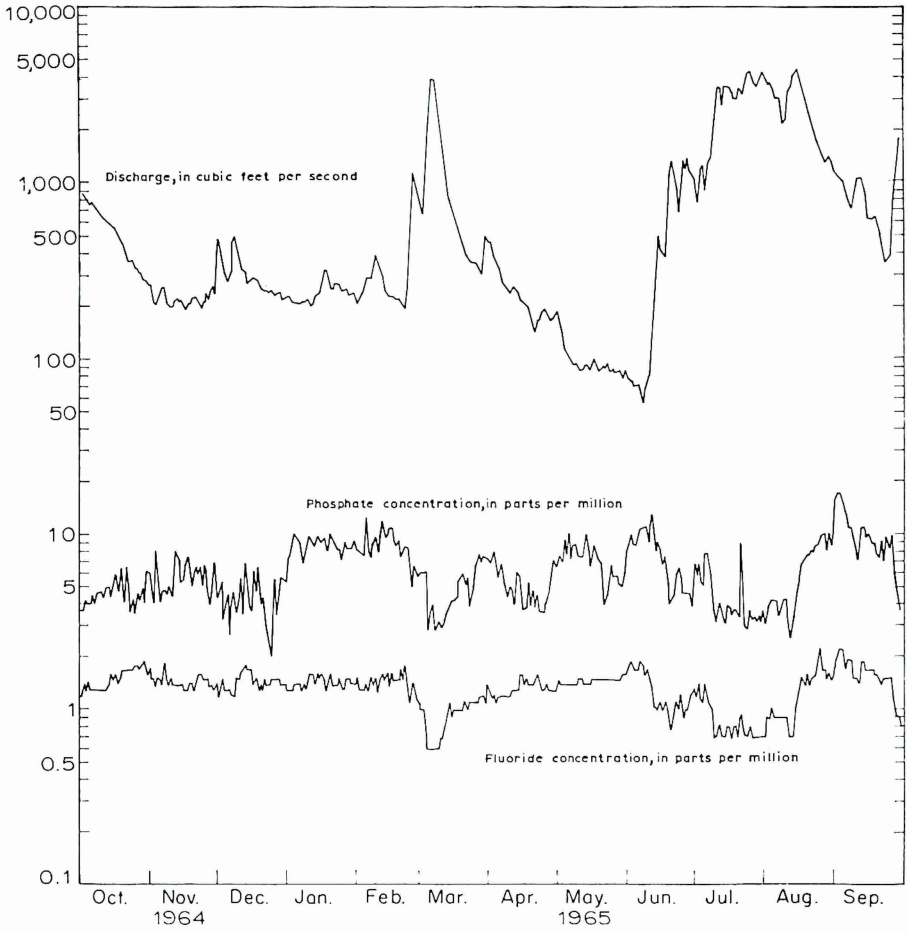


Figure 6.—Discharge and concentrations of fluoride and phosphate for the Peace River at Arcadia from October 1964 to September 1965.

materials and, consequently, contains higher concentrations of dissolved materials than water that flows on the surface to the streams.

The above are natural factors which affect the amount and kind of dissolved materials in water in a stream. During periods of little rainfall, most of the water in a stream, under natural conditions, is that which has moved through the ground to the stream. Generally, under natural conditions, there will be an inverse relation between the concentrations of dissolved solids of water in a stream and the discharge of the stream owing to most water flowing to the stream on

the surface during high discharge and most flowing through the ground during low discharge. However, the dissolved load (weight per unit time) is higher at high discharge than at low discharge because of the large volume of water that contains material dissolved from the surface.

If a stream receives waste products from municipal, industrial, or other sources, the above relations between the mineral content of water in a stream and discharge of the stream will be altered. For example, if a stream receives soluble waste at a constant rate, the mineral content of water in the stream will be higher at both low and high discharge than if no waste were being received. The inverse relation between mineral content and discharge will still occur owing to dilution at high discharge. If the waste material furnishes the larger part of any constituent in the stream, the dissolved load of that constituent should be nearly constant at all values of discharge. If the release of waste materials is controlled, so that more enters the stream at high discharge, there may be no relation between concentration and discharge and the dissolved load will be much higher at high discharge than at low discharge. If there is no consistent pattern of release of waste, there may be no consistent relation between discharge and concentration or load.

Chemical analyses of surface water in the Alafia and Peace River basins for periods of relatively low and high discharge are given in table 2. The drainage areas for stations 14, 20, and 22 (see fig. 2 for location) include no phosphate mining or processing operations and the concentrations of fluoride and phosphate in water at these sites are low. The concentration of fluoride in streams not affected by phosphate mining and processing was determined to generally be from 0.2 to 0.4 ppm from analyses of samples collected periodically at these sites and from samples collected at other sites during the early reconnaissance of the basins.

The mining and processing of phosphate rock have apparently affected the quality of water in the streams at all other stations shown on figure 2 and for which the analyses are given in table 2. The concentrations of all constituents are generally higher than for streams not affected. The analysis in table 3 shows the constituents in water from a phosphate chemical plant settling lagoon. The water from which this sample was taken was not observed entering the streams, but the analysis probably indicates the type and relative concentrations of constituents typical of the phosphate chemical plant effluents.

TABLE 2.—Chemical analyses of surface waters in the Alafia and Peace River basins during periods of relatively low and high discharge
(Analyses in parts per million. See table 1 for station name and figure 2 for location)
Analyses by the U. S. Geological Survey

Station	Date of Collection	Discharge (cfs)	Silica (SiO_2)	Iron (Fe)	Aluminum (Al)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Nitrate (NO_3)	Phosphate (PO_4)	Dissolved Solids	Hardness as $CaCO_3$: Calcium, Magnesium	Hardness as $CaCO_3$: Non-Carbonate	Specific Conductance (Micromhos at 25° C.)	pH	Color	Temperature °F.
ALAFIA RIVER BASIN																						
1	6-02-65	I 35	80	.14	—	56	102	52	3.0	0	472	35	17	13	224	1,050	560	560	1,150	4.4	20	81
	9-13-65	I 77	98	.20	2.6	111	15	66	3.0	0	340	22	24	3.6	112	810	338	338	1,000	4.6	40	82
2	6-02-65	M 79	64	.17	.9	126	20	53	2.8	0	300	42	16	.9	158	802	397	397	930	6.5	20	80
	9-14-65	M 128	70	.21	—	94	13	62	4.1	1	232	48	19	9.9	108	661	288	287	788	4.7	40	80
3	6-02-65	I 0.2	14	.00	—	27	19	12	2.5	134	29	21	3.1	.0	5.8	199	144	34	310	7.8	10	79
	9-13-65	I 10	19	.05	.6	22	7.6	26	8.4	54	19	48	5.2	.8	13	196	86	42	350	7.0	40	79
4	6-02-65	M 20	15	.23	.0	46	12	30	1.2	0	100	32	7.8	.2	86	369	164	164	465	6.6	40	80
	9-14-65	M 117	30	.14	2.3	40	8.8	26	2.9	1	88	26	11	.0	88	326	136	135	370	5.9	100	81
5	6-02-65	—	3.3	.03	—	25	4.4	15	.2	79	32	10	.5	.0	.7	130	76	11	230	7.6	20	80
	9-14-65	M 6	8.4	.19	—	12	4.5	8.9	1.0	37	20	12	.7	.4	1.8	88	48	18	150	7.0	90	—
6	6-02-65	M 137	54	.10	—	106	18	44	1.9	0	250	35	13	.0	143	665	338	338	810	6.5	20	80
	9-14-65	M 341	45	.16	2.5	63	9.9	40	3.4	3	152	36	14	7.9	86	461	198	195	688	5.4	85	80
7	9-14-65	—	21	.05	—	199	18	3230	507	63	772	5470	7.4	5.6	8.7	10,300	570	519	16,800	6.7	40	80
PEACE RIVER BASIN																						
[a]9	6-01-65	0	14	.02	—	38	19	27	1.4	100	116	7.0	3.1	.1	8.0	283	173	91	470	7.3	5	85
	9-14-65	M 188	14	.04	—	22	6.4	20	2.7	68	37	21	1.1	1.5	2.7	161	82	26	242	7.0	80	83
10	6-01-65	I 9.4	18	.09	—	58	19	23	.6	94	122	34	2.9	1.1	16	340	224	147	525	7.7	10	91
	9-13-65	I 19	19	.00	2.6	3.5	1.3	258	5.0	[b]227	280	32	11	.6	18	664	14	0	1,400	9.9	20	80
11	6-01-65	M 23	12	.05	—	46	15	34	1.0	91	119	32	2.6	.0	6.8	313	177	102	515	7.5	10	86
	9-14-65	M 248	17	.04	—	31	8.2	21	2.6	50	64	23	2.1	3.2	16	213	111	70	320	6.8	80	82
12	6-01-65	I 8.5	13	.01	—	43	20	54	.4	154	144	15	3.2	.4	1.8	371	190	64	635	7.8	5	87
	9-14-65	I 32	5.5	.01	.5	39	12	30	.3	92	105	11	2.6	.4	4.5	255	147	72	480	7.2	20	85
13	6-01-65	—	18	.07	—	43	15	15	1.0	138	70	10	1.1	1.2	2.0	244	169	56	405	7.5	10	—
	9-14-65	—	14	.09	—	27	9.8	19	2.4	63	51	18	1.4	5.7	6.4	186	108	56	280	6.9	80	83
14	9-14-65	M 6.4	6.3	.22	—	3.0	2.8	6.4	.3	6	4.0	12	.2	3.3	.7	43	19	14	79	5.7	160	78

TABLE 2.—Continued

Station	Date of Collection	Discharge (cfs)	Silica (SiO_2)	Iron (Fe)	Aluminum (Al)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Nitrate (NO_3)	Phosphate (PO_4)	Dissolved Solids	Hardness as $CaCO_3$		Specific Conductance (Micromhos at 25° C.)	pH	Color	Temperature ° F.
																	Calcium, Magnesium	Non-Carbonate				
15	6-02-65	I .8	15	.00	—	42	15	5.8	.5	120	64	5.5	3.8	.1	1.7	212	168	70	340	7.9	5	108
	9-14-65	I .7	20	.00	—	62	16	6.8	.8	140	83	8.0	3.1	.1	13	282	220	106	455	7.5	5	87
16	6-02-65	I 3.2	33	.08	—	30	81	44	.8	0	392	15	7.3	1.1	156	760	408	408	885	6.3	15	82
	9-14-65	I 5.2	33	.18	3.1	64	18	34	1.0	0	210	12	7.0	.2	131	511	234	234	620	4.6	70	87
17	6-02-65	I 24	18	.01	—	50	30	24	.4	81	184	16	2.6	.4	33	398	248	182	576	7.7	15	76
	9-14-65	I 69	18	.05	.6	40	13	16	1.2	28	106	13	4.2	.1	36	311	154	154	390	7.0	40	—
18	6-01-65	M 5.2	2.5	.19	—	16	7.5	11	.1	42	34	12	.8	5.2	2.0	112	71	36	210	7.4	20	78
	9-14-65	M 52	7.8	.32	—	13	4.9	8.0	.8	25	24	14	.9	1.4	3.7	91	52	32	152	6.7	110	78
19	6-01-65	M 59	12	.05	—	49	17	26	1.2	101	119	16	2.0	1.0	9.7	302	192	109	515	7.6	10	84
	9-14-65	M 531	14	.09	—	30	9.0	16	2.4	47	64	16	1.7	2.9	8.5	264	112	74	280	6.8	95	81
20	6-02-65	M 4.0	3.9	.12	—	16	6.2	8.8	.6	62	14	14	.7	.0	2.2	98	66	14	185	7.4	40	80
	9-14-65	M 87	8.8	.27	—	7.0	4.5	7.5	1.0	21	4.8	18	.3	.2	1.6	64	36	19	98	6.5	240	83
21	6-02-65	M 74	11	.03	—	48	17	25	1.8	105	126	18	1.7	.9	6.3	308	190	104	495	7.6	10	81
	9-14-65	M 837	12	.12	—	25	8.6	13	1.8	55	46	16	1.7	1.4	8.8	161	98	53	245	6.8	110	83
22	9-14-65	M 28	8.8	.46	—	33	6.7	16	2.1	91	29	29	.4	.6	1.2	172	110	36	288	7.0	100	83
23	9-14-65	—	11	.17	—	23	7.2	12	1.9	56	37	14	1.5	1.0	5.8	143	87	41	232	6.9	100	83

M Average daily discharge
I Discharge measurement
a Chemical analyses for Station 9, discharge data for Station 8
b Includes 80 ppm as Carbonate (CO_3)

TABLE 3.—Chemical analysis of water from a phosphate chemical plant settling lagoon, Polk County, Florida
(Analysis by the U. S. Geological Survey)

	parts per million (except specific conductance, pH, and color)
Silica (SiO_2)	1,180
Iron (Fe)	87
Aluminum (Al)	64
Manganese (Mn)	2.7
Calcium (Ca)	1,110
Magnesium (Mg)	50
Sodium (Na)	155
Potassium (K)	12
Total Acidity as H+	123
Bicarbonate (HCO_3)	0
Sulfate (SO_4)	2,710
Chloride (Cl)	37
Fluoride (F)	1,410
Nitrate (NO_3)	0.5
Phosphate (PO_4)	7,540
Dissolved Solids	14,400
Total Hardness as $CaCO_3$	2,980
Non-Carbonate hardness as $CaCO_3$	2,980
Specific electrical conductance in micromhos	10,100
pH	2.0
Color	140

Most of the phosphate chemical plants are located in the headwater areas of the Alafia River basin (fig. 2), and the water from streams in the basin contains higher concentrations of fluoride and phosphate than the streams in the Peace River basin. Drainage to the tributaries in the flat headwater areas is controlled, in large part, by the mining operations. No attempt was made to determine the amount of waste water contributed to the streams by an individual plant.

Table 2 shows that the concentrations of fluoride and phosphate in surface water may be as high or higher at high discharge as at low discharge. The hydrographs for stations 6 and 21 (figs. 5 and 6) also show that the concentration of fluoride or phosphate may be the same with wide ranges in discharge. This indicates that the streams do not receive fluoride and phosphate at a constant rate.

The load the stream carries shows the amount of waste and indicates the period during which most of the waste is received by the stream. The dissolved fluoride loads of streams in the Alafia and Peace River basins at relatively low and high discharge are shown in figure 7. The figure illustrates that a relatively high dissolved fluoride load is carried by the Alafia River as compared to the Peace River. It also indicates there is no major loss of fluoride from the streams.

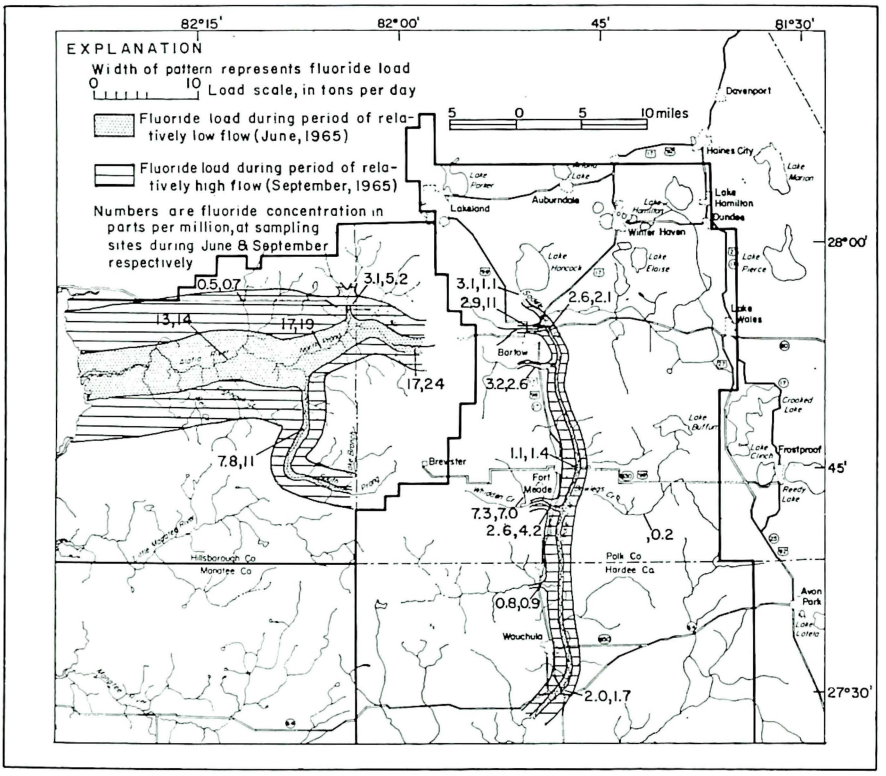


Figure 7.—Fluoride load in streams in Alafia and Peace River basins during periods of low and high flow 1965.

The fluoride load of each stream at the daily sampling sites was calculated using the fluoride concentrations of the daily sample and the mean daily discharge for the station. Hydrographs of fluoride load are shown in figure 8 for the Peace River at Arcadia and the Alafia River at Lithia. The calculations of daily samples also show that the Alafia River carries much more fluoride than the Peace River. The fluoride load hydrographs closely parallel the shape of the discharge hydrograph (figs. 5 and 6) showing that much more fluoride is carried by the streams at high discharge than at low discharge. The fluoride load hydrographs have the peak loads in August coincident with the discharge peaks. Of the approximately 4,000 tons of fluoride carried by the Alafia River at Lithia from October 1964 to September 1965, slightly more than one-fourth was during the month of August. During this year, 781 tons of fluoride was measured on the Peace River at Zolfo Springs and 900 tons at Arcadia. The larger amount at Arcadia

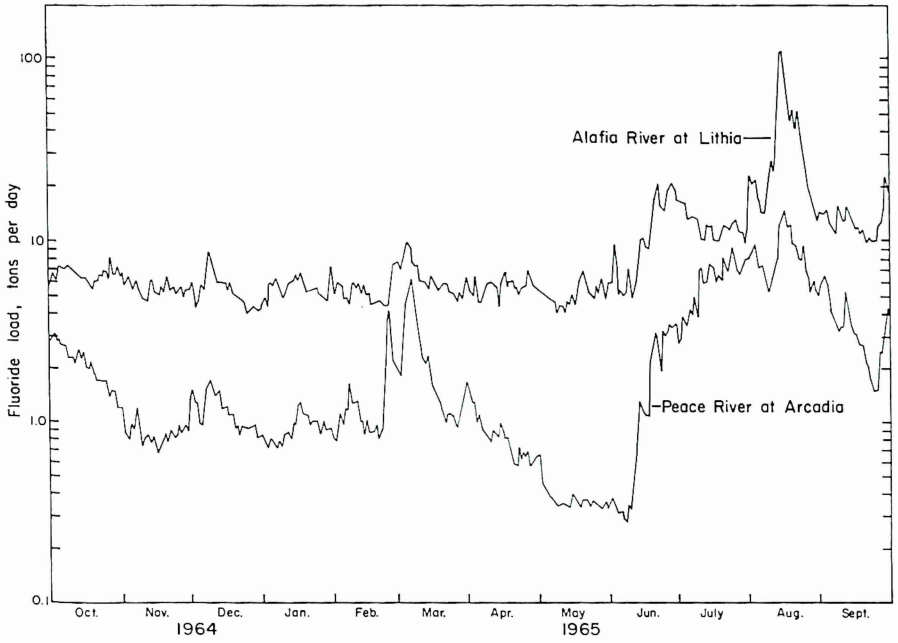


Figure 8.—Dissolved fluoride load of the Alafia River at Lithia and the Peace River at Arcadia from October 1964 to September 1965.

is of the magnitude to be expected as contribution from the uncontaminated tributaries between the two stations. Apparently, fluoride is not lost from the stream to the ground water between the two stations.

Much of the difference in fluoride load carried by the Alafia and Peace rivers may be accounted for by the greater number of chemical processing plants in the Alafia basin. Other differences undoubtedly are due to differences in the size and type of plant and to methods of waste disposal.

The high fluoride load of the streams at high discharge is probably caused, in large part, by either controlled or accidental release of larger amounts of waste water from the settling lagoons during these periods. Some of the load during high discharge periods may be due to natural ponding of waste water in flat, swampy upland areas during periods of low rainfall and subsequent flushing of these areas during periods of high rainfall.

GROUND WATER

GENERAL GEOHYDROLOGY[1]

The geologic formations which form the aquifer systems in the Alafia and Peace River Basins range in age from Eocene to Recent. The Floridan aquifer is the principal water producer. It includes the lower part of the Hawthorn Formation and the Tampa Formation of Miocene age, the Suwannee Limestone of Oligocene age and the limestones of the Ocala Group, the Avon Park Limestone, and the Lake City Limestone, of Eocene age. Generally, the upper sandy and clayey part of the Hawthorn Formation serves to confine water in the underlying formations under artesian pressure.

Overlying the Hawthorn Formation are the sands, clays, and marls of Pliocene to Recent age that may contain water under water-table conditions and which serve to supply many small domestic wells.

The Floridan aquifer is at or near the surface in the northeastern part of the area and dips to the southwest. In the southwestern part of the area, the Floridan aquifer is at depths of several hundred feet. Menke, Meredith, and Wetterhall (1961, p. 75) reported the depth of the confining beds of the Floridan aquifer in Hillsborough County to range from a few feet in the north-central part of the county to about 300 feet in the southeastern part. Woodard (1964, p. 20) stated, "The bottom of the [Hawthorn] Formation, which in most cases marks the top of the Floridan aquifer, ranges from about 200 feet below sea level in north Hardee County to about 450 feet below sea level in south DeSoto County." Surface elevations in southern DeSoto County range from about 25 to 125 feet above sea level and the depth to the Floridan aquifer is as much as 575 feet.

Regionally, the Floridan aquifer in peninsular Florida functions as an aquifer system. Water enters the aquifer in the central peninsular area where the aquifer is at or near the surface, and in areas where it may leak through the confining beds, and moves radially away from the central part of the peninsula toward the coast. Figure 9 shows the piezometric surface of the Floridan aquifer in the study area. The general direction of ground-water movement is considered to be from the areas of high to low pressures or south and west from north-central Polk County.

Locally, the Floridan aquifer may sometimes function as two or more hydraulic units. In Hillsborough County (Menke, Meredith, and Wetterhall, 1961, p. 72) the limestones of the Ocala Group tend to

[1]The stratigraphic nomenclature in this report conforms to the usage of the Florida Geological Survey and not necessarily to that of the U. S. Geological Survey.

restrict the vertical flow of water and the aquifer functions as two units, one above and one below the Ocala Group. Woodard (1964) found similar conditions in Hardee and DeSoto counties. In Hardee County, most of the water pumped is from the zone below the Ocala Group. South of Hardee County, in DeSoto County, where the Tampa Formation and Suwannee Limestone above the Ocala Group are deeper and thicker, they form the most used zone. Sutcliffe and Joyner (1966) used packers in wells in Sarasota County to show three producing zones.

Generally, the upper, permeable zones have a better quality of water

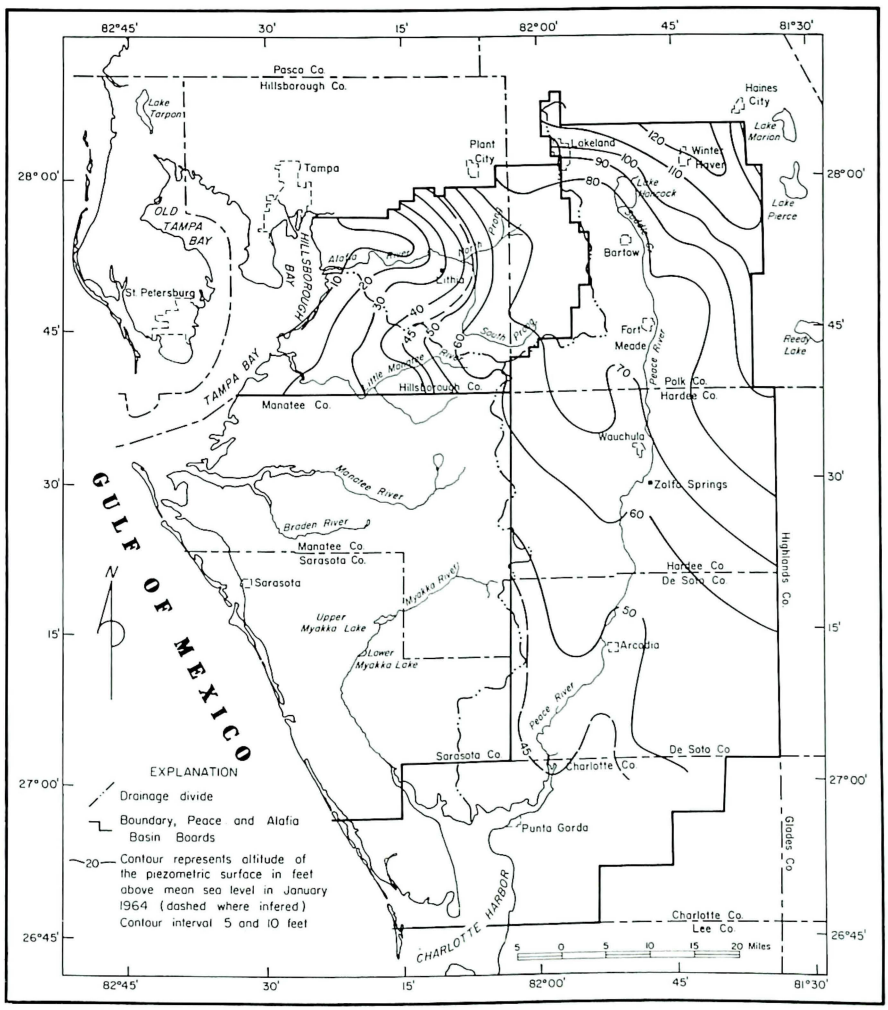


Figure 9.—Piezometric surface of the Floridan aquifer in southwest Florida in January 1964.

than the lower zones where circulation of water is inhibited. Figure 10 shows the general distribution of dissolved solids in the Floridan aquifer. The map is prepared from maps and data presented by Shattles (1965), Peek (1958), N. P. Dion and M. Kaufman (personal communication, 1966), B. F. Joyner (personal communication, 1965), and supplementary data collected during this investigation. The maps were prepared from chemical analyses that generally represent water from wells open to a large section of the aquifer and do not show differences in the dissolved solids in the different zones of the aquifer. Evidence in the literature shows that differences in the chemical quality of water occur with depth of penetration into the aquifer. Peek (1958, p. 66-67) shows large differences in his dissolved solids maps in water from the Tampa Formation and water from the Suwannee and older formations.

Differences in artesian pressure in the different zones of the aquifer in some locations affect the general flow pattern of the water. In order for water to move downward into an aquifer, the water level in the aquifer must be lower than the water level in the sediments overlying the aquifer. For the water to move downward through the aquifer, the water level from a well deep into the aquifer must be lower than in a well which only penetrates the upper part of the aquifer. Woodard (1964, p. 28) reported that the water table stands as much as 45 feet above the piezometric surface in northwest Hardee County, and that the artesian water level becomes lower with depth. The Floridan aquifer is being recharged in the ridge section of Hardee County southward to the Hardee-DeSoto county line where the water table and piezometric surface are at about the same elevation.

Along the Peace and Alafia rivers, an opposite relation of water level with depth prevails. Water is released from the aquifer through springs along the river valleys. This release of water lowers the pressure of the upper part of the aquifer to a level below that of the lower part of the aquifer. This reversal allows water to move from the lower part to the upper part of the aquifer. Dion and Kaufman (personal communication, 1966) have shown this condition to exist for the Peace River, and Menke, Meredith, and Wetterhall (1961) have discussed it for some springs in Hillsborough County. The manner in which these areas of recharge and discharge affect the chemical quality of water by altering the general flow pattern can be observed on figure 10 by the upstream indentation of the high dissolved solids patterns along the river valleys in Hardee and Hillsborough counties.

The natural zonation and local alteration of the general flow pattern in the Floridan aquifer are significant in explaining the variations in natural chemical quality of water. They also illustrate the need for a

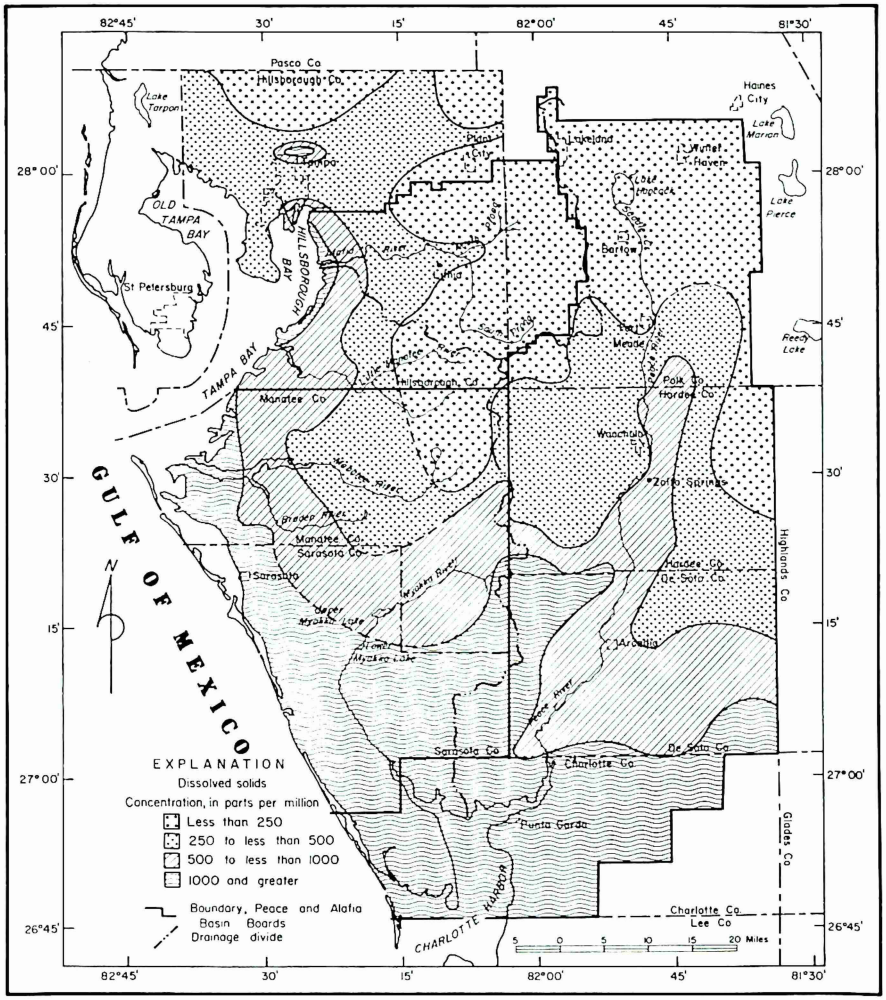


Figure 10.—Dissolved solids concentration in the Floridan aquifer in southwest Florida.

very detailed knowledge of local hydrologic conditions to locate and to predict the effects of introducing a contaminant into the aquifer at any point.

FLUORIDE DISTRIBUTION

The distribution of fluoride in ground water in the Alafia and Peace river basins and adjacent coastal areas was mapped to determine the natural concentrations of fluoride, to determine if contamination of ground water by fluoride effluent from phosphate processing plants has occurred,

and to provide a base from which any future changes in fluoride concentration can be detected.

Figure 11 is a map of fluoride concentrations in ground water. The wells shown range widely in depth and in the section of the aquifer system they penetrate. All wells except those that penetrate only the surficial sands are included.

Some general trends in the distribution of fluoride can be noted. In the northern part of the area, the concentration of fluoride in ground water generally ranges from 0.0 to 1.0 ppm. The concentration of

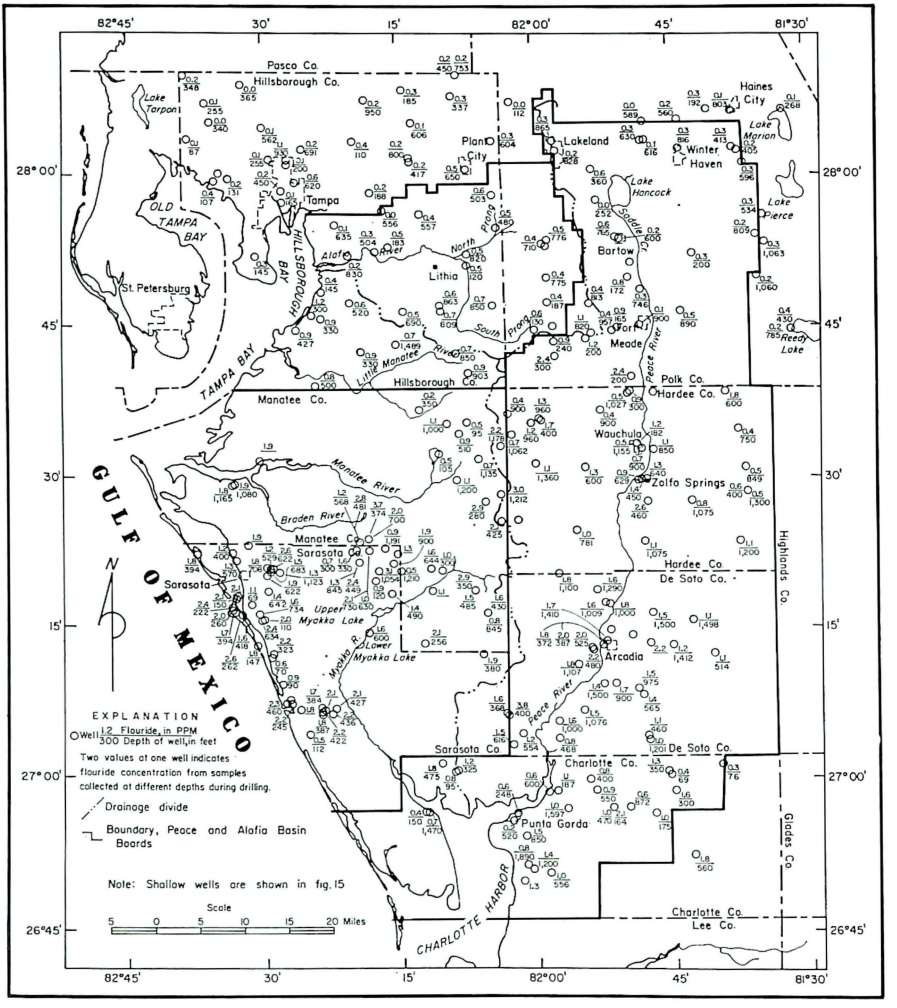


Figure 11.—Concentration of fluoride in ground water in southwest Florida.

fluoride generally increases from the northern boundary of the Peace River basin district, both westward into Hillsborough County and southward into Hardee County.

In Hardee County the concentration of fluoride is slightly higher than in Polk and Hillsborough and generally ranges from 0.5 to 1.5 ppm. The fluoride concentration in the western part of the county is slightly higher than in the eastern part. Further south in DeSoto County, the concentration of fluoride may be more than 2.0 ppm. The concentration of fluoride in many wells in Charlotte, Sarasota, and Manatee counties ranges from about 1.0 to 3.0 ppm.

There are many exceptions to these generalities on areal distribution of fluoride in ground water. Most of the variations can probably be attributed to vertical hydrologic zonation of the aquifer system and the amount of water produced from each zone in a particular well, to local deviations from the generalized areal ground water flow patterns, and to variations in the amount of fluoride source minerals available in the rocks.

North-south cross sections, located along the lines shown in figure 12, are shown in figures 13 and 14 to illustrate the vertical zoning of concentrations of fluoride in ground water. These sections also substantiate the general southward increase in concentrations of fluoride shown on the map in figure 11. The higher concentrations of fluoride generally occur at shallower depths.

Because the sections were constructed by projecting well locations as much as 5 miles and because only a few geologic control points were used, the wells are not all finished in the geologic formations exactly as shown. It is evident, however, that the higher fluoride concentrations are in water from the Hawthorn Formation and Tampa Formation and possibly from the upper part of the Suwannee Limestone. This is best shown by wells with only a small producing interval or where samples were collected at different depths while the well was being drilled.

This zonation of high fluoride concentrations in the more shallow formations strengthens the conclusions of Woodard (1964) that the most probable source of the fluorides are the fluoride-bearing phosphate minerals in the Hawthorn Formation and Tampa Formation. No attempt was made to relate the fluoride concentration in ground water to the percent of phosphate minerals in the rock at different locations; however, such a relation appears likely.

It is also evident from figures 13 and 14 that the fluoride concentration in any location may depend on the vertical movement of ground

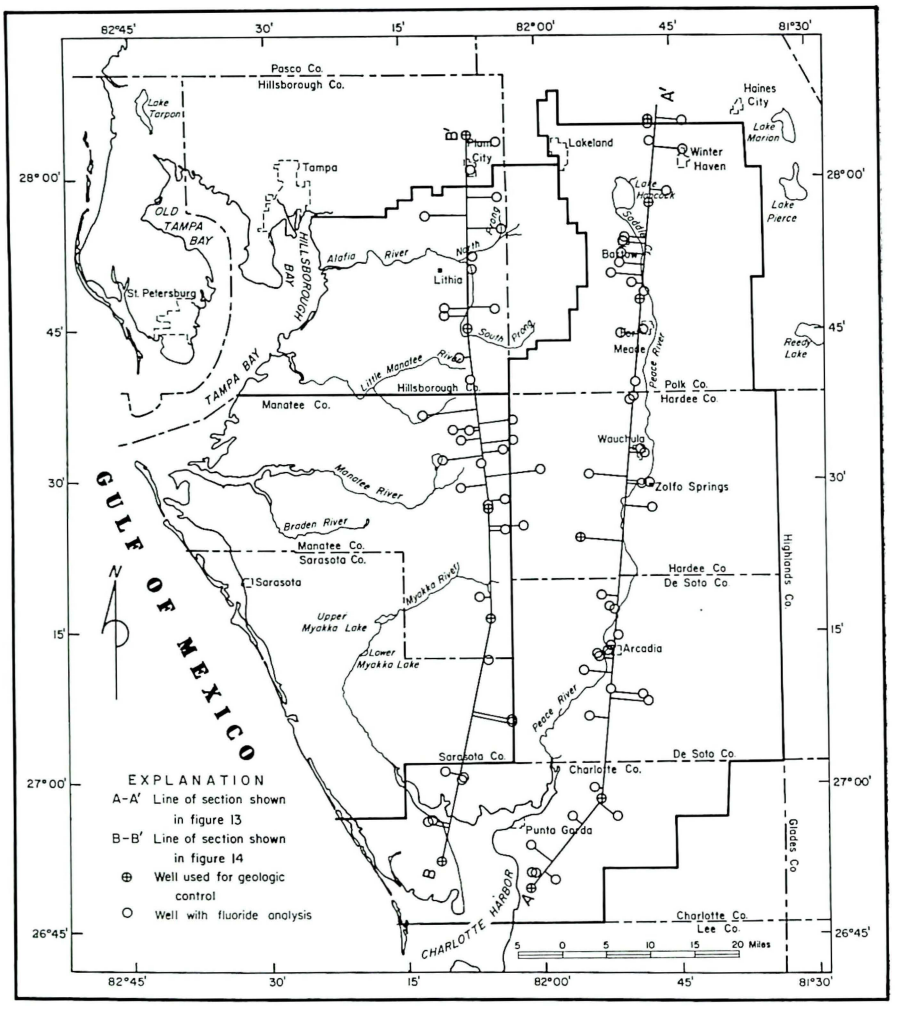


Figure 12.—Location of cross sections A-A′ and B-B′.

water as well as the lateral movement. If there is vertical hydraulic connection between all formations and water movement is downward (recharging conditions), fluoride in water would tend to move downward to the underlying formations. If the vertical movement is upward (discharge conditions), however, the fluoride concentration should represent, in part, that from water which has moved upward from the lower formations. Geohydrologic environments favorable to both conditions occur in the area. Discharge occurs through springs and prob-

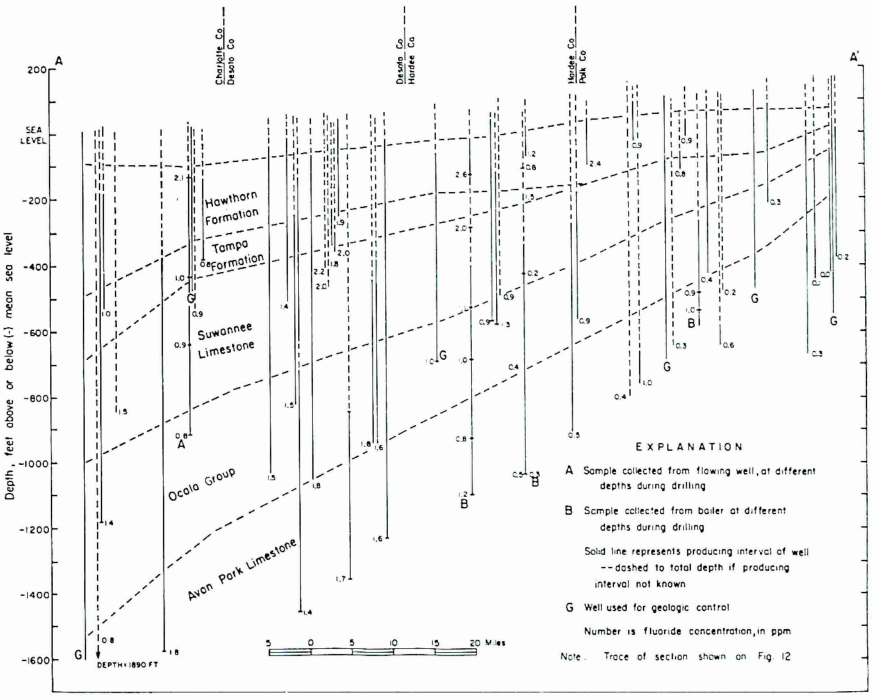


Figure 13.—Cross section A-A′ showing geologic formations and fluoride concentrations in ground water.

ably directly to the streams along the lower reaches of both the Alafia and Peace rivers. Recharge occurs along much of the ridge section away from the river. The general effect of these opposing conditions on water quality has been noted in figure 10 by the indentation of the contours of high dissolved solids along the lower reaches of the rivers. As concentrations of fluoride in ground water are relatively low and variable, it is difficult to evaluate these various factors on the concentration of fluoride at a particular location.

The fluoride content of water from shallow wells in the surficial sands was determined at 30 locations near the active phosphate mining areas. The distribution of wells sampled and the concentrations of fluoride are shown in figure 15. Fluoride in water from the surficial material ranged from 0.0 to 1.0 ppm. The number of shallow wells available for sampling is limited, because most wells are finished in the underlying limestone; however, it can be concluded from figure 15 that there is no widespread occurrence of high fluoride concentration in water in the surficial sands. However, the data shown in figure 15 do not pre-

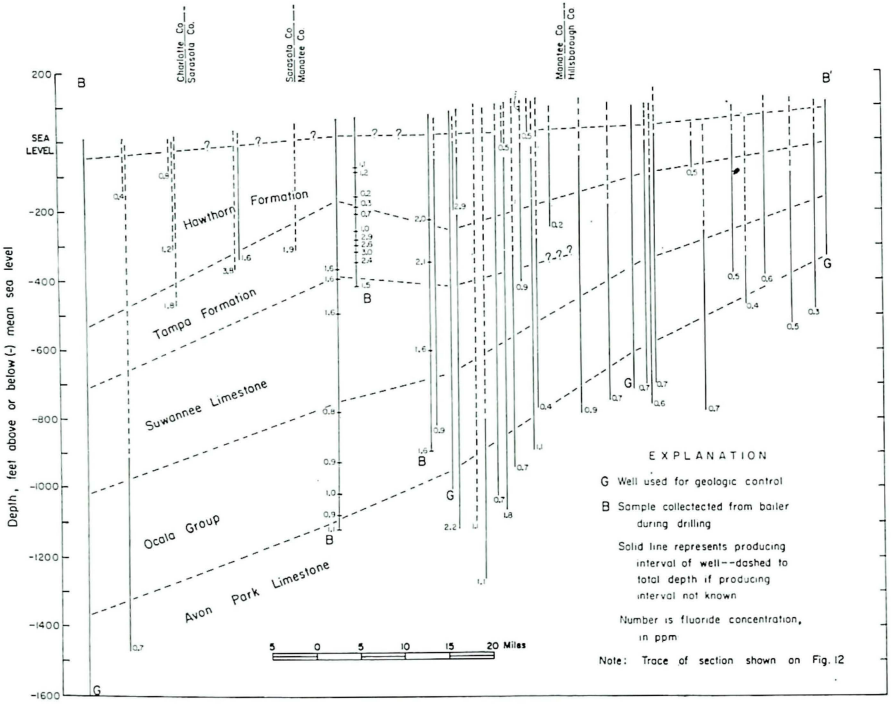


Figure 14.—Cross section B-B′ showing geologic formations and fluoride concentrations in ground water.

clude any contamination of the shallow ground water on a local scale. Generally, there are no wells available for sampling near the phosphate mines, chemical plants, and settling lagoons, the places where local contamination of shallow ground water would be expected.

From the maps (figs. 11 and 15) and sections (figs. 13 and 14), the following general conclusions can be made about the occurrence of fluoride in ground water in southwest Florida. Fluoride concentrations of 2 ppm or more are confined to waters in the Hawthorn Formation and Tampa Formation and possibly in the upper part of the Suwannee Limestone; fluoride concentrations in the surficial materials and in the underlying limestone in the areas of active phosphate mining are low (generally less than 1.0 ppm); widespread pollution of the ground water by fluoride is not evident; and the formations that have high fluoride concentrations in interstitial water are the formations that contain phosphatic minerals, and these are the probable source of the fluoride in the water. If contamination of ground water by fluoride

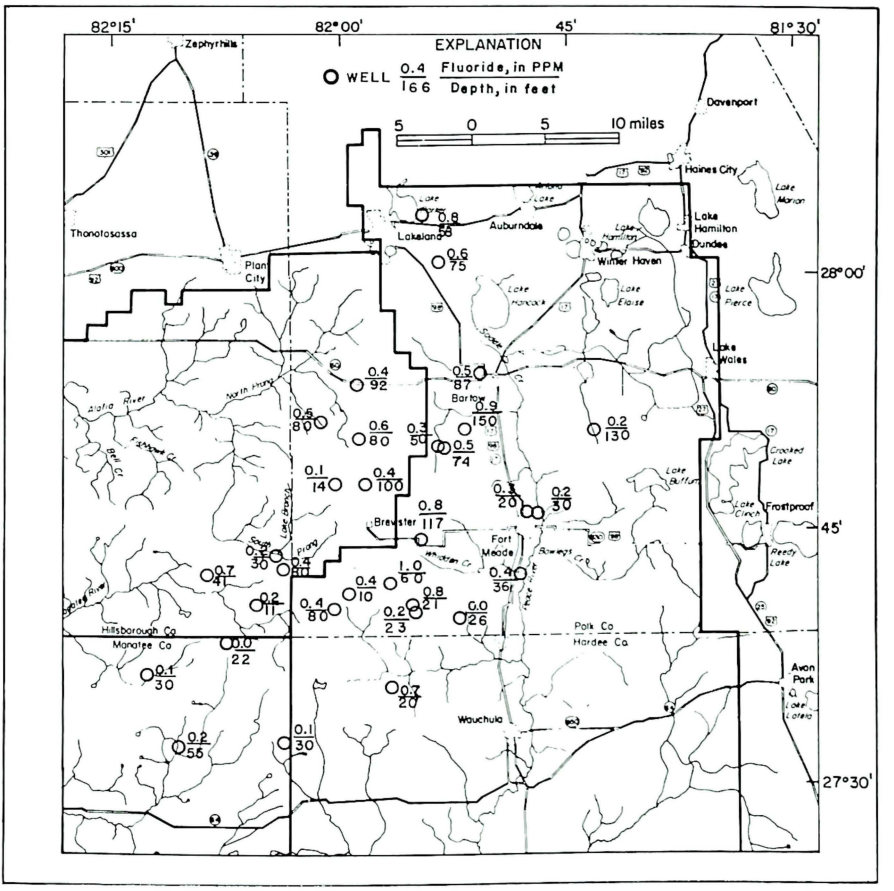


Figure 15.—Fluoride concentrations in shallow wells in the phosphate mining area in southwest Florida.

occurs from the mining and processing of phosphate rock, such contaminations apparently are local and not evident from the areal approach used for this investigation.

POLLUTION POTENTIAL AND PHYSICAL CHEMISTRY OF FLUORIDE

The general mining and processing of the phosphate ore do not appear to be causing widespread contamination of the ground water supplies. The greatest potential hazard to ground water would appear to be the settling lagoons at the chemical plants which receive water containing several hundred ppm fluoride (see analysis table 3). The

lagoons become lined with the fine waste material from the operation which inhibits leakage to the aquifer. Even if leakage does not occur, waste waters might enter the aquifer by collapse of the surficial materials into solution chambers in the underlying limestone as happens in the formation of many sinkholes in Florida and has happened in Polk County.

Prediction of what would happen to the fluoride, should it enter the aquifer from the lagoons, involves (1) a detailed knowledge of the hydrology and geology of the aquifer near and down gradient from the lagoons and (2) knowledge of the chemical changes exacted upon the wastes by the laws of chemical equilibrium when they reach the aquifer environment.

The flow patterns in the aquifer near the waste disposal lagoons probably could be delineated satisfactorily by detailed hydrologic investigations. This would involve extensive drilling and testing to determine the direction a contaminant would move away from a point where it was injected into the aquifer and the general geometric shape the moving mass would assume.

Little experimental work has been done, however, on the role of chemical reactions of contaminants with the minerals and water which they encounter, particularly on what may happen to a fluoride contaminant in a limestone aquifer.

Aumeras (1927), reported in Hem (1959), states that fluoride is soluble in pure water at 25° C. to the extent of 8.7 ppm fluoride. For such a sparingly soluble compound as calcium fluoride, this information is sufficient to calculate a "solubility product" for the compound. The principle of a solubility product is useful in investigating the geochemistry of ground water and recently has been applied to saturation studies of calcium carbonate in ground water (Back, 1961, 1963; Hem, 1961).

The significance of the solubility product is that "when a solution is at equilibrium with a given salt, the product of the activities (or concentrations) of its constituent ions, raised to the appropriate powers, must be constant" (Glasstone, 1946, p. 490). Because calcium fluoride (CaF_2) requires two fluoride ions to balance each calcium ion the appropriate power for the fluoride concentration is 2 and the equation for the solubility product (K) is

$$K_{CaF_2} = Ca_{++} \times (F^-)^2$$

where Ca^{++} and F^- represent the molal concentrations of calcium and fluoride.

Both temperature and the concentration of all constituents in solution affect the solubility constant (K). For the range of temperature of most ground water the effect is small and the standard temperature of 77° F. may be used for this area. The effect of concentrations of other ions in solution requires the use of activities of Ca^{++} and F^{-} instead of concentrations as given in the above equation.

The effect of other constituents in solution is to suppress the effective activity of an ion below that expressed by the concentration of the ion. This effect is related to the ionic strength of the solution which can be calculated from the concentration and the valence of the ion in the solution by:

$$\mu = \tfrac{1}{2}M_1Z_1^2 + \tfrac{1}{2}M_2Z_2^2 + \tfrac{1}{2}M_3Z_3^2 \ldots$$

where μ = ionic strength
M = molal concentration of each constituent
Z = valence of the ion in solution

From the ionic strength a number can be calculated which, when multiplied by the concentration of an ion, will give its effective activity. This number will be less than 1.0 and is called the activity coefficient.

Hem (1961) gives in detail the calculations to obtain ionic strengths and resulting activity coefficients along with nomographs to eliminate many of the calculations.

Figure 16 shows the relation of the activity coefficient of calcium and fluoride to the ionic strength of a solution. The ionic strength may be obtained from the above quotation or from nomographs given in Hem (1961, plate I), either of which requires a chemical analysis and considerable calculations. As the ionic strength depends only on the type and amount of dissolved material and as most natural water contains only a relatively few major constituents, a fair approximation of the ionic strength can usually be obtained from a measure of the dissolved solids.

Pure water is a poor conductor of electricity. The dissolved material in the water that conducts electricity and the specific electrical conductance is a good indicator of the amount of dissolved solids. Figure 17 shows the relation of ionic strength to specific electrical conductance of several ground water analyses. Most of the points on the graph represent samples of ground water from Florida except those above 2,000 micromhos which are analyses from the literature and which had relatively high fluoride concentrations. The specific electrical conductance multipled by a factor of 0.60 gives a good approximation of the dissolved solids content of ground water in southwest Florida.

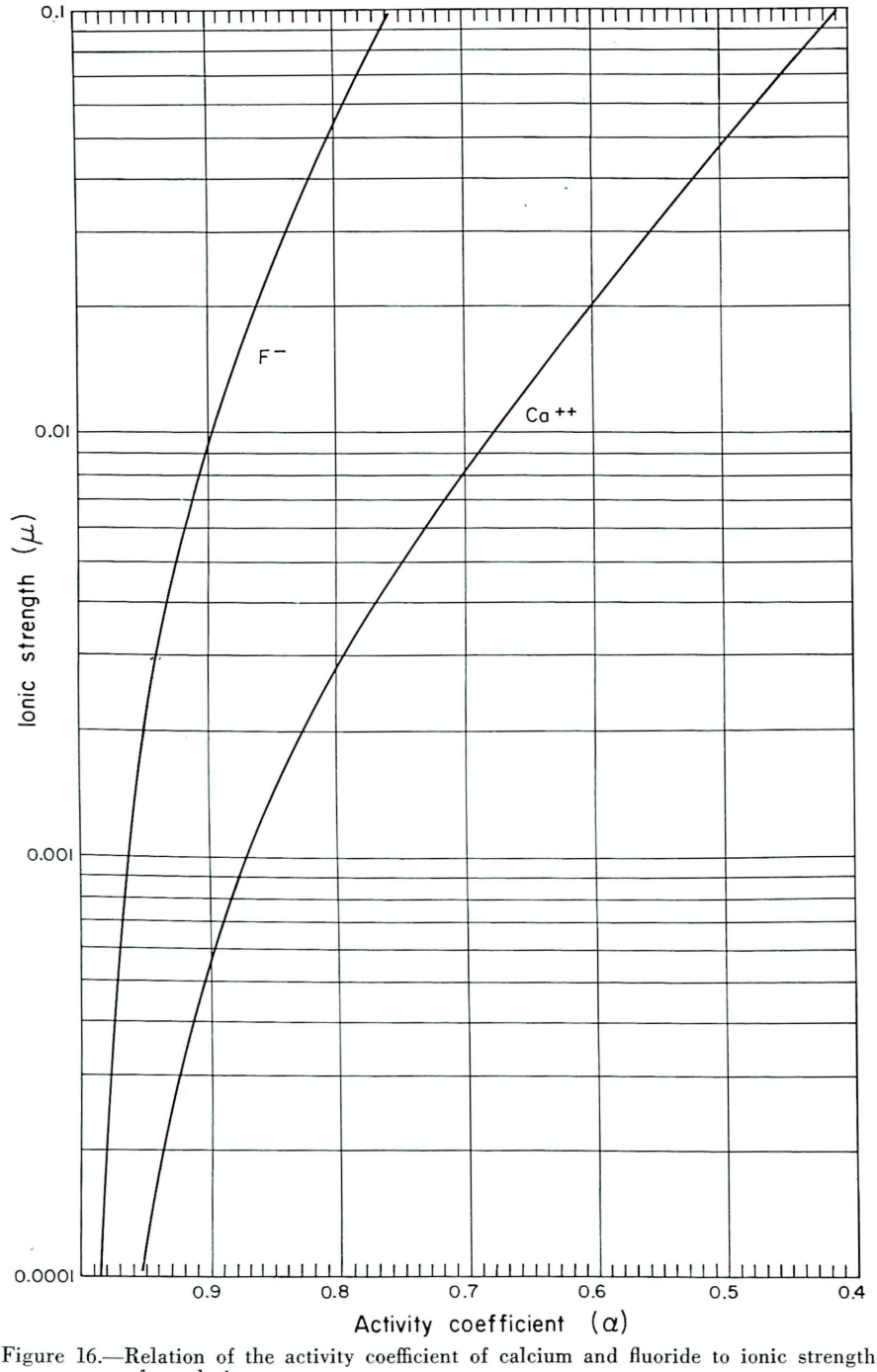


Figure 16.—Relation of the activity coefficient of calcium and fluoride to ionic strength of a solution.

Utilizing the activities of the ions in solution, the solubility product for calcium fluoride becomes

$$K_{CaF_2} = a_{Ca}Ca^{++} \times (aF^-)^2$$

where K_{CaF_2} = equilibrium constant for calcium fluoride

a = activity coefficient for the ions
Ca^{++} and F^- = molal concentrations of the ions

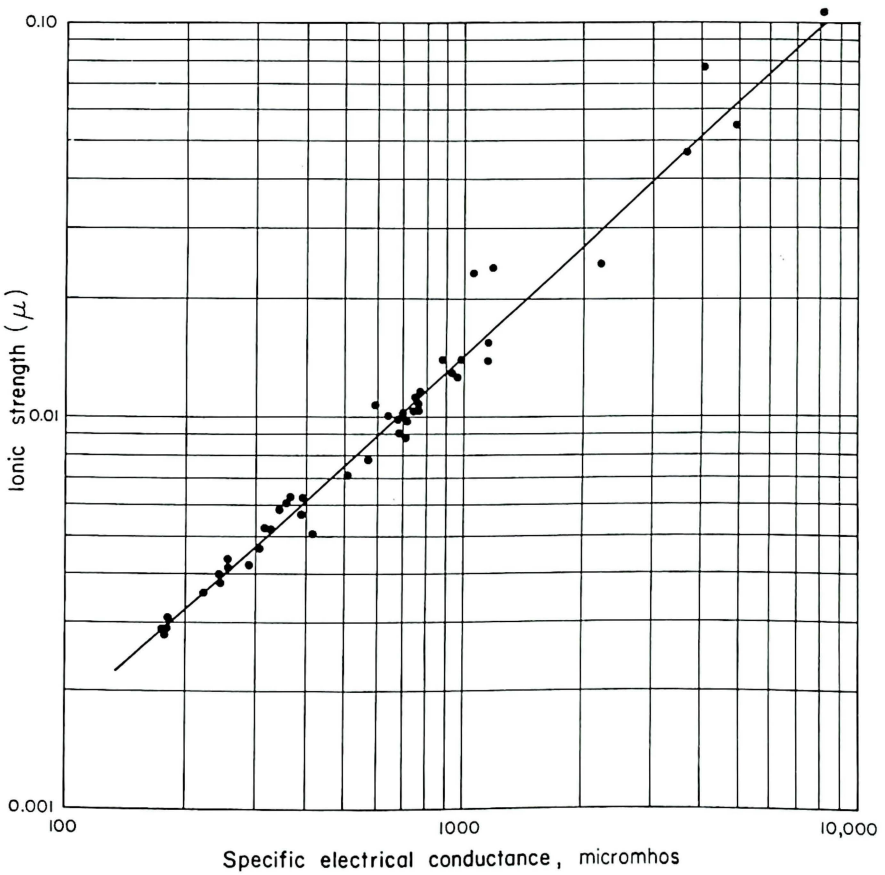


Figure 17.—Relation of ionic strength to the specific conductance of some ground waters.

The Handbook of Chemistry and Physics (1954, p. 1634) gives the solubility product of calcium fluoride at 26° C. (78.8° F.) as 3.95 x 10^{-11}. Using this value and assuming that ground water system is at

chemical equilibrium, the maximum fluoride concentration for any given calcium concentration in a saturated solution may be calculated by:

$$F^- = \frac{\sqrt{\frac{3.95 \times 10^{-11}}{a\,Ca^{++}}}}{a^{F^-}}$$

Figure 18 shows a set of curves for a saturated solution of calcium fluoride with respect to fluorite at several ionic strengths. An ionic strength of 0.10 is considered about the maximum at which the above calculations hold (Hem, 1961). From figure 17 this is seen to be at a specific conductance of about 8,000 micromhos (4,800 ppm dissolved solids). The lowest curve is a theoretical curve for ionic strength (μ) equal zero and activity coefficients (a) equal one. For potable ground water in southwest Florida, the practical curves to consider are from about ionic strength of 0.002 to 0.02 or about 70 to 900 ppm dissolved solids.

Figure 18 shows analyses of fluoride versus calcium from ground water in Florida. The dots represent samples from the Peace and Alafia River basins that contain more than 0.5 ppm fluoride. The triangular points represent samples from northwest Florida (Toler, 1966) and are included to show that the solubility product principle apparently holds for higher fluoride concentrations.

Most of the points in figure 18 plot to the left of the family of equilibrium curves showing the water to be undersaturated in fluoride with respect to fluorite. Those points falling within the family of curves are from analyses of ground water of relatively high ionic strength. They also plot to the left of the saturation position for the ionic strength of that sample and are undersaturated. Figure 18 shows graphically that the product of the activities of calcium and fluoride in ground water in Florida approaches, but does not exceed, the theoretical values based on the concept of chemical equilibrium.

From the concept of the solubility product principle and the analysis of the graph in figure 18, it is apparent that large concentrations of fluoride in ground water at equilibrium are limited by the amount of calcium present. This is significant in southwest Florida where ground water is obtained from limestone rocks and generally has high calcium concentrations. For a calcium concentration of 40 ppm and an ionic strength of 0.01 (dissolved solids about 420 ppm), the maximum fluoride concentration at equilibrium would be 5 ppm. The role that solubility would play in event of contamination by water of extremely high fluoride concentrations makes the reaction important. If contaminating water, high in fluorides entered the aquifer, the water would quickly become

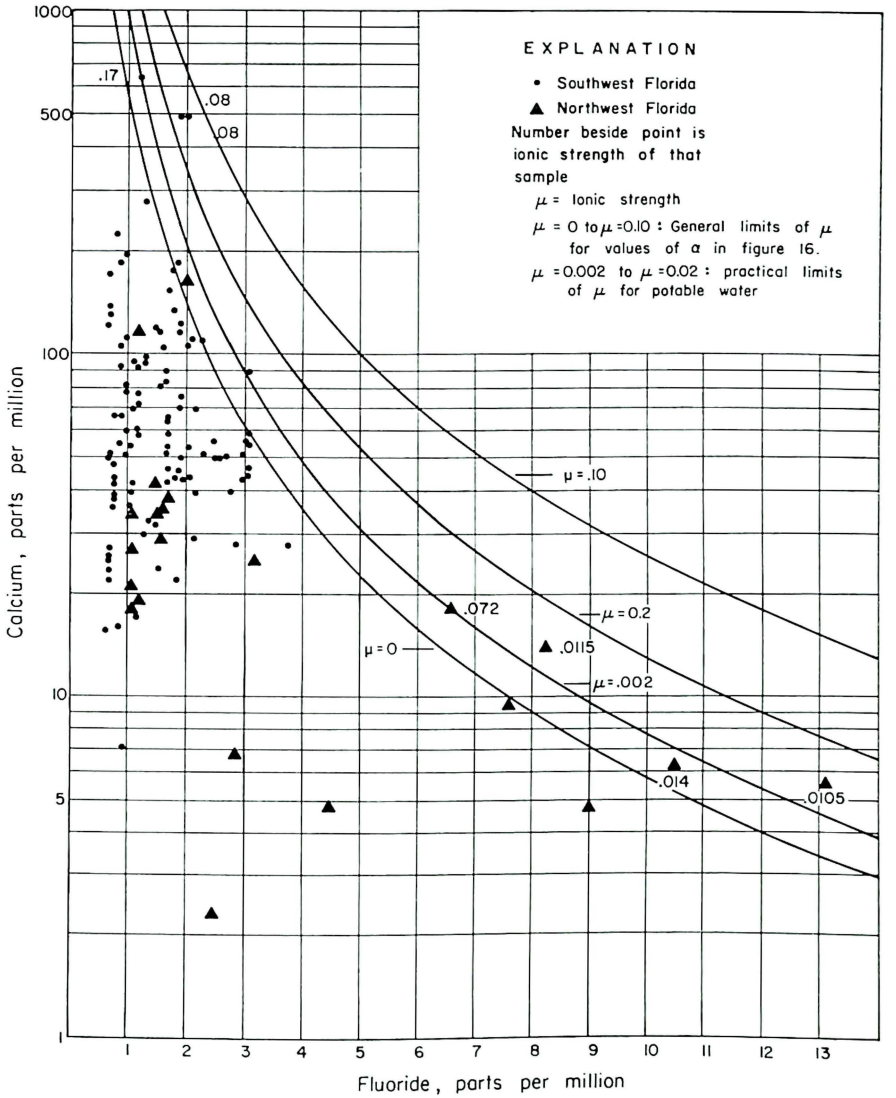


Figure 18.—Scatter diagram of calcium versus fluoride for analyses of ground water in southwest and northwest Florida and graphs showing the relation of calcium to fluoride in solutions of different ionic strength saturated with respect to fluoride.

supersaturated with respect to fluorite. The tendency for the water to reach equilibrium and satisfy the solubility product should cause chemical precipitation of calcium fluoride in the aquifer and thereby remove

fluoride from solution. Both chemical precipitation and dilution should act to reduce the concentration of fluoride.

If the assumption is made that, because of its slow movement, ground water has sufficient time to come to equilibrium with the solid phases it contacts, and that an unlimited supply of calcium is available from the limestone aquifer, then the concept of chemical equilibrium can aid in making a first approximation about the fate of a fluoride contaminant that might be introduced into the aquifer.

Many other factors must be considered to predict what might happen to a contaminant after it enters ground water. LeGrand (1965) discussed the difficulties involved in making such predictions, and summarizes the present knowledge about the patterns of contaminated zones of water in the ground. His interpretations of various types of contaminated zones are generally some modification of a rectangular prism or a wedge which forms in the upper part of the zone of saturation. LeGrand states (p. 83): "Two opposing tendencies need be in focus before an evaluation of contaminated zones is undertaken: (1) the tendency of contaminants to be entrained in ground water flow and (2) the tendency for contaminants to be attenuated to varying degrees by dilution in water, decay with time, or some other 'die-away' mechanism, and sorption on earth materials." The mechanisms of attenuation of a fluoride contaminant in a limestone aquifer would be largely dilution and chemical precipitation of fluoride as calcium fluoride.

MONITORING OF FLUORIDE IN GROUND WATER

The areal (fig. 11) and vertical (figs. 13 and 14) distribution of fluoride in ground water gives no indication of any significant contamination of the ground-water supplies. Because there is presently (1966) no indication of widespread contamination, any feasible system of monitoring fluoride in ground water that was designed to include all the phosphate mining area would probably be ineffective and fail to quickly detect a contaminating mass of fluoride should it enter the aquifer.

If any system of monitoring any contaminant in ground water is to be effective, it must be capable of quickly detecting the contaminant near its point of entry into the ground. Therefore, any system of monitoring fluoride in ground water that will quickly and effectively detect any contamination of the ground-water supplies should be designed individually around the greatest potential hazards, the chemical plant settling lagoons.

The lagoons may cover several hundred acres. A detailed investigation of one or more lagoons would be desirable to (1) firmly establish

whether there is leakage to the aquifer or through the banks to the surrounding area, (2) determine effects of leakage, if any, on the gradient of the water table and piezometric surface, and (3) acquire data to prepare hydrogeologic maps adequate for making accurate predictions of local ground-water flow patterns. After sufficient detail of the hydrology in the vicinity of a lagoon is established, monitoring wells could be located so they would be most effective. They should be along the down gradient side of the lagoons with respect to the piezometric surface and the water table and be constructed to enable collection of water samples from the surficial materials, the top of the artesian aquifer and from a deeper zone in the aquifer.

SUMMARY

Fluoride concentrations of several parts per million occur in the surface waters of the Alafia and Peace River basins as a result of waste water disposal from the mining and processing of phosphate deposits. The Alafia River carries more fluoride waste than the Peace River and usually has a fluoride concentration several times as high as the Peace River.

The Alafia River discharged about 4,000 tons of fluoride from October 1964 to September 1965 compared to about 900 tons for the Peace River. During this same period, the fluoride concentration of the Alafia River at Lithia ranged from 3.2 to 30 ppm and the Peace River at Arcadia ranged from 0.6 to 2.2 ppm. There was no apparent loss of fluoride from the river to the ground water.

Fluoride occurs naturally in ground water in southwest Florida in concentrations from 0.0 to about 4.0 ppm. The concentration of fluoride in ground water is generally lowest in northern and central Polk County and is generally highest in the southern part of the area. There is both areal and vertical variability in fluoride concentrations. The highest concentrations are usually found in water from the Hawthorn Formation and Tampa Formation of Miocene age. The source of the fluoride is apparently the phosphate minerals within the formations.

The waste water in the settling lagoons at the phosphate chemical processing plants contains fluoride concentrations of several hundred ppm. Fine waste material deposited in these lagoons appears to retard leakage of the waste water to the aquifer. The lagoons are a potential pollution hazard if the fine waste material is not effective in preventing leakage, or if solution of the underlying limestone should allow collapse of the surface materials into solution chambers to breach the fine deposits. If such should occur, the fluoride could contaminate the ground-

water supplies for several miles from the point of entry into the aquifer.

Any system of monitoring fluoride in ground-water should be designed about the chemical plant settling lagoons to best detect a possible fluoride contaminant. A detailed investigation is desirable to firmly establish the geologic-hydrologic conditions in the vicinity of one or more of the lagoons. Such an investigation would establish the best procedures to be followed in designing an effective monitoring system for ground water. Experimental investigation of the fate of solutions containing high concentrations of fluoride when they enter a limestone environment is esssential to predict the effects on ground water should water from the lagoons enter the ground.

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