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THE EFFECT OF CARBONATE KARST TERRAIN  
ON WATER QUALITY

by

ROBERT RUSSELL KILGO - 1935

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A

THESIS

submitted to the faculty of the

UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN CIVIL ENGINEERING

Rolla, Missouri

1965

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## ABSTRACT

The ever increasing use of water and unabated pollution of streams have made necessary increased research efforts into the quality and quantity of the available national water resources. Karst terrain is prevalent in several sections of the United States, however, little work has been done on the effect of this topography on water quality.

The purpose of this investigation was to determine the effect of carbonate karst terrain on the quality of water. The Meramec spring area, east of Rolla, Missouri, was selected for study. This area was underlain with dolomite formations and contains both karst and non-karst drainage basins which made possible comparative studies. Stream, well, and spring waters from the study area were characterized using chemical, physical, and bacteriological determinations and the results obtained were evaluated.

Water in carbonate karst terrain was found to contain primarily calcium and magnesium bicarbonate, with nitrate ions and iron often reaching significant concentrations in underground supplies. Increases in the mineral content of stream waters at some locations after rainfall indicated that subsurface discharges were feeding the streams. Direct pathways from the surface to the groundwater were established when coliform organisms were found in the spring and well water samples.

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## I. INTRODUCTION

The population explosion in the United States and the ever increasing use of water for industrial, agricultural, municipal, and recreational purposes has prompted the United States Senate Select Committee on National Water Resources (1) to predict in 1961 that the estimated 300 billion gallons of water required per day at that time would approximately double by 1980 and triple by the year 2000. Although the United States has vast water resources, the geographic distribution of these resources and the uncontrolled pollution of surface waters have already caused problems in several areas. To meet the present and especially the future water demands, there is a need for stream pollution abatement, greater utilization of underground water supplies, and increased research effort on the quality and quantity of the national water resources.

An area of investigation which is of interest to many sections of the United States, and which has received little attention to date, is the effect of carbonate karst terrain on water. Extensive portions of this country are underlain with karst terrain; among them is the state of Missouri where karst development is prevalent in the large metropolitan areas of St. Louis and Springfield, the counties of Boone, Phelps, Pulaski, Dent, Shannon, St. Genevieve, Perry, Howell, Wright, and the Bennett Springs area (2).

The karst topography received its name (3) from the region known as Karst on the eastern side of the Adriatic Sea

in Yugoslavia where the terrain consists of limestone rocks which have become dissolved by groundwaters causing large sinkholes to develop. Much of the drainage is underground and it is characterized by dry streams and streams which disappear and later reappear as large springs. The name of karst has been applied to other areas of the world whose topography is similar to this region.

The development of karst topography occurs where limestone and dolomite are dissolved by the action of water containing carbon dioxide; the rate of solution is enhanced by increased amounts of this chemical (4). Long and continued solvent action on these formations by the water as it percolates through the ground creates caverns and solution cavities by carrying away significant portions of the calcium and magnesium carbonate of the rocks. Caverns may become so enlarged by this solvent action that their roofs become too thin to support the overburden and collapse forming sinkholes (5).

Although the effect of karst terrain on water quality has not been thoroughly investigated at the present time, certain of its aspects may be anticipated.

Water passing through limestone or dolomite formations would become enriched with the calcium and magnesium of the rocks. Other ions which exist as impurities in the terrain may also be carried into solution. Solution cavities and other openings which might exist in bedrock would make the pollution of groundwater from the surface a distinct

possibility due to the loss of natural purification by filtration through the ground. Sinkholes would be another direct route for contamination to reach underground water supplies.

The surface water characteristics might be changed through surface and subsurface discharges. The mineralization and biological quality of the water would undoubtedly vary as a result of these sources.

The object of this study was to determine through systematic investigation the effect of carbonate karst terrain on the chemical, physical, and biological quality of surface and underground water and its availability for domestic, industrial, and recreational use.

The Meramec spring area, east of Rolla, Missouri, was chosen for study. This area was known to be partially underlain with carbonate karst topography and included karst and non-karst drainage basins which made possible comparative studies. The quality of the surface and underground water in the study area was extensively investigated and the results correlated.

## II. REVIEW OF LITERATURE

The literature review was made to determine previous research studies conducted on the effects of karst terrain on water resources. Little material was found, all of which was contributed by Russian and Eastern European investigators. Due to language barriers the information derived was of limited value because only the abstracted contents of these publications were available in English.

Koldyazhnaza (6) studied over a period of years 2000 samples of surface and subsurface waters from the Sos avi-Vagranka watershed and adjacent regions in order to determine the solubility of limestones in the area and quantitatively evaluate karst formations. From the data collected, Koldyazhnaza found that the water which flowed through karstized limestone became enriched with calcium and bicarbonate ions. He calculated that 1800 to 5000 tons of calcium carbonate was leached from the area each year.

Gorbunova (7) studied the chemical composition of karst waters in the Ufa region and found it to be controlled by the same factors contributing to the formation of other groundwaters. The lithology of the Ufa area consisted of carbonate and sulfate rocks, and its main feeding source was the Ufa plateau where the waters moved westward in a territory containing gypsum. The composition of the waters was found to change gradually and regularly from the carbonate to the sulfate zone. Four components of the waters were determined, and were the calcium, magnesium, bicarbonate, and sulfate ions.

Gorbunova separated the waters into five groups: "(1)HCO<sub>3</sub>-Ca-Mg, (2)HCO<sub>3</sub>-Ca-SO<sub>4</sub>, (3)HCO<sub>3</sub>-SO<sub>4</sub>-Ca, (4)SO<sub>4</sub>-HCO<sub>3</sub>-Ca and (5)SO<sub>4</sub>-Ca-HCO<sub>3</sub>". The sulfate ion content of these waters was found to be less than 27, 22 to 100, 100 to 350, 330 to 700, and 700 to 1600 mg/l, respectively.

Gorbunova (8) surveyed a large number of gypsum lakes in the Ufa area and the Ufa-Solikamsk syncline and found the dissolved solids content of their waters to range from 60 to 2076 mg/l and at these two values consist of the following ions:

Dissolved solids, mg/l.....	60	2076
Calcium, mg/l.....	8	372
Magnesium, mg/l.....	5	148
Sodium and Potassium, mg/l.....	3	48
Bicarbonate, mg/l.....	36	244
Sulfate, mg/l.....	-	1248
Chloride, mg/l.....	7	49

Gorbunova (9) also studied the effect of gypsum karst on the chemical composition of waters in oxbow lakes in the vicinity of the village of Ust Kishert and found the mineral composition to vary from 118 to 1488 mg/l. He reported that "As mineralization increases the composition of the water changes from HCO<sub>3</sub>-Ca-SO<sub>4</sub> to HCO<sub>3</sub>-SO<sub>4</sub>-Ca (or Na), SO<sub>4</sub>-HCO<sub>3</sub>-Ca, and SO<sub>4</sub>-Ca." Bicarbonate, calcium, and sulfate ions were the main ions in the water.

Vaschenko (10) reported that the hydrochemical conditions of carbonate-gypsum lakes on the Chusov peninsula in

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\*The writer of this thesis has not been able to determine the meaning of the water groups given by the abstractor and can only surmise that the ions indicated were listed in decreasing order of concentration.

the Kama reservoir were quite varied and depended upon depth and the distance from the shore toward the center of the reservoir. "All water types were  $\text{HCO}_3$ ; Na and  $\text{NO}_3$  associations were observed in only 2 cases.  $\text{HCO}_3$ -Ca,  $\text{HCO}_3$ -Na and  $\text{HCO}_3$ - $\text{NO}_3$  waters predominated the lakes. Cl was often the 3rd component." The presence of chloride and nitrate ions was attributed to contamination and decomposition of organic substances. The pH of the waters ranged from 6 to 7.5.

Maksimovich (11) studied the chemical composition of underground karst lakes in the U.S.S.R. and found that their hydrochemical phases depended on mineral concentration. The calcium bicarbonate, calcium sulfate and bicarbonate, and calcium sulfate phases corresponded to mineral concentrations of less than 550, 650 to 1250, and greater than 1250 mg/l, respectively.

Kashtavov, et al (12) reported the calcium, magnesium, sodium and potassium, chloride, sulfate, bicarbonate, and total hardness content of 2800 small rivers in the Tatar Autonomous S.S.R. This study was made primarily to determine the karst development of that area and its effect on the engineering properties of the soils. They reported that because the chemical composition of those rivers in summer and winter depended greatly on subsurface discharges, changes in the river waters could be used in the application of soil mechanics in the territory.

Ernst (13), on the basis of the carbon dioxide content of the normal air and the carbon dioxide content of the air at

the temperature generally prevailing in Hungarian wells, concluded that the equilibrium concentration of calcium was proportional to the cube root of the carbon dioxide partial pressure. He also assumed that additional carbon dioxide was obtained from the humus soil resulting in a water which was significantly harder than would have been anticipated on the basis of the previous formula.

Although only a small amount of research material was found in the literature, certain conclusions of value to this investigation were drawn. Water which flowed through karst topography became enriched with the principal ions of which the rock was composed and the composition of the water changed as the rock formations changed. The mineral concentration of underground carbonate karst waters was also found to be less than 550 mg/l.

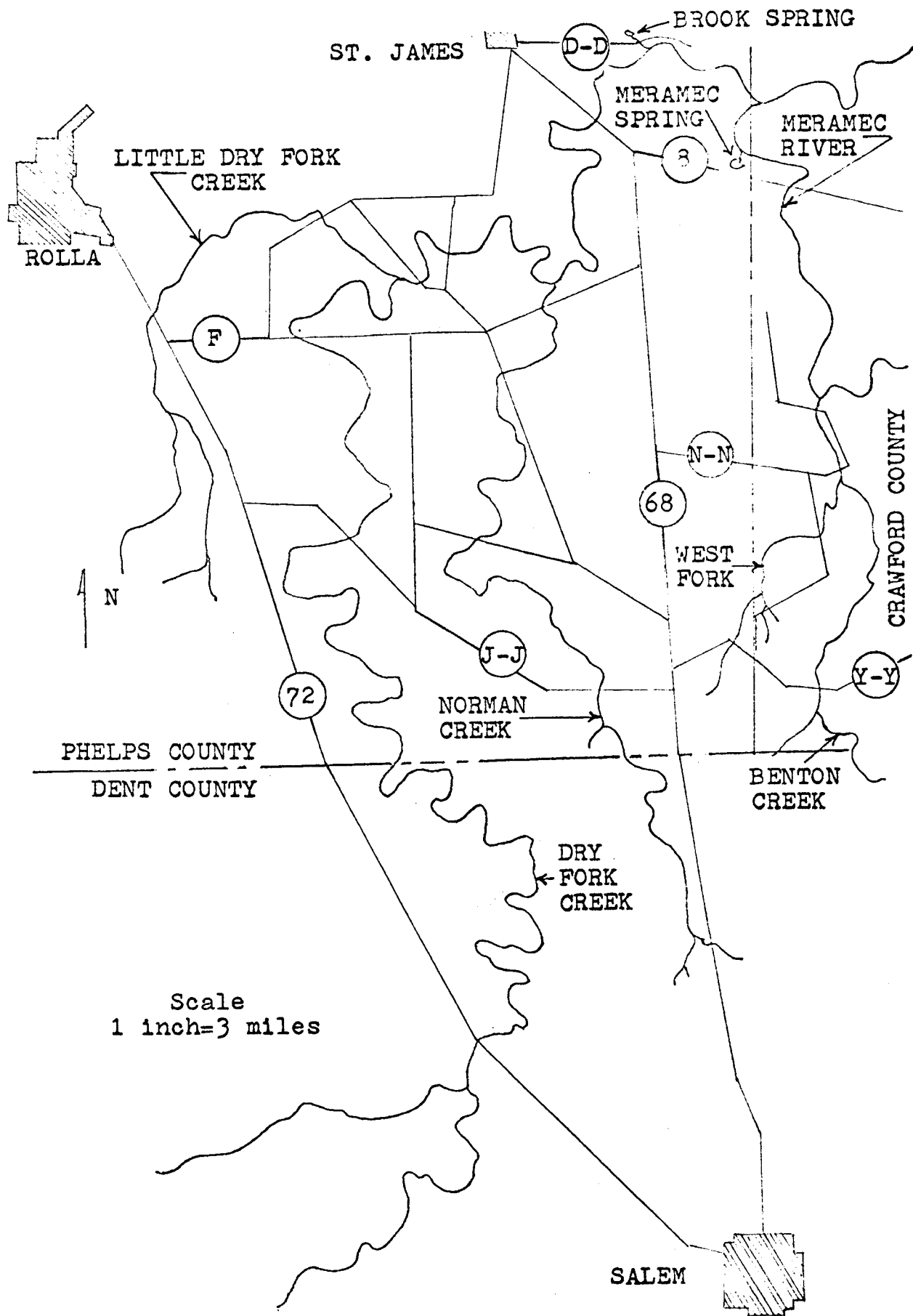


### III. MODE OF STUDY

#### A. FIELD AREA

The field area selected for this investigation was a carbonate karst terrain east of Rolla, Missouri and included portions of Phelps, Crawford, and Dent counties. A map of this area is shown in Figure 1. The chemical, physical, and biological quality of numerous water samples obtained from the Dry Fork, Little Dry Fork, Norman, Benton, and West Fork Benton creeks as well as from the wells and springs in the immediate vicinity was analysed and the results evaluated. This field area was chosen because karst topography existed in the Dry Fork and Norman creek drainage basins, while adjacent to these basins Benton creek had perennial flow and was not considered karst. In addition, the streams in the area were tributaries of Meramec river, one of the major rivers in Missouri, while the water lost in the karst topography was believed to contribute part of the flow of the Meramec spring which supplies part of the base flow of the Meramec river. The convenience afforded by the short distance of the area from the University of Missouri at Rolla was also considered an asset for sample collection.

After the area had been selected, several reconnaissance field trips were made to it in order to decide on sampling points. Property owners were also contacted and the permission to sample well or spring supplies along with available access points to the streams governed the selection of the initial sampling locations.



Scale  
1 inch=3 miles

FIGURE 1. FIELD AREA

## B. SAMPLING POINTS

The stream sampling points were originally selected uniformly over the area of investigation. However, after the first sampling trips had been made it became evident that the upper portion of Dry Fork and most of Norman creek were dry, except during and immediately following heavy rainfalls. Only Little Dry Fork, and the lower portions of Dry Fork, Benton, and West Fork Benton creeks were found to have perennial flow and, consequently, intense sampling over these areas was undertaken.

The well points were chosen near the stream drainage areas, and whenever possible those which were on file with the Missouri Geological Survey were employed. To detect any correlation which might have existed between the well and stream waters the distance of the well sampling points to the nearest stream was maintained below approximately 1500 feet. The wells sampled were all of drilled construction and pumps were used for water extraction. In all cases the water was sampled at a water faucet.

Springs in the immediate study area were also sampled as another source of underground water. The Meramec spring was of particular interest because it has been postulated that much of the water lost in the area may eventually resurface at this point.

## C. NUMBERING SYSTEM FOR SAMPLING POINTS

A four digit numbering system was used to locate and identify the sampling points with ease. It was designed to

enable the addition of points without disruption of the system.

The first digit located the sampling point by stream drainage area as follows:

- 1 - Dry Fork Creek
- 2 - Little Dry Fork
- 4 - Norman Creek
- 7 - Benton Creek
- 8 - West Fork Benton Creek

Numbers were left out to provide space for tributaries of the major streams to be added at a later time.

The second digit indicated the type sample which was collected:

- 1 - Stream
- 2 - Spring
- 3 - Well

The third and fourth digits identified the location of the sampling point by its position along the stream. The low numbers began at the mouth of the stream and increased upstream to the origin.

#### D. SAMPLE COLLECTION

Three separate samples were collected at each point to enable the determinations of the chemical, physical, and bacteriological quality of the water and measure its dissolved oxygen content. Special precautions had to be taken in collecting the bacteriological and dissolved oxygen samples.

##### 1. General Sample.

The main sample, which was used for the determination of the physical and chemical characteristics of the water, was

collected in a 5 pint glass bottle equipped with a plastic cap. The bottle had been previously cleaned with a chromic acid cleaning solution consisting of potassium dicromate dissolved in sulfuric acid, and was thoroughly rinsed with tap and distilled water.

At the well sampling points water was allowed to run until the system had been flushed out and a representative sample was insured, before filling the bottle. At streams and springs the bottle was partially submerged and the water allowed to flow in. The samples were collected at locations which seemed to be most representative of the particular point.

The samples were stored in a 5° C walk-in incubator until the completion of the analyses in order to provide as much assurance as possible that the water quality was not changed.

## 2. Bacteriological Sample.

It was necessary to obtain this sample free from outside contamination; consequently, it was collected in sterile bottles. Wide mouth bottles of 125 ml capacity which had been thoroughly cleaned, stoppered, wrapped in kraft paper, and sterilized in dry heat at 170° C for one and one-half hours were used.

Before collection of well samples, the faucet was flamed with a propane torch to kill any microorganisms present and the water was allowed to run for a period of three to four minutes.

When sampling streams and springs the bottle was held with the mouth forward and quickly passed through the water against the direction of flow to guard against contamination from the hand of the sampler.

After collection, the stopper with the kraft paper cover was replaced and tied securely to avoid any outside contamination.

The bacteriological samples were analysed as soon as possible after collection, however, they were refrigerated at 5° C upon return to the laboratory to retard any bacterial action until the analyses were made.

### 3. Dissolved Oxygen Sample.

Precautions were necessary in the collection of this sample to insure oxygen was neither lost nor introduced into the water. A standard 300 ml biochemical oxygen demand bottle constructed with a well which extended above its neck was used. After the sample had been collected and the stopper replaced, the well was filled with water to insure an airtight seal until the oxygen in the sample had been fixed.

Fixing was accomplished in the field by addition of 2 ml each of manganous sulfate and alkali-iodide-azide in that order. When oxygen was present some of the  $Mn^{++}$  was oxidized to  $MnO_2$  and precipitated as a brown floc. To insure that all the oxygen was converted to the stable form, the sample was shaken vigorously 20 times and the floc allowed to settle, then 2 ml of sulfuric acid was added and in its presence  $MnO_2$  oxidized the iodide to free iodine.

The sample was again shaken to dissolve the floc. This procedure was employed to arrest all biological activity which could change the oxygen content of the sample. The liberated iodine was stable and could be titrated when the sample was brought to the laboratory.

When dissolved oxygen samples were taken from a faucet a rubber tube was inserted from the faucet to the bottom of the bottle and the water in the bottle was displaced several times. The tubing was slowly withdrawn while the water was kept running and then the bottle was tightly stoppered. The water-seal well was filled with water until the oxygen in the sample was fixed.

Collection of samples from springs and streams presented a problem because they were not deep enough to use a standard collection apparatus and a galvanic cell oxygen analyser was not available for use. This made it necessary to submerge the bottle by hand as carefully as possible and allow it to fill beneath the water surface. The sample was then treated in the manner explained above.

#### E. PARAMETERS AND THEIR MEASUREMENT

Several parameters were employed in order to determine the characteristics of the various waters and successfully evaluate the effect of the carbonate karst terrain on water quality. In general the procedures outlined in the Standard Methods for the Examination of Water and Wastewater (14) were used. Certain determinations were so lengthy however that short-cut methods considered to be entirely satisfactory were substituted.

## 1. Calcium.

Calcium is one of the major minerals in the dolomite formation which comprised a large percentage of the rocks which underlie the area under investigation. Since dolomite is known to be dissolved by water flowing in karst topography, calcium was expected to be one of the main cations in the water. Calcium is one of the two principal divalent metals which impart hardness to water.

Calcium was determined by the EDTA Titrimetric method (14, p.67) using special reagents supplied by the Hach Chemical Company, Ames, Iowa. One ml of 8N potassium hydroxide solution and 0.1 gram of Calver II indicator powder were added to 50 ml of sample. The sample was then titrated with standard EDTA (disodium dihydrogen ethylenediaminetetracetate) solution of which one ml was equivalent to one mg calcium carbonate. Calcium was calculated by multiplying the number of ml of titrant by 1000/50 and was expressed as mg/l of equivalent calcium carbonate.

## 2. Magnesium.

Magnesium is also plentiful in dolomite formations and is the other major divalent metal which causes hardness in water. This cation was expected to be present, in conjunction with calcium, in significant concentrations in the waters of the study area.

Magnesium was computed using the calculation method employed by the United States Geological Survey (15, p.197). The procedure consisted of subtracting calcium from the total



hardness to obtain magnesium. Since both hardness and calcium were measured as mg/l of equivalent calcium carbonate, magnesium was also expressed as mg/l of equivalent calcium carbonate.

### 3. Hardness.

Hardness is defined as that property of water which requires large amounts of soap to produce lather. It is therefore generally unacceptable from an economic standpoint due to the high soap consumption it causes. Hard water is also associated with scaling problems.

Hardness was measured by the EDTA Titration Method (14, p.133) using special reagents prepared by Hach Chemical Company, Ames, Iowa. Fifty ml of sample to which one gram Univer II indicator powder had been added was titrated with standard EDTA solution. Hardness was calculated by multiplying the ml of titrant used by 1000/50 and was expressed as mg/l of equivalent calcium carbonate.

### 4. Alkalinity.

Alkalinity in natural waters is mainly due to the bicarbonate ions present, however, in certain cases it is also caused by the presence of carbonate and hydroxide ions. Alkalinity plays an important part in corrosion control and imparts buffering capacity to water. Because of the abundance of carbonate minerals expected in the carbonate karst terrain of the field area, it was believed that the solvent action of water containing carbon dioxide would make bicarbonates one of the major anions in the water.

The potentiometric titration method (14, p.44) was used to determine alkalinity; a Beckman Zeromatic pH meter was employed. The electrodes were immersed in a 50 ml volume of the sample which was then titrated with 0.02N sulfuric acid to the equivalence pH point of 4.8. This equivalence point was selected because it was recommended for alkalinities in the range of 150 mg/l as calcium carbonate which was anticipated in these waters. The ml of sulfuric acid used in the titration were multiplied by 1000/50 to obtain alkalinity as mg/l of calcium carbonate.

#### 5. Chloride.

Chloride ions are found in natural waters and their concentration usually increases with increased mineralization. Significant quantities are added by sewage or sewage treatment plant effluent discharged into receiving streams. Chlorides may impart a brackish taste if present in excessive quantities. The United States Public Health Service Drinking Water Standards (16, p.7) limit the chloride concentration in drinking water to 250 mg/l. In the past this ion has been used as a basis for detecting contamination of groundwaters.

Chloride was determined using a Beckman Zeromatic pH meter equipped with a silver billet electrode coated by electrolysis with silver chloride\* and a standard calomel reference electrode. The special chloride electrode was

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\*Silver Electrodes, Beckman Instruments 1203-A.

designed for use with an expanded scale pH meter and because the model available was of the standard type it became necessary to expand its millivolt scale. The procedure outlined by Keegan and Matsuyama (17) was employed. It involved the addition of an external resistor, plugged in the thermocompensator jack, to increase meter sensitivity. Difficulty was encountered in selecting the proper size resistor for best scale expansion. Finally, a 1400 ohm resistor was found to be the optimum size for millivolt readings in the range of 0 to 280 which enabled measurement of chloride ion concentrations from 1.0 to 10,000 mg/l.

The resistor was plugged into the thermocompensator of the pH meter. The "1400 millivolt" button was depressed and the "read" button was engaged when readings were taken.

A calibration curve was prepared using a standard solution of sodium chloride from 1.0 to 10,000 mg/l; the readings were plotted on semilogarithmic graph paper and gave a straight-line. Prior to a series of determinations, the instrument was calibrated against two chloride ion solutions of known concentration. Readings were then taken on the unknown solutions and their chloride content was determined from the calibration curve. Recoating of the silver billet electrode became necessary when the proper millivolt potential differential, as shown on the calibration curve, was not measured when checking solutions of known concentrations.

## 6. Ammonia Nitrogen.

Nitrogen is an essential element for the growth of microorganisms, and is therefore important in stream pollution and self purification. Ammonia nitrogen is a product of microbial activity and has been used as indication of recent sanitary pollution (14, p.167). In quantities as low as 2.5 mg/l it has been found to be detrimental to fish (15, p.211). Ammonia nitrogen is important in water treatment from the standpoint of chlorination.

Ammonia nitrogen was measured by direct nesslerization (14, p.173). One hundred ml of sample was treated with 2 ml of zinc sulfate and 0.5 ml of hydroxide solution to precipitate any substances which might have caused turbidity with the nessler's reagent. Two ml of nessler's reagent was then added to 50 ml of the clear supernatant, the sample was mixed, and the yellow-green color was measured spectrophotometrically after 30 minutes using a Bausch and Lomb Spectronic 20 colorimeter at a wavelength of 410 m $\mu$ . The ammonia nitrogen content was computed using a calibration curve.

## 7. Nitrate Nitrogen.

Nitrate nitrogen is the end product of the aerobic decomposition of ammonia nitrogen. Nitrates in water have been associated with pollution because they are one of the major components of human and animal excreta. When present in large quantities nitrate causes methemoglobinemia in infants (15, p.216), and therefore, its concentration is limited to 45 mg/l (as NO<sub>3</sub>) in drinking water (16, p.7). Nitrates are also important for the growth of algae in water.

Nitrate nitrogen was determined by the phenoldisulfonic acid method (14, p.175). A sample, containing less than 2 mg/l nitrate nitrogen, was evaporated to dryness on a water bath, after removal of nitrites and chlorides which would have interfered with the analysis. The residue was dissolved in 2 ml of phenoldisulfonic acid and treated with 7 ml of ammonium hydroxide to full color development. The color was measured spectrophotometrically using a Bausch and Lomb colorimeter at 410 m $\mu$  and the nitrate nitrogen content computed by means of a calibration curve.

#### 8. Nitrite Nitrogen.

Nitrite nitrogen is the intermediate stage in the nitrogen cycle between ammonia and nitrate nitrogen. Its presence is considered an indicator of organic pollution (15, p.221).

Nitrite nitrogen was measured by the diazotization method (14, p.180). The procedure consisted of adding 1 ml of sulfanilic acid to 50 ml of a sample clarified, when necessary, with an aluminum hydroxide solution. After 3 to 10 minutes 1 ml of naphthylamine hydrochloride reagent and 1 ml of sodium acetate buffer solution were added. At the end of 30 minutes, the reddish-purple color developed was measured spectrophotometrically at 520 m $\mu$  and the nitrite nitrogen concentration found using a calibration curve.

## 9. Orthophosphate.

Phosphorus together with nitrogen is necessary for the growth of algae and other microorganisms. Algae, although essential in sewage lagoons, are troublesome in water supplies because they impart undesirable taste and odors. Phosphorus determinations are useful in assessing possible biological activity in surface waters and important in stream pollution studies (18, p.330).

Phosphates were determined by the amino naphthol sulfonic acid method (14, p.199). Two ml of a strong acid solution containing ammonium molybdate followed by 2 ml of amino naphthol sulfonic acid solution was added to a 50 ml sample. The blue color developed was measured spectrophotometrically at a wavelength of 690 m $\mu$ . A red filter was necessary for use at this wavelength. The orthophosphate present was determined from a calibration curve.

## 10. Iron.

Iron is seldom present in large quantities in water supplies unless dissolved oxygen is absent (18, p.311). Even small concentrations are troublesome however, since it stains clothing and porcelain and at high concentrations causes a noticeable taste (15, p.183). The U.S. Drinking Water Standards (16, p.7) limit its concentration in drinking water to 0.3 mg/l.

This determination was performed by the phenanthroline method (14, p.140). The procedure consisted of reducing iron to the ferrous state by boiling for 5 minutes a 50 ml

sample to which 2 ml of hydrochloric acid and 2 ml of hydroxylamine solution had been added. The sample was cooled and 2 ml of phenanthroline was added to develop an orange red color which was measured spectrophotometrically after 15 minutes at a wavelength of 510 m $\mu$ . The iron present was determined through a calibration curve.

#### 11. Manganese.

Like iron, manganese requires the absence of dissolved oxygen to be present in large amounts in water supplies. Manganese causes objectionable stains to laundry and plumbing fixtures even in small amounts (15, p.205), therefore, its concentration should not exceed 0.05 mg/l in drinking water (16, p.7).

The waters were analysed for manganese according to the persulfate method (14, p.155). This method consisted of the addition of 5 ml of a special solution containing mercuric sulfate, nitric acid, phosphoric acid, and silver nitrate to 90 ml of sample. One gram of ammonium persulfate was then added and the sample was brought to boiling in 2 minutes, quickly cooled and the purple color formed measured spectrophotometrically at 525 m $\mu$ . The manganese content was then found using a calibration curve.

#### 12. Sodium.

Sodium is usually found in very low concentrations in carbonate rocks and normally minor amounts of the metal are present in waters associated with the rocks (19, p.86). Sodium is added in significant amounts to water by discharge

of domestic and industrial wastes, or by softening with ion exchange units. Although not very important from the standpoint of natural waters, it was determined to enable a more complete balance of the cationic content of the waters.

Sodium was measured using a Beckman pH meter equipped with a special sodium ion electrode\* and a calomel reference electrode. The millivolt scale on the pH meter was expanded as described in the chloride determination. A calibration curve was prepared using solutions of known sodium chloride concentrations and the results were plotted on semilogarithmic graph paper. Before measuring an unknown sample the instrument was checked against two solutions of known sodium ion strength and the asymmetry control adjusted, if necessary. The millivolt reading was then obtained for the sample and the sodium concentration determined from the calibration curve. In all cases, care was taken to insure that the pH values of the solutions tested were between 7 and 10 because values outside these limits gave erratic results.

### 13. Silica.

Silica has little physiological significance to human, livestock, or fish life and most industries can tolerate silica at the concentrations normally found in most natural waters which are often below 10 mg/l; however, silica is particularly harmful in boiler feed waters (15, p.259).

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\* Laboratory Sodium Ion Electrodes, Beckman Instructions 1155-B.



Silica was determined by the molybdate blue method used by the U.S. Geological Survey (15, p.259). This method consisted of adding 5 ml each of 0.025N hydrochloric acid, five percent ammonium molybdate, one percent sodium salt of EDTA, and 10 ml of seventeen percent sodium sulfite to a 10 ml sample. The molybdate blue color developed was measured spectrophotometrically at a wavelength of 700 m $\mu$ . A red filter was utilized at this wavelength. The silica content was found from a previously prepared calibration curve.

#### 14. Dissolved Oxygen.

Dissolved oxygen is essential in water from the standpoint of fish and other aquatic life and is needed to maintain the aerobic stabilization of the wastes discharged to streams (self purification). Surface and underground water without dissolved oxygen may contain significant amounts of troublesome iron and manganese (18, 261).

The dissolved oxygen content of the samples was determined by the Alsterberg (azide) modification of the Winkler Method (14, P.309). The oxygen in the sample was fixed in the field as described in Part D. Sample Collection (p.13). The free iodine in the fixed samples was titrated in the laboratory with 0.025N sodium thiosulfate using starch as the indicator and the dissolved oxygen content computed.

#### 15. Chemical Oxygen Demand.

Chemical oxygen demand (COD) is the amount of oxygen needed to chemically stabilize a waste and involves the

oxidation of the organic matter present to carbon dioxide, water, and other compounds. This test was utilized to provide a measure of the amount of organic material present and enable the detection of any unusual wastes which might have been discharged to the streams.

The test was performed by the dilute method outlined in Standard Methods (14, p.399) with modifications suggested by Moore and Walker (20). The method consisted of refluxing the sample with potassium dicromate in a sulfuric acid solution for two hours. The excess dicromate was then titrated with 0.025N ferrous ammonium sulfate using ferroin indicator. The departure from Standard Methods entailed the use of 70 rather than 50 ml of sample and 2.5 ml of 0.25N potassium dicromate instead of the usual 25 ml of 0.025N solution. In addition, the outlets of the reflux condensers were plugged with glass wool and the wash water was acidified with one ml of concentrated sulfuric acid per liter. A distilled water blank was prepared in the same manner as the samples. The chemical oxygen demand was calculated from the amount of dicromate used after the blank correction had been applied.

#### 16. Anionic Surfactants.

Surfactants are widely used for domestic purposes and therefore are present in the sewage at significant concentrations. The microbial treatment of sewage has little effect in breaking down certain forms of these detergents.

This feature can lead to undesirable stream conditions through the discharge of treatment plant effluents containing synthetic detergents and the entrance of surfactants into groundwater thus effecting the drinking water quality.

The determination for anionic surfactants was performed in accordance with Degens modification of the methylene blue method (21). Ten ml of sample in a separatory funnel was treated with one ml of 5N sulfuric acid, 100 ml of distilled water, 5 ml methylene blue solution and 10 ml of chloroform. The sample was shaken for one minute and the chloroform layer was collected in a nessler tube through a funnel containing glass wool; the chloroform extraction was repeated twice using 10 ml of chloroform each time. The volume in the nessler tube was made up to 50 ml with chloroform. The resultant mixture was read at 600 m $\mu$  using a Bausch and Lomb colorimeter and the surfactant concentration was determined by means of a calibration curve.

#### 17. Color.

Most color is imparted to natural waters by decaying vegetation (18, p.192). The presence of color in water is significant for aesthetic reasons and because of the public's association of color with impurity. The U.S. Public Health Service Drinking Water Standards (16, P.6) limit color to 15 units in drinking water.

Color analyses were made by visual comparison with standards prepared from potassium chloroplatinate and

cobaltous chloride (14, p.111). The sample was placed in a nessler tube and the color of the standard which most closely approximated that of the sample recorded.

#### 18. Turbidity.

Turbidity is the optical property of water which inhibits the transmission of light; suspended particles reflect light rays and result in a turbid water (18, p.185). The presence of turbidity in water is undesirable from many standpoints and the U.S. Public Health Service Drinking Water Standards have set a limit of 5 units for drinking water (16, p.6). Even higher standards are required for waters used by several industries (15, p.289).

Turbidities in excess of 25 units were measured using the Jackson candle turbidimeter (14, p.261). The sample was carefully poured into a calibrated glass tube above the standard candle flame until the image of the flame just disappeared. The tube was removed and the turbidity read directly in units. When turbidities less than 25 units were encountered, the bottle standards method was used (14, P.261). The sample was placed in a bottle similar to those containing standards having known amounts of turbidity. The sample and the standards were shaken vigorously and the sample compared to the standards. The turbidity of the sample was recorded as that of the standard which produced the same visual effect.

#### 19. Total Residue.

This term is also referred to as the total solids and is important in determining the suitability of a water supply for domestic and industrial use. A high solids content is generally associated with a hard water and if the water is to be softened the method utilized often depends on the concentration of solids present (18, p.304).

Total solids were measured (14, p.213) by evaporating 50 ml of sample in a tared porcelain dish on a steam bath. The residue was then dried at 103° C to a constant weight, cooled in a dessicator and the dish reweighed on an analytical balance. The increase in weight was used to compute the solids.

#### 20. Nonfilterable and Filterable Residue.

Filterable residue, often called dissolved solids, is a major parameter for the characterization of water supplies. It is a measure of the total chemical composition of a water. The limit placed on total dissolved solids in drinking water by the U.S. Public Health Service Drinking Water Standards (16, p.7) is 500 mg/l, however this limit can be exceeded if no other source of water is available. Nonfilterable residue, also referred to as suspended solids, is not usually determined in water because of the small amount generally found. However, this parameter is extremely valuable in polluted water where suspended solids indicate the amount of matter that could settle over a period of time through deposition and biological precipitation (18, p.306).

Suspended solids were measured (14, p.215) by filtering a known volume of water through a preweighed filter with pore sizes less than 0.5  $\mu$ . The filter and suspended matter were then oven-dried at 103° C, cooled and reweighed. The increase in weight was used to calculate the suspended solids. During drying and weighing the filter was placed in an aluminum foil dish.

Dissolved solids were determined by subtracting suspended solids from total solids. This method was chosen so that it would not be necessary to evaporate samples to obtain both the total and dissolved solids content and therefore reduce the time required for these determinations.

#### 21. pH.

pH is important to water resources for several reasons. In drinking water it should generally be maintained in the range of 6 to 10 units; in surface waters it should be maintained between 4.5 and 9 units to protect fish and other aquatic life; in water treatment it must be controlled in chemical coagulation, water softening, and corrosion control; in biological waste treatment it must be maintained at a level suited for microbial life.

pH was determined using a Beckman Zeromatic pH meter.

#### 22. Bacteriological Examination.

The importance of determining the sanitary quality of water is evident. It becomes of particular interest in karst terrain where solution cavities are present through

which surface contamination may find a direct route to underground supplies. The presence of the coliform group of microorganisms in a water supply implies direct contamination by waste material from men or warm blooded animals. Although the coliforms are not harmful in themselves, they originate in the intestinal tract of warm blooded animals and their presence may mean that pathogens are also present leading to the possibility of water borne disease.

The membrane filter technique (14, p.508) was used to test for the presence of coliforms. This method consisted of filtering a known amount of sample through a membrane filter having pore sizes of less than  $0.5 \mu$ . The filter was then placed in a petri dish on an adsorbent pad to which 2 ml of M-Endo Broth MF\* differential medium had been added. The petri dish was incubated in an inverted position for  $20 \pm 2$  hours at  $35^{\circ} \text{C}$  in 100 percent humidity. The coliform colonies developed were identified by their green metallic sheen and were counted. The volume of sample filtered was selected to produce between 20 and 80 coliform colonies and not more than 200 colonies of all types.

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\* A product of Difco Laboratories, Detroit, Michigan.

#### IV. PRESENTATION OF RESULTS

The quality of stream, well, and spring waters in the study area was analysed in order to determine the effect of the karst terrain environment on these supplies. The results of these analyses are presented in tabular form by sample points and each analysis is listed under the date the sample was collected. Tables with average results for each point are also given, while significant changes in water characteristics are pointed out in graphs. To simplify the presentation, the results are divided into three groups: (a) stream studies, (b) well studies, and (c) spring studies.

The water samples analysed for this study were collected during the months of June and July, 1965. Each set of tests required approximately six days from sample collection to completion.

##### A. STREAM STUDIES

The streams chosen for investigation were Dry Fork, Norman, and Benton creeks and their main tributaries. The Benton creek drainage area was not considered karst but was investigated to provide a basis for comparison.

A map of the area indicating the location of the stream sampling points is given in Figure 2. The location of these points is also described in Table XXIII, Appendix A. Sampling was initiated on Dry Fork creek at sampling point 1140 where the stream was fed by a water source referred to by local residents (22) as the "spring at the head of Stedman's lake". After several observations of the spring, it was



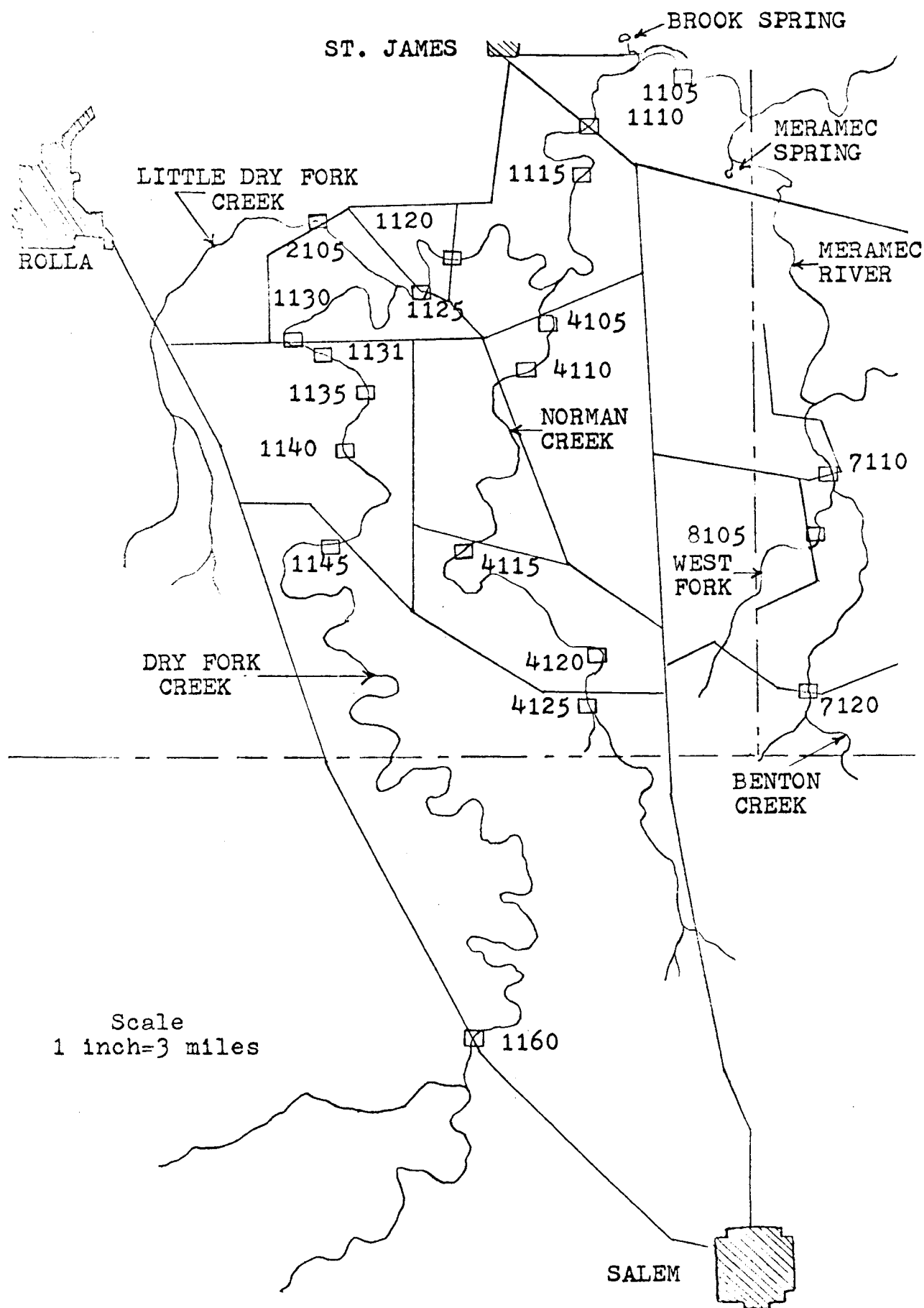


FIGURE 2. STREAM SAMPLING POINTS

concluded that the water was contributed to the stream primarily by seepage. Water was seen from point 1140 to the mouth of Dry Fork creek, while above this point the stream appeared to be dry. The absence of water in the Dry Fork creek above point 1140 was concluded after walking approximately two miles upstream from this point in the dry creek bed. Further investigation was made by checking the creek at all available access points to the Route 72 crossing. Figure 3a shows the "spring at the head of Stedman's lake". It was approximately 200 feet upstream from this spring that water was first observed on Dry Fork where it had backed up because of the non-uniform stream bed gradient. The location of this water is pictured in Figure 3b.

The characteristics of the Dry Fork creek water at the various points sampled are presented in Tables I through VII; in Table I average values are given. In general, the quality of the water fluctuated significantly between sampling points.

As previously stated point 1140 on Dry Fork creek derived its water from a spring. The water flowed at such a low velocity that it was difficult to detect movement. Abundant decaying vegetation made it highly colored. This decaying material was thought to be the main source of the chemical oxygen demand measured. A significant number of coliforms were present and their presence was attributed to the cattle droppings seen in the vicinity. The water at this sampling location was moderately hard and contained a notable quantity of iron. Its dissolved oxygen content was moderately high, while the turbidity, chloride, and sodium



a. Spring at the Head of Stedman's Lake



b. Beginning of Water on Dry Fork Creek

FIGURE 3. DRY FORK CREEK AT POINT 1140

TABLE I

## SURFACE WATER STUDIES

## AVERAGE CHARACTERISTICS OF DRY FORK AND LITTLE DRY FORK CREEK WATERS

PARAMETER	SAMPLE POINT				
	1140	1135	1131	1130	2105*
Calcium, mg/l as CaCO <sub>3</sub>	45	44	27	53	102
Magnesium, mg/l as CaCO <sub>3</sub>	44	31	21	44	98
Total Hardness, mg/l as CaCO <sub>3</sub>	89	75	48	97	200
Alkalinity, mg/l as CaCO <sub>3</sub>	86	71	48	94	178
Chloride, mg/l	2.7	2.9	3.0	5.2	56
Ammonia Nitrogen, mg/l	0.28	0.25	0.16	0.18	0.32
Nitrate Nitrogen, mg/l	0.05	0.03	0.01	0.28	1.5
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.06
Orthophosphate, mg/l	0.0	0.0	0.0	0.0	7.4
Iron, mg/l	0.48	0.32	0.97	0.62	0.31
Manganese, mg/l	0.00	0.06	0.30	0.00	0.00
Sodium, mg/l	1.1	1.8	2.3	2.3	27
Silica, mg/l as SiO <sub>2</sub>	3.4	0.9	5.1	5.0	9.4
Dissolved Oxygen, mg/l	6.3	4.6	8.1	8.3	7.3
COD, mg/l	8.4	7.4	7.7	4.8	10.4
Anionic Surfactants, mg/l as ABS	0	0	0	0	0
Color, units	55	45	40	25	15
Turbidity, units	8	8	15	25	35
Total Solids, mg/l	106	115	58	138	360
Dissolved Solids, mg/l	99	104	47	124	338
pH, units	7.6	7.6	7.5	8.0	8.1
Coliforms, organisms/100 ml.	160	73	10	93	822

\*Sample collection point on Little Dry Fork creek

TABLE I (Continued)

## SURFACE WATER STUDIES

## AVERAGE CHARACTERISTICS OF DRY FORK AND LITTLE DRY FORK CREEK WATERS

PARAMETER	SAMPLE POINT				
	1125	1120	1115	1110	1105
Calcium, mg/l as CaCO <sub>3</sub>	89	82	83	76	93
Magnesium, mg/l as CaCO <sub>3</sub>	84	74	79	71	96
Total Hardness, mg/l as CaCO <sub>3</sub>	173	156	162	147	189
Alkalinity, mg/l as CaCO <sub>3</sub>	157	142	152	131	172
Chloride, mg/l	37	38	41	18	26
Ammonia Nitrogen, mg/l	0.30	0.32	0.35	0.35	0.58
Nitrate Nitrogen, mg/l	0.44	0.27	0.10	0.18	0.05
Nitrite Nitrogen, mg/l	0.03	0.05	0.01	0.01	0.00
Orthophosphate, mg/l	4.2	3.5	2.5	0.8	0.8
Iron, mg/l	0.65	0.69	0.19	0.70	0.33
Manganese, mg/l	0.00	0.00	0.00	0.08	0.00
Sodium, mg/l	16	17	18	13	15
Silica, mg/l as SiO <sub>2</sub>	6.6	6.8	3.2	5.6	4.5
Dissolved Oxygen, mg/l	6.7	6.5	9.6	7.2	7.9
COD, mg/l	8.0	6.1	6.9	10.2	6.4
Anionic Surfactants, mg/l as ABS	0	0	0	0	0
Color, units	25	30	7	24	5
Turbidity, units	75	65	15	55	30
Total Solids, mg/l	292	301	278	264	283
Dissolved Solids, mg/l	249	253	268	240	260
pH, units	8.2	8.0	8.7	8.0	8.2
Coliforms, organisms/100 ml	463	280	263	482	320

TABLE II

## SURFACE WATER STUDIES

## CHARACTERISTICS OF DRY FORK CREEK WATER AT SAMPLE POINTS 1140 AND 1135

PARAMETER	POINT 1140			POINT 1135		
	SAMPLE COLLECTION DATE					
	7-7-65	7-12-65	7-19-65	7-7-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	44	45	46	42	47	43
Magnesium, mg/l as CaCO <sub>3</sub>	40	37	53	32	28	31
Total Hardness, mg/l as CaCO <sub>3</sub>	84	82	99	74	75	74
Alkalinity, mg/l as CaCO <sub>3</sub>	88	82	86	66	74	72
Chloride, mg/l	3.6	3.7	1.0	3.9	3.4	1.5
Ammonia Nitrogen, mg/l	0.17	0.47	0.20	0.06	0.55	0.15
Nitrate Nitrogen, mg/l	0.07	0.02	0.05	0.05	0.02	0.03
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	0.0	0.0	0.0	0.0
Iron, mg/l	0.44	0.36	0.64	0.34	0.32	0.28
Manganese, mg/l	0.00	0.00	0.00	0.18	0.00	0.00
Sodium, mg/l	1.2	0.9	1.3	1.9	1.4	2.2
Silica, mg/l as SiO <sub>2</sub>	3.0	3.3	4.0	0.8	0.8	1.0
Dissolved Oxygen, mg/l	5.5	6.5	6.8	3.3	5.6	4.9
COD, mg/l	3.2	13.9	8.0	5.6	5.6	11.2
Anionic Surfactants, mg/l as ABS	0	0	0	0	0	0
Color, units	80	30	60	60	20	60
Turbidity, units	5	10	10	10	10	10
Total Solids, mg/l	103	114	96	132	98	116
Dissolved Solids, mg/l	103	107	89	124	92	99
pH, units	7.5	7.8	7.6	7.4	7.7	7.6
Coliforms, organisms/100 ml	70	40	370	100	0	120

TABLE III

## SURFACE WATER STUDIES

## CHARACTERISTICS OF DRY FORK CREEK WATER AT SAMPLE POINTS 1131 AND 1130

PARAMETER	POINT 1131			POINT 1130			
	SAMPLE COLLECTION DATE						
	6-14-65	6-21-65	6-28-65	6-6-65	7-7-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	29	26	27	44	52	55	61
Magnesium, mg/l as CaCO <sub>3</sub>	20	25	17	43	42	32	58
Total Hardness, mg/l as CaCO <sub>3</sub>	49	51	44	87	94	87	119
Alkalinity, mg/l as CaCO <sub>3</sub>	50	48	46	78	94	84	118
Chloride, mg/l	2.2	1.4	2.4	3.4	7.0	6.6	4.0
Ammonia Nitrogen, mg/l	-	0.18	0.30	0.10	0.03	0.60	0.00
Nitrate Nitrogen, mg/l	0.00	0.00	0.03	0.78	0.15	0.05	0.15
Nitrite Nitrogen, mg/l	0.01	0.00	0.00	0.01	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	-	0.0	0.0	0.0
Iron, mg/l	1.16	1.10	0.64	0.70	0.68	0.72	0.36
Manganese, mg/l	0.50	0.32	0.08	0.00	0.00	0.00	0.00
Sodium, mg/l	-	3.5	1.0	-	2.4	1.4	3.2
Silica, mg/l as SiO <sub>2</sub>	5.1	5.1	5.2	6.2	5.0	5.0	3.7
Dissolved Oxygen, mg/l	6.2	7.5	10.9	-	8.9	10.6	7.8
COD, mg/l	8.3	-	7.0	-	2.4	9.3	2.8
Anionic surfactants, mg/l as ABS	-	-	0	-	0	0	0
Color, units	50	30	-	-	30	30	10
Turbidity, units	20	10	-	60	10	10	10
Total Solids, mg/l	-	-	58	-	136	138	140
Dissolved Solids, mg/l	-	-	47	-	122	119	130
pH, units	7.5	7.3	7.8	7.2	7.9	8.3	8.0
Coliforms, organisms/100 ml	10	0	20	-	110	110	60

TABLE IV

## SURFACE WATER STUDIES

CHARACTERISTICS OF LITTLE DRY FORK WATER AT POINT 2105 AND DRY FORK WATER AT POINT 1125

PARAMETER	POINT 2105			POINT 1125		
	SAMPLE COLLECTION DATE					
	7-7-65	7-12-65	7-19-65	7-7-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	98	91	118	83	78	106
Magnesium, mg/l as CaCO <sub>3</sub>	90	88	114	84	76	91
Total Hardness, mg/l as CaCO <sub>3</sub>	188	179	232	167	154	197
Alkalinity, mg/l as CaCO <sub>3</sub>	180	152	201	152	131	189
Chloride, mg/l	46	42	80	40	32	40
Ammonia Nitrogen, mg/l	0.31	0.43	0.23	0.17	0.47	0.27
Nitrate Nitrogen, mg/l	0.83	1.0	2.6	0.33	0.81	0.18
Nitrite Nitrogen, mg/l	0.03	0.10	0.06	0.01	0.07	0.01
Orthophosphate, mg/l	7.0	5.0	10.3	4.5	3.8	4.2
Iron, mg/l	0.30	0.52	0.12	0.48	0.82	0.64
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	20	16	44	14	13	19
Silica, mg/l as SiO <sub>2</sub>	8.6	10.8	8.7	5.5	9.4	5.0
Dissolved Oxygen, mg/l	9.7	7.6	7.0	7.2	6.2	6.8
COD, mg/l	3.5	8.7	19.1	3.8	9.5	10.8
Anionic Surfactants, mg/l as ABS	0	0	0	0	0	0
Color, units	20	5	20	30	20	20
Turbidity, units	15	65	30	30	130	70
Total Solids, mg/l	318	334	428	218	318	340
Dissolved Solids, mg/l	307	293	415	212	248	296
pH, units	8.3	8.0	8.2	8.2	8.0	8.4
Coliforms, organisms/100 ml	625	1140	700	90	860	440



TABLE V

## SURFACE WATER STUDIES

## CHARACTERISTICS OF DRY FORK CREEK WATER AT SAMPLE POINTS 1120 AND 1115

PARAMETER	POINT 1120			POINT 1115		
	SAMPLE COLLECTION DATE					
	7-7-65	7-12-65	7-19-65	7-7-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	98	65	83	91	79	78
Magnesium, mg/l as CaCO <sub>3</sub>	85	57	80	89	88	60
Total Hardness, mg/l as CaCO <sub>3</sub>	183	122	163	180	167	138
Alkalinity, mg/l as CaCO <sub>3</sub>	168	105	154	180	146	130
Chloride, mg/l	65	26	23	50	45	28
Ammonia Nitrogen, mg/l	0.05	0.57	0.33	0.24	0.48	0.33
Nitrate Nitrogen, mg/l	0.29	0.51	0.02	0.06	0.21	0.03
Nitrite Nitrogen, mg/l	0.08	0.07	0.00	0.00	0.03	0.00
Orthophosphate, mg/l	5.6	2.7	2.2	1.4	3.4	2.6
Iron, mg/l	0.48	1.10	0.48	0.30	0.20	0.08
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	25	9.2	16	19	16	18
Silica, mg/l as SiO <sub>2</sub>	5.8	8.8	5.8	2.3	4.8	2.5
Dissolved Oxygen, mg/l	13.0	6.5	6.5	9.5	14.1	9.7
COD, mg/l	7.7	9.5	10.7	3.7	8.6	8.3
Anionic Surfactants, mg/l as ABS	0	0	0	0	0	0
Color, units	40	5	20	15	5	5
Turbidity, units	20	120	50	15	15	10
Total Solids, mg/l	356	292	256	346	272	216
Dissolved Solids, mg/l	340	193	229	336	260	209
pH, units	8.1	7.9	8.1	8.5	8.9	8.8
Coliforms, organisms/100 ml	60	360	420	700	30	60

TABLE VI

## SURFACE WATER STUDIES

## CHARACTERISTICS OF DRY FORK CREEK WATER AT SAMPLE POINT 1110

PARAMETER	SAMPLE COLLECTION DATE						
	6-6-65	6-14-65	6-21-65	6-28-65	7-7-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	52	47	71	81	81	105	97
Magnesium, mg/l as CaCO <sub>3</sub>	43	36	82	77	84	89	86
Total Hardness, mg/l as CaCO <sub>3</sub>	95	83	153	158	165	194	183
Alkalinity, mg/l as CaCO <sub>3</sub>	72	70	120	146	156	179	173
Chloride, mg/l	6.2	7.5	7.0	11	20	45	26
Ammonia Nitrogen, mg/l	0.29	-	0.52	0.33	0.13	0.43	0.38
Nitrate Nitrogen, mg/l	0.45	0.46	0.00	0.03	0.08	0.05	0.02
Nitrite Nitrogen, mg/l	0.04	0.04	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	-	0.4	0.4	1.6	0.9
Iron, mg/l	1.28	0.92	0.84	0.56	0.52	0.48	0.32
Manganese, mg/l	0.00	0.24	0.00	0.32	0.00	0.00	0.00
Sodium, mg/l	-	-	6.9	6.6	9.6	22	18
Silica, mg/l as SiO <sub>2</sub>	8.4	7.8	6.4	5.0	3.3	3.8	4.4
Dissolved Oxygen, mg/l	-	4.6	8.4	6.7	8.1	9.1	6.3
COD, mg/l	-	18.3	-	8.4	4.1	10.8	9.2
Anionic Surfactants, mg/l as ABS	0	0	0	0	0	0	0
Color, units	-	50	20	-	20	10	20
Turbidity, units	100	120	50	-	10	40	15
Total Solids, mg/l	-	-	-	220	254	320	261
Dissolved Solids, mg/l	-	-	-	194	235	294	243
pH, units	7.2	7.4	8.0	8.0	8.1	8.3	8.0
Coliforms, organisms/100 ml	-	830	1100	160	200	360	240

TABLE VII  
SURFACE WATER STUDIES  
CHARACTERISTICS OF DRY FORK CREEK  
WATER AT SAMPLE POINT 1105

PARAMETER	COLLECTION DATE	
	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	88	97
Magnesium, mg/l as CaCO <sub>3</sub>	89	104
Total Hardness, mg/l as CaCO <sub>3</sub>	177	201
Alkalinity, mg/l as CaCO <sub>3</sub>	162	182
Chloride, mg/l	32	20
Ammonia Nitrogen, mg/l	0.84	0.32
Nitrate Nitrogen, mg/l	0.05	0.05
Nitrite Nitrogen, mg/l	0.00	0.00
Orthophosphate, mg/l	1.0	0.7
Iron, mg/l	0.46	0.20
Manganese, mg/l	0.00	0.00
Sodium, mg/l	15	16
Silica, mg/l as SiO <sub>2</sub>	4.2	4.8
Dissolved Oxygen, mg/l	8.3	7.6
COD, mg/l	7.4	5.4
Anionic Surfactants, mg/l as ABS	0	0
Color, units	5	5
Turbidity, units	50	10
Total Solids, mg/l	304	261
Dissolved Solids, mg/l	268	253
pH, units	8.2	8.3
Coliforms, organisms/100 ml	540	100

contents were found to be low. Generally only slight changes in the characteristics of the water at this point were detected between samplings. An exception was the iron content of the sample collected on July 19, 1965, which did show a sizeable increase; this sample was collected immediately after a rainfall. The hardness of the water also increased under those circumstances.

The water characteristics at point 1135 approximate those found at point 1140. The only significant differences occurred in the slightly lower hardness and dissolved oxygen content and the decrease in the number of coliforms noted at point 1135. The land at this location was fenced, thus greatly reducing the possibility of contamination by cattle. The results obtained showed only slight differences from one sample collection to the next.

At point 1131, the hardness of the water was again found to decrease, this time significantly. Other important changes in characteristics were the increase in dissolved oxygen content, the detection of manganese for the first time, the very high iron concentrations, and the low number of coliforms present. Generally the water characteristics did not change between samplings, however, a decrease in iron and manganese was noted.

A pronounced change occurred in the quality of the Dry Fork water between points 1131 and 1130. The calcium, magnesium, hardness, and alkalinity (bicarbonate ion) concentrations doubled in a distance of approximately 400 feet. These characteristics are presented in bar-graph form in

Figure 4. The change in water quality was attributed to subsurface discharges, because no surface tributaries were in this area. This occurrence is common in karst terrain. The iron concentration at this point was still high and manganese was found to be absent. The total solids content increased as would be expected. Although still quite low, the amount of nitrate detected increased substantially over the amount found at other locations. The characteristics of point 1130 remained relatively the same between samplings except for hardness, which varied to a considerable degree. The largest increase occurred when the sample was collected shortly after a rainfall (July 19, 1965). The stream velocity was still almost undetectable at this location.

The next sampling point on Dry Fork was selected below its junction with Little Dry Fork. Little Dry Fork was perennial in the area of study and carried the sewage plant effluent from Rolla. It was felt that this tributary should also be chosen for sampling to determine the quality of the water it discharged into Dry Fork. The water collected at this sample location (point 2105), which was approximately a mile above Dry Fork, contained a significant amount of phosphorus which had not been found previously. Chloride, sodium, nitrate, and even nitrite ions were present in considerable concentrations for surface water. Coliforms were also found in large numbers. The COD and silica measured were the highest in the area, although they did not exceed the amounts normally found in surface water.

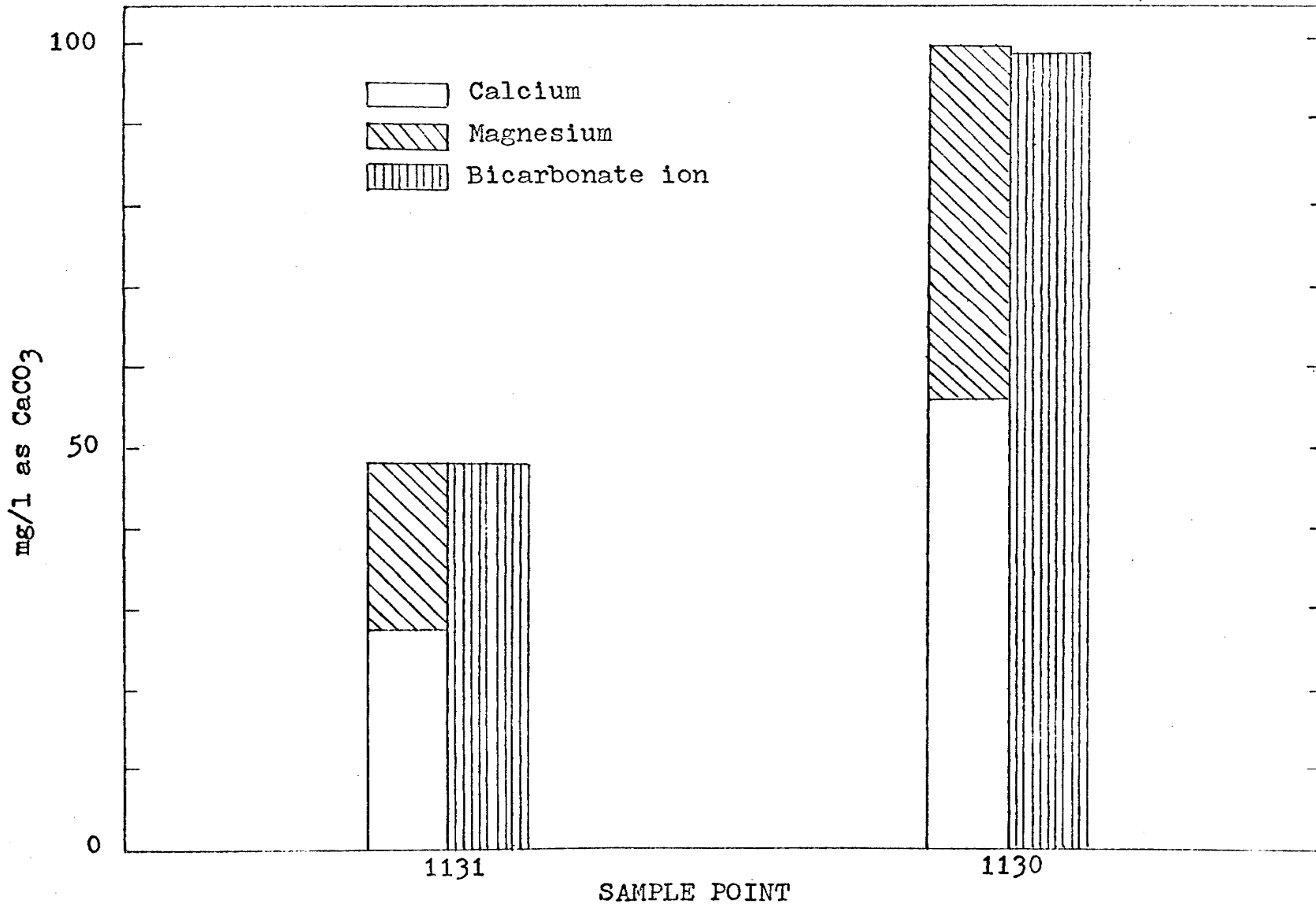


FIGURE 4. VARIATION IN WATER CHARACTERISTICS  
IN DRY FORK OVER A SHORT DISTANCE

These characteristics can be attributed to the sewage plant effluent in the water. Variations were noted between samplings, probably the result of the varying strength of the treatment plant effluent being discharged. The water at point 2105 was classified as hard and showed an appreciable amount of iron but an absence of manganese. The hardness of the water changed between samplings and increased significantly following a rainfall. Possible subsurface discharges may have caused this variation in the hardness content. The stream flow at this point was swift and the shallow depth of the creek provided sufficient aeration to keep a relatively high amount of dissolved oxygen in the water.

Point 1125 below the confluence of Dry Fork with Little Dry Fork was effected by the introduction of the Little Dry Fork waters but due to the dilution involved the concentration of the minerals present was less pronounced. The turbidity and suspended solids content increased prominently over other locations. This increase was probably caused by the turbulence created by Little Dry Fork upon its discharge into Dry Fork. Increases also occurred in the concentration of iron and the intensity of color. The velocity of the stream still appeared low, however the water was constricted as it flowed beneath a low water bridge and this caused the current to become swift for a short distance. After passing under the bridge the flow was again difficult to detect. The hardness of the water collected at point 1125 decreased

in relation to Little Dry Fork, but increased substantially over the preceding point on Dry Fork. Subsurface discharges, characteristic of karst terrain, were again considered responsible. Fluctuations in water quality were noticed from one sample collection to the next and were comparable to those seen in the analyses made on samples from point 2105.

The effect of Little Dry Fork on the chemical characteristics of the Dry Fork water decreased at point 1120. The hardness, calcium, magnesium, and alkalinity content of the sample collected on the 12th of July was significantly lower than that of the sample collected on the preceding (July 7) or following (July 19) sampling trip. This observation applies to most of the sampling points above this location. Rainfall occurred prior to the 7th of July, the last rain falling on July 3rd. Between that time and the 12th of July no significant precipitation occurred and, as stated above, the mineralization of the water decreased. Rain again fell on the 19th of July and the mineral content was found to increase over that measured in the preceding sample. These facts suggested the possibility that Dry Fork at point 1120, as well as at most locations above this point, was receiving subsurface discharges which had become enriched with calcium and magnesium from the rock formations through the solvent action of rainwater. The stream at these locations would be classified as effluent in as much as it appeared to receive subsurface discharges. Figure 5 shows the



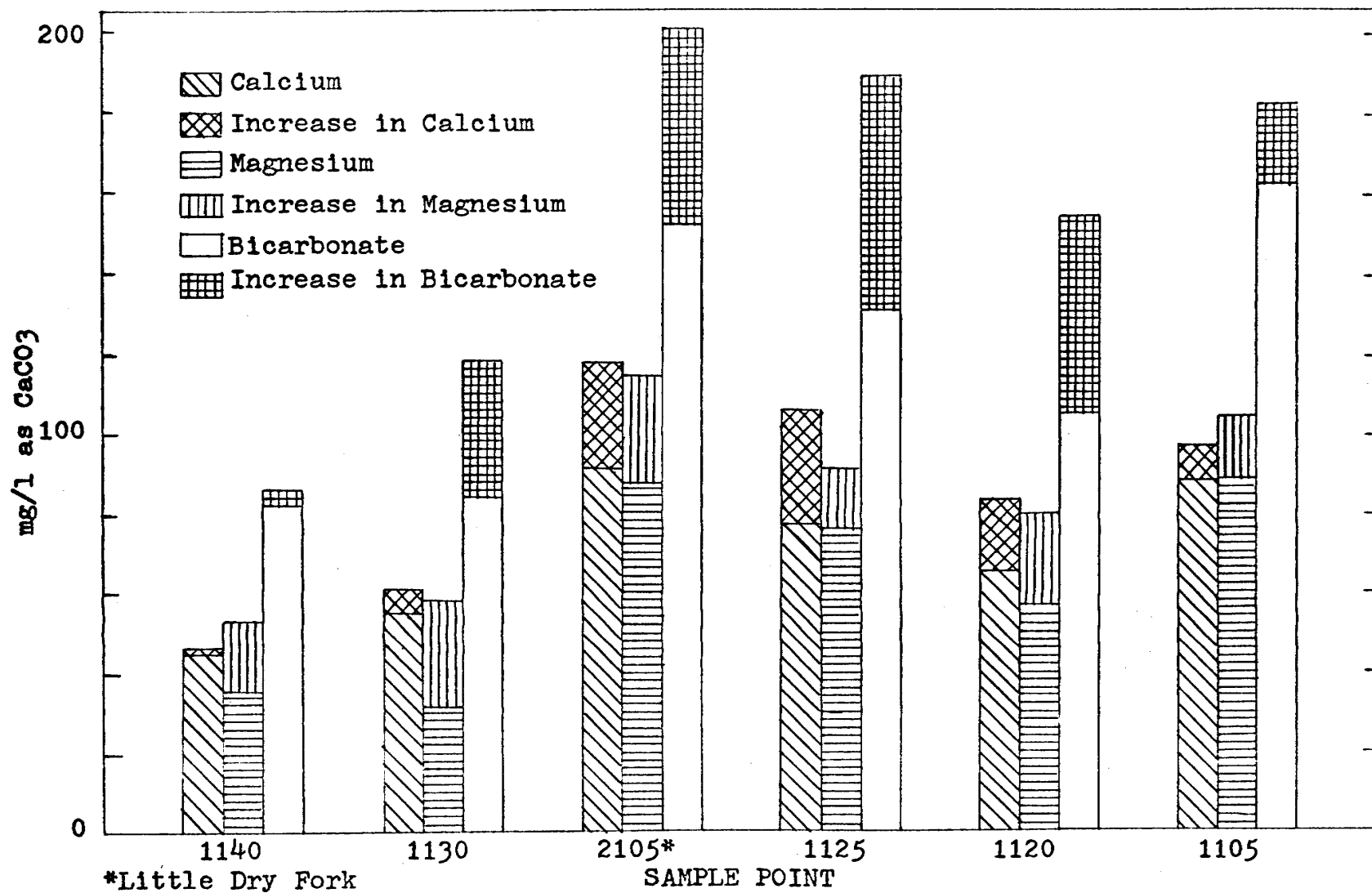


FIGURE 5. INCREASE IN THE MINERALIZATION

OF DRY FORK CREEK WATER FOLLOWING A RAINFALL (PERIOD JULY 12-19, 1965)

increase of calcium, magnesium, and bicarbonate ion (alkalinity) concentration in the Dry Fork water collected at several sampling points on the 19th of July over the concentration of the same components in the samples collected seven days earlier. The velocity of the stream at point 1120 appeared to be the same as that observed at previous points. No significant changes in water characteristics were noted between samplings except those listed above.

Below point 1120 a major change was seen in the physical appearance of Dry Fork. Above this point the stream was relatively broad and deep, had a slow velocity, and its bank was lined with trees. Further downstream at point 1115 the creek appeared shallow and swift with boundaries which were not sharply defined. The water at this point was less colored, the iron content dropped sharply, while the pH value increased. The concentration of the phosphate, nitrate, nitrite, chloride, and sodium ions which were introduced by Little Dry Fork continued to decrease. The hardness content decreased consistently between sampling times, as opposed to the fluctuations found in samples collected above this location. Since the mineral concentration of the water at this point decreased following rainfall, it was believed that no subsurface discharge was contributing to the flow. The rainfall was thought to have a diluting effect on the stream waters which was most significant when the sample was collected shortly following a rain. The stream at this location would be classified as influent,

or one which loses water to the ground, however, the losses were considered negligible in this case. The coliform content of the water varied considerably between samplings and is attributed to the cattle seen feeding in the area.

Point 1110 was sampled extensively from the first part of June. There appeared to be water losses somewhere in this area since the flow did not seem to be directly dependent on the rainfall. This occurrence would suggest that the immediate terrain had karst characteristics and the stream bed was influent. The mineral content of the water increased throughout the summer, except when a sample was collected immediately after a rainfall, when it decreased. Iron was found here in large quantities and manganese was present on two sampling occasions. Color increased over the previous locations and the concentration of the substances contributed by Little Dry Fork continued to decrease. The pH of the water at this point was lower than that measured in samples collected at the preceding sampling location while turbidity significantly increased and dissolved oxygen was plentiful. The COD was nearly as high as in Little Dry Fork. The hardness, turbidity, color, and coliform content varied between samplings.

The final sampling point on Dry Fork, 1105, was approximately one mile upstream from the Meramec river. The velocity of the stream at this point was swift. The water here was further diluted and the concentration of the materials contributed by Little Dry Fork again diminished. The hardness

was similar to that found at point 1110. There were few changes in the water quality between points 1110 and 1105.

Surfactants were not detected at any of the sample locations on either Dry Fork or Little Dry Fork.

Norman creek is generally considered to be a dry stream bed which contains no water except during and immediately following heavy rainfall. The access points checked on this creek substantiated this belief, however, one location was found to have flowing water. Professor V.A.C. Gevecker of the Civil Engineering Department first observed the flow when he was walking the Norman creek bed while doing field work on a research project to determine water losses in the area. He informed this writer and the location was made a sampling point. This water flow ceased during the month of July. Figure 6a shows the running water at point 4120, while Figure 6b was taken from the same position but after the flow had ceased. Subsurface flow was considered to be the source of this water, since water could be reached at a depth of about one foot below the creek bed when there was no surface flow. Figure 7 points out this feature.

The results of the analyses run on Norman creek water are presented in Table VIII. Iron was present in considerable amounts and manganese reached very high concentrations. Manganese is seldom found at this level in surface waters. The water was colored and its chloride, nitrogen, sodium, and turbidity content was low as was its chemical oxygen demand. The calcium, magnesium, and alkalinity



a. Water Flowing



b. Dry Stream by the End of July

FIGURE 6. NORMAN CREEK AT POINT 4120



FIGURE 7. WATER LOCATED ONE FOOT BELOW  
DRY BED OF NORMAN CREEK AT POINT 4120

TABLE VIII

## SURFACE WATER STUDIES

## CHARACTERISTICS OF NORMAN CREEK WATER AT SAMPLE POINT 4120

PARAMETER	SAMPLE COLLECTION DATE			AVERAGE
	7-7-65	7-26-65	7-30-65	ANALYSIS
Calcium, mg/l as CaCO <sub>3</sub>	41	50	38	43
Magnesium, mg/l as CaCO <sub>3</sub>	45	46	30	40
Total Hardness, mg/l as CaCO <sub>3</sub>	86	96	68	83
Alkalinity, mg/l as CaCO <sub>3</sub>	75	95	65	78
Chloride, mg/l	3.4	2.0	1.7	2.4
Ammonia Nitrogen, mg/l	0.11	0.13	0.00	0.08
Nitrate Nitrogen, mg/l	0.09	0.00	0.07	0.05
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	0.0	0.0
Iron, mg/l	0.52	0.40	0.32	0.41
Manganese, mg/l	0.84	1.68	1.00	1.17
Sodium, mg/l	2.4	2.3	2.3	2.3
Silica, mg/l as SiO <sub>2</sub>	5.4	7.2	3.0	5.2
Dissolved Oxygen, mg/l	5.1	5.0	5.5	5.3
COD, mg/l	0.0	2.7	5.5	2.7
Anionic Surfactants, mg/l as ABS	0	0	0	0
Color, units	50	10	10	20
Turbidity, units	2	5	5	4
Total Solids, mg/l	140	108	82	110
Dissolved Solids, mg/l	132	103	80	105
pH, units	7.6	7.5	7.6	7.6
Coliforms, organisms/100 ml	520	120	140	260

fluctuated between samplings and the coliform content, as well as the dissolved solids and color, decreased throughout the summer. The samples taken at the end of July are not considered as representative of the water as the sample collected during flow. These samples were taken where deep depressions in the creek bed had been filled by subsurface water. They were tested to confirm the previous analysis.

Benton and West Fork Benton creek are considered to be perennial streams, but during the month of July the upper portion of Benton creek became dry as shown in Figure 8. These two creeks were not considered to be influenced by karst development and were studied for this reason in order to provide a source of comparison. Water characteristics are presented in Tables IX through XII; average characteristics are given in Table IX.

Most of the water found in Benton and West Fork Benton creek was derived from springs. It was cool, clear, did not contain any phosphates or surfactants, or exhibit a chemical oxygen demand. The iron present was low and manganese was not found. The streams were swift and shallow and the water contained significant concentrations of dissolved oxygen. The coliform content of the water was relatively high although its physical appearance was as good as that taken from a municipal supply. The coliforms were traced to cattle in the area. Mineralization of the water increased throughout the summer as the stream flow decreased. This





FIGURE 8. DRY STREAM BED  
AT POINT 7120 ON BENTON CREEK

TABLE IX  
SURFACE WATER STUDIES  
AVERAGE CHARACTERISTICS OF BENTON  
AND WEST FORK BENTON CREEK WATERS

PARAMETER	SAMPLE POINT		
	7120	7110	8105
Calcium, mg/l as CaCO <sub>3</sub>	53	85	93
Magnesium, mg/l as CaCO <sub>3</sub>	55	85	92
Total Hardness, mg/l as CaCO <sub>3</sub>	108	170	185
Alkalinity, mg/l as CaCO <sub>3</sub>	101	166	185
Chloride, mg/l	1.6	1.7	2.0
Ammonia Nitrogen, mg/l	0.26	0.20	0.12
Nitrate Nitrogen, mg/l	0.11	0.13	0.10
Nitrite Nitrogen, mg/l	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	0.0
Iron, mg/l	0.17	0.12	0.19
Manganese, mg/l	0.00	0.00	0.00
Sodium, mg/l	1.2	1.3	1.6
Silica, mg/l as SiO <sub>2</sub>	9.3	10.0	10.2
Dissolved Oxygen, mg/l	7.2	8.8	7.4
COD, mg/l	0.6	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	0
Color, units	0	0	0
Turbidity, units	0	0	0
Total Solids, mg/l	130	191	222
Dissolved Solids, mg/l	130	191	221
pH, units	7.6	8.1	8.1
Coliforms, organisms/100 ml	298	69	216

TABLE X

## SURFACE WATER STUDIES

## CHARACTERISTICS OF WEST FORK BENTON CREEK WATER AT SAMPLE POINT 8105

PARAMETER	SAMPLE COLLECTION DATE			
	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	76	93	98	106
Magnesium, mg/l as CaCO <sub>3</sub>	72	93	100	103
Total Hardness, mg/l as CaCO <sub>3</sub>	148	186	198	209
Alkalinity, mg/l as CaCO <sub>3</sub>	144	186	200	210
Chloride, mg/l	1.9	1.4	2.0	2.6
Ammonia Nitrogen, mg/l	-	0.38	0.00	0.00
Nitrate Nitrogen, mg/l	0.12	0.02	0.12	0.12
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	0.0
Iron, mg/l	0.24	0.20	0.22	0.12
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	-	1.6	1.0	2.1
Silica, mg/l as SiO <sub>2</sub>	9.8	9.6	10.7	10.8
Dissolved Oxygen, mg/l	7.6	7.4	6.7	7.8
COD, mg/l	1.5	-	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	-	-	200	244
Dissolved Solids, mg/l	-	-	200	242
pH, units	7.9	8.1	8.1	8.2
Coliforms, organisms/100 ml	305	300	240	20

TABLE XI

## SURFACE WATER STUDIES

## CHARACTERISTICS OF BENTON CREEK WATER AT SAMPLE POINT 7120

PARAMETER	SAMPLE COLLECTION DATE			
	6-6-65	6-14-65	6-21-65	6-28-65
Calcium, mg/l as CaCO <sub>3</sub>	36	49	59	67
Magnesium, mg/l as CaCO <sub>3</sub>	38	60	60	62
Total Hardness, mg/l as CaCO <sub>3</sub>	74	109	119	129
Alkalinity, mg/l as CaCO <sub>3</sub>	68	94	110	130
Chloride, mg/l	1.6	1.7	1.2	1.7
Ammonia Nitrogen, mg/l	0.06	-	0.40	0.32
Nitrate Nitrogen, mg/l	0.22	0.10	0.09	0.05
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	-	0.0
Iron, mg/l	0.00	0.24	0.22	0.20
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	-	-	1.5	1.0
Silica, mg/l as SiO <sub>2</sub>	7.9	9.2	9.4	10.7
Dissolved Oxygen, mg/l	-	8.6	7.6	5.4
COD, mg/l	-	1.9	-	0.0
Anionic Surfactants, mg/l as ABS	-	-	-	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	-	-	-	130
Dissolved Solids, mg/l	-	-	-	130
pH, units	7.3	7.9	7.9	7.6
Coliforms, organisms/100 ml	-	185	110	600

TABLE XII

## SURFACE WATER STUDIES

## CHARACTERISTICS OF BENTON CREEK WATER AT SAMPLE POINT 7110

PARAMETER	SAMPLE COLLECTION DATE				
	6-6-65	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	78	78	83	89	100
Magnesium, mg/l as CaCO <sub>3</sub>	84	81	84	86	91
Total Hardness, mg/l as CaCO <sub>3</sub>	162	159	167	175	191
Alkalinity, mg/l as CaCO <sub>3</sub>	146	154	170	174	188
Chloride, mg/l	1.9	1.7	1.1	1.7	1.9
Ammonia Nitrogen, mg/l	0.09		0.46	0.20	0.05
Nitrate Nitrogen, mg/l	0.12	0.14	0.07	0.03	0.29
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	-	0.0	0.0
Iron, mg/l	0.00	0.24	0.16	0.22	0.00
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	-	-	1.5	0.8	1.7
Silica, mg/l as SiO <sub>2</sub>	9.2	9.4	9.4	11.7	11.0
Dissolved Oxygen, mg/l	-	8.9	9.0	8.5	8.7
COD, mg/l	-	1.5	-	0.0	0.0
Anionic Surfactants, mg/l as ABS				0	0
Color, units	0	0	0	0	0
Turbidity, units	0	0	0	0	0
Total Solids, mg/l	-	-	-	184	198
Dissolved Solids, mg/l	-	-	-	184	198
pH, units	7.8	8.1	8.2	8.1	8.1
Coliforms, organisms/100 ml	-	35	60	120	60

increase in mineral content could be attributed to evaporation and the fact that during the dryer weather the water flowing in the creek was almost completely spring water. The fluctuations encountered in the karst areas were not found, however, samples were not taken from these creeks immediately after a rainfall. The only significant changes occurring between sample collections were the continued increases in calcium, magnesium, hardness, and alkalinity concentrations.

#### B. WELL STUDIES

The well sampling points are shown in Figure 9. Table XXIV, Appendix A, lists the owner's name, the Missouri Geological Survey log number whenever applicable, the approximate depth, approximate distance from the stream, and location for each of these wells. The driller's well log of point 7305 indicated that it was drilled into the Eminence formation. This point was located near the mouth of Benton creek. The other wells for which logs were on file with the Missouri Geological Survey were terminated in the Gasconade formation. It was believed that the wells sampled which were not on file also terminated in the Gasconade. This was substantiated by the findings of Mueller (23, p.112) who reported that all wells south and east of the Dry Fork creek were drilled into the Gasconade or Eminence formations and by the work of Yorston (24, p.97) who concluded that wells drilled into the Gasconade were necessary for a dependable water supply.

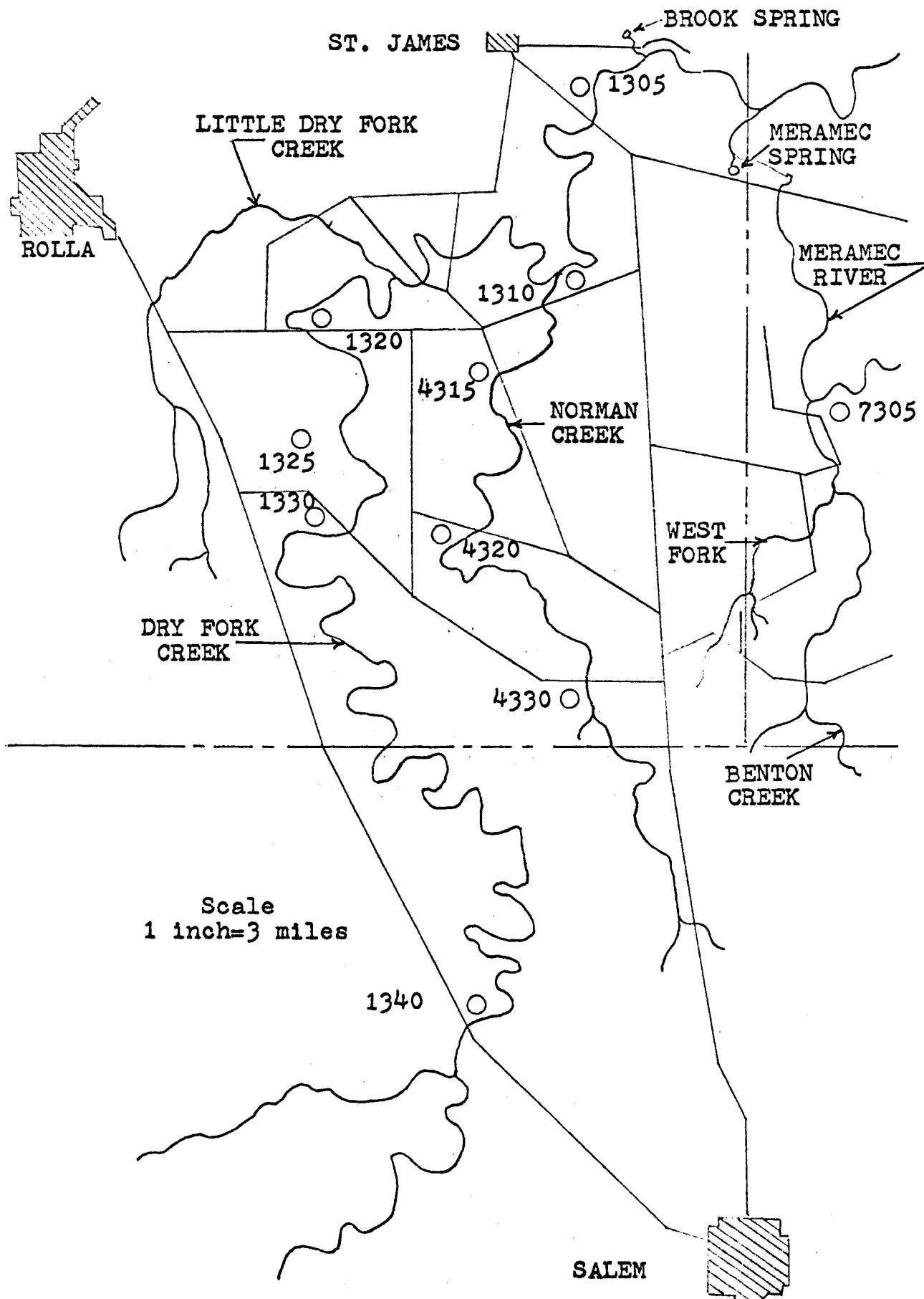


FIGURE 9. WELL SAMPLING POINTS

The characteristics of the various well waters are given in Tables XIII through XX with the average values presented in Tables XIII and XIV. The quality of the individual well waters remained essentially the same throughout the sampling period. All these waters were clear, contained no surfactants, little sodium, and did not exhibit chemical oxygen demand. Two of the wells, points 7305 and 1305, were found to be contaminated as indicated by the coliform content of their water. Since there was no evidence in the immediate well area that this contamination had entered from the surface, its entrance was attributed to lack of purification by soil filtration which is characteristic of karst terrain. The other wells sampled did not contain coliforms, although significant concentrations of nitrates and chlorides were measured. Their presence also suggested that contamination may have reached the underground water. The nitrate and chloride content of the well waters is shown in Figure 10.

Although manganese was absent, iron exceeded the 0.3 mg/l limit in several wells. As in the streams, the dissolved oxygen concentration was relatively high. The water in the wells sampled varied in calcium, magnesium, total hardness, and dissolved solids content, however, the only noticeably important changes occurred at two locations. The water from well 1330 was found to contain significantly higher concentrations of the above mentioned parameters than the majority of wells, while the water from well 1325



TABLE XIII

## WELL WATER STUDIES

## AVERAGE CHARACTERISTICS OF WELL WATERS NEAR THE DRY FORK CREEK DRAINAGE BASIN

PARAMETER	SAMPLE POINT					
	1305	1310	1320	1325	1330	1340
Calcium, mg/l as CaCO <sub>3</sub>	107	109	92	56	167	101
Magnesium, mg/l as CaCO <sub>3</sub>	93	100	84	34	163	89
Total Hardness, mg/l as CaCO <sub>3</sub>	200	209	176	90	330	190
Alkalinity, mg/l as CaCO <sub>3</sub>	127	208	162	83	240	170
Chloride, mg/l	14	2.0	8.5	2.6	19	3.3
Ammonia Nitrogen, mg/l	0.24	0.22	0.24	0.33	0.17	0.33
Nitrate Nitrogen, mg/l	19.7	1.9	3.3	1.7	21.2	5.4
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	0.0	0.0	0.0	0.0
Iron, mg/l	0.18	0.17	0.17	0.37	0.25	0.19
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	7.2	1.3	4.0	0.8	5.8	1.1
Silica, mg/l as SiO <sub>2</sub>	16.1	9.2	12.3	9.1	12.5	11.6
Dissolved Oxygen, mg/l	7.4	8.7	7.4	6.3	5.9	9.6
COD, mg/l	0.0	0.0	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	0	0	0	0
Color, units	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0
Total Solids, mg/l	255	232	209	115	395	250
Dissolved Solids, mg/l	255	232	209	113	395	250
pH, units	7.4	7.9	7.9	7.9	7.7	7.9
Coliforms, organisms/100 ml	2	0	0	0	0	0

TABLE XIV  
WELL WATER STUDIES  
AVERAGE CHARACTERISTICS OF WELL WATERS  
NEAR THE NORMAN AND BENTON CREEK DRAINAGE BASINS

PARAMETER	SAMPLE POINT			
	4315	4320	4330	7305
Calcium, mg/l as CaCO <sub>3</sub>	118	116	118	128
Magnesium, mg/l as CaCO <sub>3</sub>	110	108	109	113
Total Hardness, mg/l as CaCO <sub>3</sub>	228	224	227	241
Alkalinity, mg/l as CaCO <sub>3</sub>	212	184	208	216
Chloride, mg/l	3.5	6.6	7.0	12
Ammonia Nitrogen, mg/l	0.11	0.20	0.26	0.19
Nitrate Nitrogen, mg/l	4.8	9.0	3.9	6.7
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	0.0	0.0
Iron, mg/l	0.56	0.19	0.16	0.36
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	1.4	1.9	3.0	7.2
Silica, mg/l as SiO <sub>2</sub>	9.1	10.5	10.5	12.9
Dissolved Oxygen, mg/l	7.2	7.8	8.0	8.6
COD, mg/l	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	0	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	244	264	250	266
Dissolved Solids, mg/l	243	264	250	265
pH, units	7.9	7.8	7.8	7.8
Coliforms, organisms/100 ml	0	0	0	4

TABLE XV

## WELL WATER STUDIES

## CHARACTERISTICS OF WELL WATERS AT SAMPLE POINTS 1305 AND 1310

PARAMETER	POINT 1305				POINT 1310		
	SAMPLE COLLECTION DATE						
	6-14-65	6-21-65	6-28-65	7-30-65	6-21-65	6-28-65	7-26-65
Calcium, mg/l as CaCO <sub>3</sub>	105	110	104	112	111	108	110
Magnesium, mg/l as CaCO <sub>3</sub>	95	90	90	95	102	100	98
Total Hardness, mg/l as CaCO <sub>3</sub>	200	200	194	207	213	208	208
Alkalinity, mg/l as CaCO <sub>3</sub>	130	120	128	128	208	208	207
Chloride, mg/l	14	13	13	18	1.4	2.0	2.8
Ammonia Nitrogen, mg/l	-	0.35	0.27	0.10	0.30	0.23	0.13
Nitrate Nitrogen, mg/l	14.0	19.0	20.8	24.6	1.8	1.8	2.0
Nitrite Nitrogen, mg/l	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	0.0	-	0.0	0.0
Iron, mg/l	0.20	0.16	0.24	0.10	0.16	0.24	0.12
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	-	7.8	5.5	8.3	1.5	0.9	1.4
Silica, mg/l as SiO <sub>2</sub>	15.8	16.7	16.1	16.2	8.8	10.2	8.6
Dissolved Oxygen, mg/l	7.5	7.6	7.2	7.4	7.3	9.5	9.0
COD, mg/l	0.0	-	0.0	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0	-	0	0
Color, units	0	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0	0
Total Solids, mg/l	-	-	232	278	-	252	212
Dissolved Solids, mg/l	-	-	232	278	-	252	212
pH, units	7.4	7.4	7.4	7.3	7.9	7.8	7.9
Coliforms, organisms/100 ml	4	6	0	0	0	0	0

TABLE XVI

## WELL WATER STUDIES

## CHARACTERISTICS OF WELL WATERS AT SAMPLE POINTS 1320 AND 1325

PARAMETER	POINT 1320				POINT 1325	
	SAMPLE COLLECTION DATE					
	6-14-65	6-21-65	6-28-65	7-30-65	7-12-65	7-19-65
Calcium, mg/l as CaCO <sub>3</sub>	87	90	90	99	60	52
Magnesium, mg/l as CaCO <sub>3</sub>	93	79	83	83	36	32
Total Hardness, mg/l as CaCO <sub>3</sub>	180	169	173	182	96	84
Alkalinity, mg/l as CaCO <sub>3</sub>	156	160	162	169	84	82
Chloride, mg/l	8.8	6.4	8.7	10.0	3.4	1.7
Ammonia Nitrogen, mg/l	-	0.32	0.15	0.26	0.50	0.17
Nitrate Nitrogen, mg/l	2.4	3.4	3.5	4.1	1.6	1.7
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	0.0	0.0	0.0
Iron, mg/l	0.20	0.16	0.24	0.08	0.42	0.32
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	-	3.9	3.2	4.8	0.8	0.8
Silica, mg/l as SiO <sub>2</sub>	12.0	12.5	13.0	11.6	9.6	8.7
Dissolved Oxygen, mg/l	7.4	9.7	7.4	7.2	6.6	6.0
COD, mg/l	0.0	-	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0	0	0
Color, units	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0
Total Solids, mg/l	-	-	214	204	116	114
Dissolved Solids, mg/l	-	-	214	204	114	111
pH, units	7.9	7.9	7.8	7.9	7.9	7.9
Coliforms, organisms/100 ml	0	0	0	0	0	0

TABLE XVII

## WELL WATER STUDIES

## CHARACTERISTICS OF WELL WATERS AT SAMPLE POINTS 1330 AND 1340

PARAMETER	POINT 1330				POINT 1340	
	SAMPLE COLLECTION DATE					
	6-14-65	6-21-65	6-28-65	7-30-65	6-21-65	6-28-65
Calcium, mg/l as CaCO <sub>3</sub>	162	175	158	173	102	100
Magnesium, mg/l as CaCO <sub>3</sub>	164	159	165	162	86	92
Total Hardness, mg/l as CaCO <sub>3</sub>	326	334	323	335	188	192
Alkalinity, mg/l as CaCO <sub>3</sub>	234	238	244	244	170	170
Chloride, mg/l	20	17	19	20	2.8	3.7
Ammonia Nitrogen, mg/l		0.37	0.10	0.05	0.40	0.27
Nitrate Nitrogen, mg/l	16.6	22.0	23.3	23.1	4.5	6.2
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.01	0.01
Orthophosphate, mg/l	-	-	0.0	0.0	-	0.0
Iron, mg/l	0.28	0.22	0.26	0.24	0.22	0.16
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	-	6.0	4.6	6.9	1.5	0.8
Silica, mg/l as SiO <sub>2</sub>	12.5	12.0	13.3	12.5	10.7	12.5
Dissolved Oxygen, mg/l	6.3	5.7	6.3	5.2	9.7	9.6
COD, mg/l	0.0	-	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0	-	0
Color, units	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0
Total Solids, mg/l	-	-	404	386	-	250
Dissolved Solids, mg/l	-	-	404	386	-	250
pH, units	7.9	7.8	7.7	7.6	8.0	7.8
Coliforms, organisms/100 ml	0	0	0	0	1	0

TABLE XVIII

## WELL WATERS STUDIES

## CHARACTERISTICS OF WELL WATERS AT SAMPLE POINTS 4315 AND 4320

PARAMETER	POINT 4315		POINT 4320			
	SAMPLE COLLECTION DATE					
	7-26-65	7-30-65	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	118	118	115	119	112	119
Magnesium, mg/l as CaCO <sub>3</sub>	109	110	110	104	114	104
Total Hardness, mg/l as CaCO <sub>3</sub>	227	228	225	223	226	223
Alkalinity, mg/l as CaCO <sub>3</sub>	211	212	180	182	186	186
Chloride, mg/l	4.0	3.0	7.5	5.6	6.4	7.0
Ammonia Nitrogen, mg/l	0.13	0.08		0.37	0.24	0
Nitrate Nitrogen, mg/l	-	4.8	7.9	8.5	9.8	9.8
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.0	0.0	-	-	0.0	0.0
Iron, mg/l	0.64	0.48	0.24	0.24	0.16	0.12
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	1.2	1.6	-	2.5	1.2	1.9
Silica, mg/l as SiO <sub>2</sub>	9.2	9.0	10.0	10.3	10.8	10.8
Dissolved Oxygen, mg/l	7.7	6.7	7.7	7.8	7.2	8.7
COD, mg/l	0.0	0.0	0.0	-	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	-	-	0	0
Color, units	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0
Total Solids, mg/l	244	244	-	-	268	260
Dissolved Solids, mg/l	244	244	-	-	268	260
pH, units	7.9	7.9	7.8	7.8	7.7	7.7
Coliforms, organisms/100 ml	0	0	0	0	0	0

TABLE XIX

## WELL WATER STUDIES

## CHARACTERISTICS OF WELL WATER AT SAMPLE POINT 4330

PARAMETER	SAMPLE COLLECTION DATE			
	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	119	119	114	119
Magnesium, mg/l as CaCO <sub>3</sub>	112	102	112	110
Total Hardness, mg/l as CaCO <sub>3</sub>	231	221	226	229
Alkalinity, mg/l as CaCO <sub>3</sub>	216	206	207	204
Chloride, mg/l	9.0	5.6	6.4	7.0
Ammonia Nitrogen, mg/l	-	0.57	0.18	0.03
Nitrate Nitrogen, mg/l	3.0	3.8	4.5	4.3
Nitrite Nitrogen, mg/l	0.02	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	0.0
Iron, mg/l	0.20	0.20	0.24	0.00
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	-	3.0	2.5	3.4
Silica, mg/l as SiO <sub>2</sub>	9.4	10.3	11.7	10.6
Dissolved Oxygen, mg/l	8.0	8.0	8.0	8.2
COD, mg/l	0.0	-	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	-	-	252	248
Dissolved Solids, mg/l	-	-	250	248
pH, units	7.7	8.0	7.8	7.8
Coliforms, organisms/100 ml	0	0	0	0

TABLE XX

## WELL WATER STUDIES

## CHARACTERISTICS OF WELL WATER AT SAMPLE POINT 7305

PARAMETER	SAMPLE COLLECTION DATE			
	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	126	134	123	129
Magnesium, mg/l as CaCO <sub>3</sub>	109	111	118	113
Total Hardness, mg/l as CaCO <sub>3</sub>	235	245	241	242
Alkalinity, mg/l as CaCO <sub>3</sub>	210	218	220	214
Chloride, mg/l	14	11	12	13
Ammonia Nitrogen, mg/l	-	0.30	0.24	0.03
Nitrate Nitrogen, mg/l	4.8	6.3	7.2	8.2
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	-	-	0.0	0.0
Iron, mg/l	0.26	0.34	0.34	0.40
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	-	8.0	5.1	8.5
Silica, mg/l as SiO <sub>2</sub>	14.4	12.0	12.9	12.2
Dissolved Oxygen, mg/l	7.4	9.6	8.7	8.9
COD, mg/l	0.0	-	0.0	0.0
Anionic Surfactants, mg/l as ABS	-	-	0	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	-	-	250	282
Dissolved Solids, mg/l	-	-	249	282
pH, units	7.8	7.7	7.8	7.9
Coliforms, organisms/100 ml	30	12	0	0



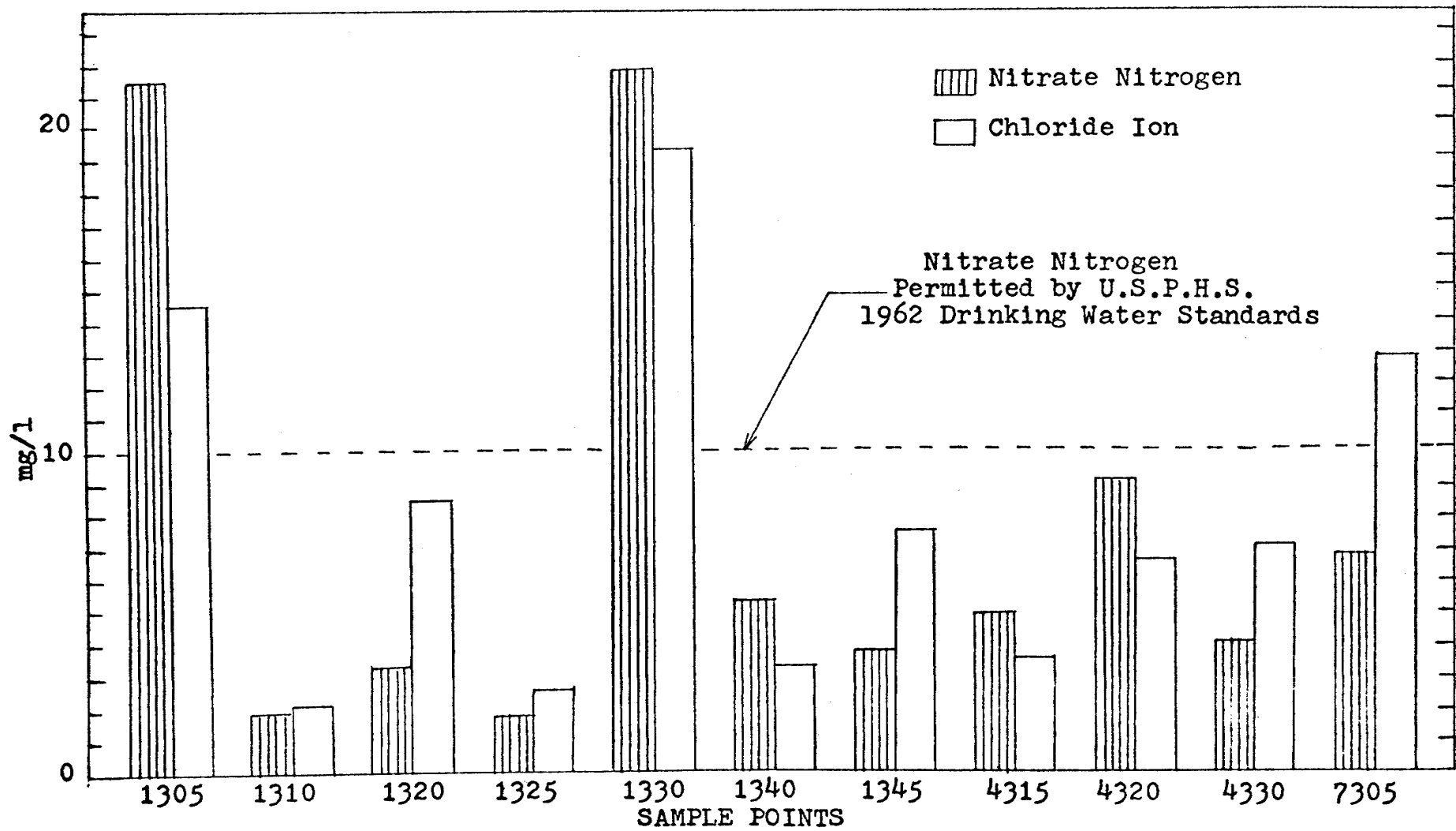


FIGURE 10. NITRATE NITROGEN AND CHLORIDE ION CONCENTRATIONS IN WELL WATERS

contained greatly reduced amounts. Contrary to the other wells investigated, the alkalinity of the samples collected at points 1330 and 1305 was considerably lower than the corresponding hardness, however, the nitrate and chloride ion content was the highest measured in the wells sampled and would account for the majority of the differences.

### C. SPRING STUDIES

The location of the springs sampled is shown in Figure 11 with details given in Table XXV, Appendix A. The average characteristics of the spring waters are given in Table XXI. Individual tables were not prepared for spring points 1215 and 7209 because only one sample was analysed for each of these locations, however, several samples were collected at points 1210 and 7210 and their individual analyses are listed in Table XXII under the date of sample collection. The quality of the water varied with location. The samples collected in the Benton Creek drainage basin contained significantly higher concentrations of calcium, magnesium, hardness, and dissolved solids, while those collected near the Dry Fork creek area had higher nitrate and chloride contents. Color, turbidity, and surfactants were absent from all spring waters; the sodium was low and there was no chemical oxygen demand. Phosphorus was found in Meramec spring yet was conspicuously absent in the other wells and springs. The only source of phosphorus found in the area was the Little Dry Fork water which carried treatment plant effluent from Rolla and discharged into the Dry

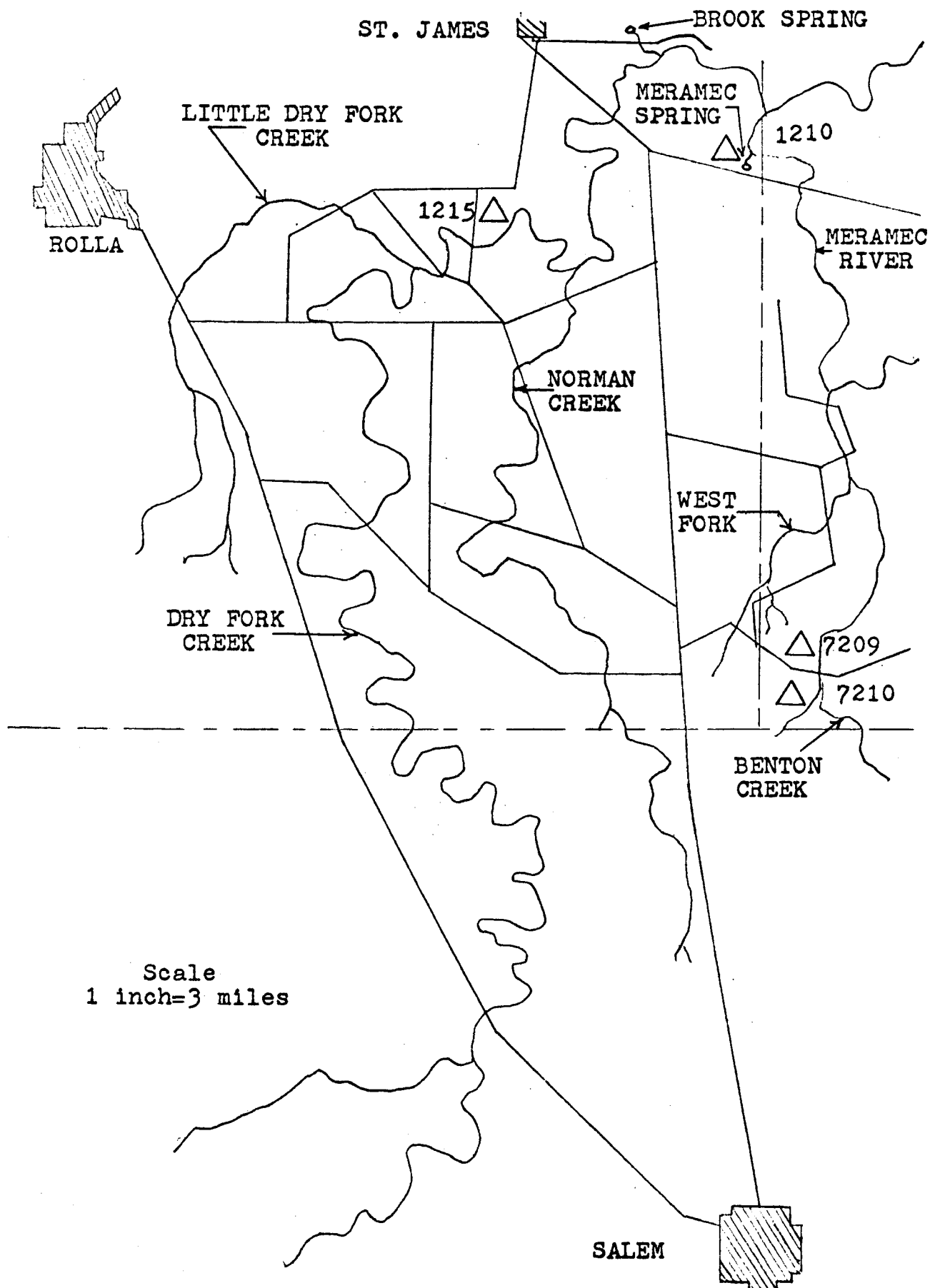


FIGURE 11. SPRING SAMPLING POINTS

TABLE XXI

## SPRING WATER STUDIES

## AVERAGE CHARACTERISTICS OF SPRING WATERS AT VARIOUS SAMPLING POINTS

PARAMETER	SAMPLE POINTS			
	1210	1215	7210	7209
Calcium, mg/l as CaCO <sub>3</sub>	79	97	123	126
Magnesium, mg/l as CaCO <sub>3</sub>	72	83	118	107
Total Hardness, mg/l as CaCO <sub>3</sub>	151	180	241	233
Alkalinity, mg/l as CaCO <sub>3</sub>	144	167	245	230
Chloride, mg/l	4.1	6.0	1.6	1.7
Ammonia Nitrogen, mg/l	0.24	0.15	0.19	0.05
Nitrate Nitrogen, mg/l	0.97	2.4	0.17	0.47
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.2	0.0	0.0	0.0
Iron, mg/l	0.15	0.16	0.16	0.24
Manganese, mg/l	0.00	0.00	0.00	0.00
Sodium, mg/l	2.5	3.2	2.1	2.5
Silica, mg/l as SiO <sub>2</sub>	8.8	8.3	10.9	11.2
Dissolved Oxygen, mg/l	6.7	9.0	5.1	8.1
COD, mg/l	0.0	0.0	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	0	0
Color, units	0	0	0	0
Turbidity, units	0	0	0	0
Total Solids, mg/l	171	210	250	244
Dissolved Solids, mg/l	169	201	250	243
pH, units	7.6	7.6	7.8	7.7
Coliforms, organisms/100 ml	13	48	14	18

TABLE XXII

## SPRING WATER STUDIES

## CHARACTERISTICS OF SPRING WATERS AT SAMPLE POINTS 1210 AND 7210

PARAMETER	POINT 1210			POINT 7210			
	SAMPLE COLLECTION DATE						
	7-7-65	7-12-65	7-19-65	6-14-65	6-21-65	6-28-65	7-30-65
Calcium, mg/l as CaCO <sub>3</sub>	73	79	85	119	123	129	123
Magnesium, mg/l as CaCO <sub>3</sub>	71	73	72	124	118	113	118
Total Hardness, mg/l as CaCO <sub>3</sub>	144	152	157	243	241	242	241
Alkalinity, mg/l as CaCO <sub>3</sub>	138	145	153	240	242	248	248
Chloride, mg/l	5.2	4.5	2.5	1.9	1.0	1.7	1.9
Ammonia Nitrogen, mg/l	0.06	0.47	0.21	-	0.37	0.18	0.03
Nitrate Nitrogen, mg/l	1.00	0.94	0.97	0.15	0.17	0.10	0.27
Nitrite Nitrogen, mg/l	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Orthophosphate, mg/l	0.2	0.0	0.4	-	-	0.0	0.0
Iron, mg/l	0.16	0.20	0.10	0.20	0.16	0.26	0.00
Manganese, mg/l	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sodium, mg/l	2.4	2.5	2.5	-	2.5	1.4	2.5
Silica, mg/l as SiO <sub>2</sub>	8.8	9.2	8.3	10.2	10.6	12.0	10.8
Dissolved Oxygen, mg/l	6.8	6.7	6.7	5.6	5.1	4.8	4.8
COD, mg/l	0.0	0.0	0.0	0.0	-	0.0	0.0
Anionic Surfactants, mg/l as ABS	0	0	0	-	-	0	0
Color, units	0	0	0	0	0	0	0
Turbidity, units	0	0	0	0	0	0	0
Total Solids, mg/l	166	182	166	-	-	240	260
Dissolved Solids, mg/l	163	180	164	-	-	240	260
pH, units	7.7	7.6	7.6	7.7	7.9	7.8	7.8
Coliforms, organisms/100 ml	10	15	15	1	0	6	40

Fork creek. All springs were contaminated, with varying quantities of coliforms present.

The calcium content of Meramec spring was observed to increase at each sampling. This is shown in Figure 12. Rain occurred three days before the first increase in calcium and the night before the second. An increase was not noted in the magnesium content although it was anticipated because the formations feeding the spring were reported to be dolomite.

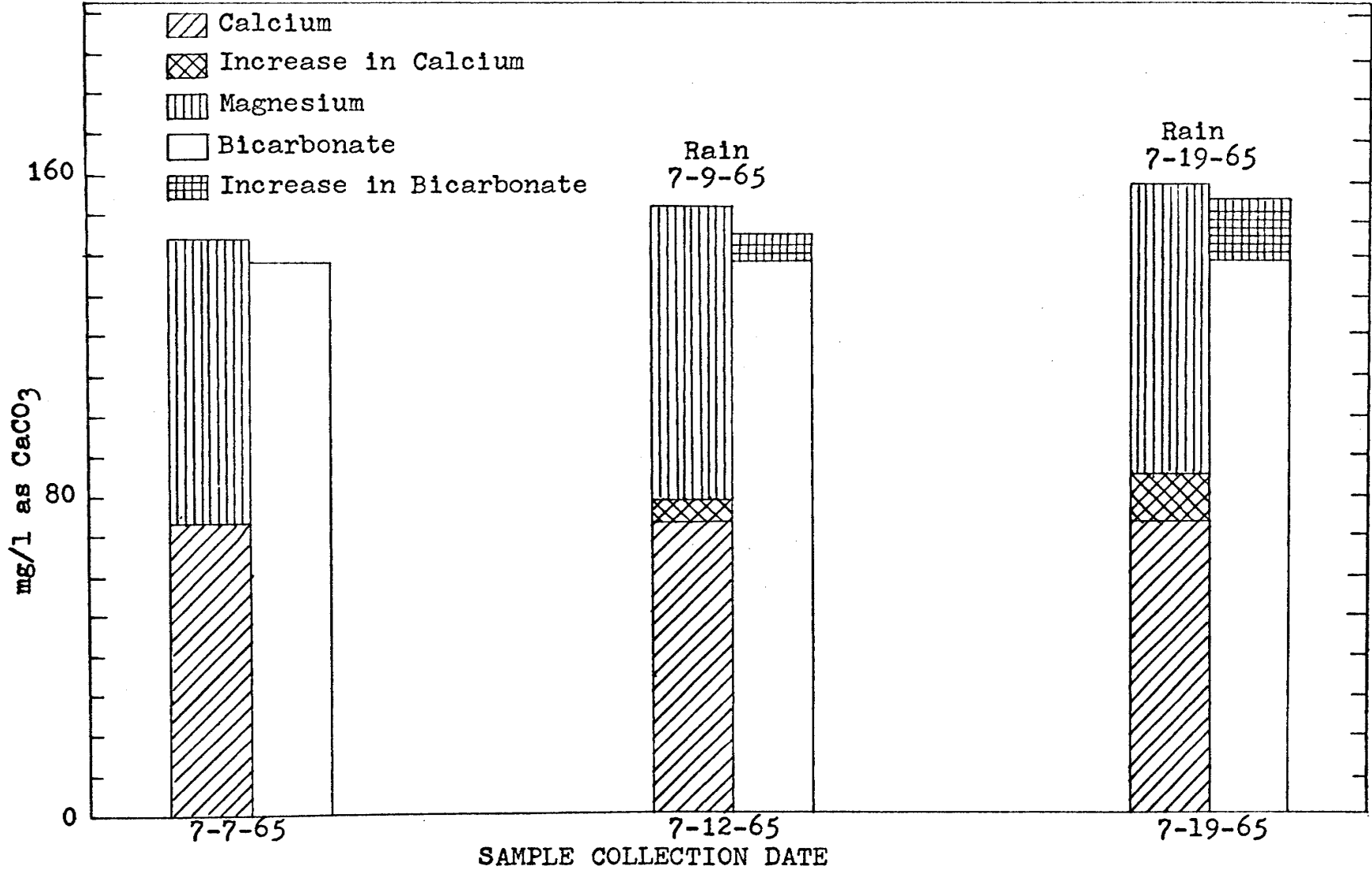


FIGURE 12. INCREASED CONCENTRATIONS OF CALCIUM BICARBONATE  
IN MERAMEC SPRING FOLLOWING RAINFALL

## V. DISCUSSION

The quality of the waters in the study area varied, however, it was generally characterized by a high hardness and iron content, and the frequent presence of nitrate ions. Well waters were usually harder and contained more nitrates. Contamination was present in the surface and spring waters, and in some well waters.

The waters in the study area were moderately hard to very hard\*. Moderately hard water was found in Dry Fork to its confluence with Little Dry Fork, in Benton to its junction with West Fork Benton, and in Norman creek, while hard water was found in the remaining locations. The well and spring waters were hard with two exceptions; the well at point 1325 had moderately hard water and the water in the well at point 1330 was very hard. In all cases, the hardness consisted largely of calcium and magnesium bicarbonate, and this was anticipated because the study area was underlain with dolomite formations (23, p.24 and 24, p.14) which consist of calcium and magnesium carbonate. The calcium and magnesium concentrations in the water were approximately the same when expressed as equivalent calcium carbonate.

Iron was present at considerable concentrations in both surface and subsurface waters, while manganese was only found

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\* Sawyer in "Chemistry for Sanitary Engineers"(18, p.235) classifies waters in terms of degree of hardness, as follows:

0 - 75	mg/l as CaCO <sub>3</sub>	Soft
75 -150	mg/l as CaCO <sub>3</sub>	Moderately Hard
150 -300	mg/l as CaCO <sub>3</sub>	Hard
300 and over	mg/l as CaCO <sub>3</sub>	Very Hard



in some surface waters. Iron and manganese are normally reported together because of their similar troublesome staining characteristics. Dissolved oxygen was also abundant in the water samples, and this was not expected because iron and dissolved oxygen are rarely found in the same water. Hem (19, p.65) reported that fully aerated water seldom contains more than 0.5 mg/l iron, however, ferric iron may form complexes with organic substances rather than precipitating out of solution (19, p.61). Since it was observed that surface waters containing iron in excess of 0.5 mg/l also contained color, these high values were attributed to complexes formed between ferric iron and the color-causing organic matter. Benton creek water which contained no color was very low in iron. The well waters were also colorless, yet they contained iron in excess of the 0.5 mg/l limit. It is believed that air was introduced into the water during sampling through the pumping and water procurement facilities, thus giving inaccurate dissolved oxygen results.

The surface waters were found to exhibit little chemical oxygen demand which indicated that the streams were able to overcome any organic pollution that they might have received. Decaying vegetation was probably responsible for the oxygen demand measured in the Dry Fork and Norman creeks because its presence was associated with colored water. On the other hand, the Benton creek water and the well and spring waters which were colorless had no oxygen demand.

Of primary concern in karst terrain would be the lack of filtration through the soil formations. As a result of

the sinkholes and solution cavities which exist in this type terrain direct routes might be available for contamination and pollution to reach underground water supplies. This characteristic of the karst topography was fairly well substantiated when two wells were found on at least two different occasions to contain coliforms, and high concentrations of nitrate and chloride ions were detected in several others. The wells where coliforms were found were over 200 feet deep and, consequently, the microorganisms could not have reached the water by usual infiltration. In addition, all the springs sampled showed contamination, and this evidence further strengthened the theory that direct pathways existed between the surface and underground supplies. It should be noted that two of these springs were unprotected, however, the other two were covered and were used as drinking water sources. Significant numbers of coliforms were also present in most surface water; animal discharges and the effluent from the Rolla sewage treatment plants were considered to be the source of this contamination.

The presence of high nitrate ion concentrations in most wells may well be characteristic of karst water. Waters containing high concentrations of these ions are unsafe for infants, therefore, nitrates are limited to 45 mg/l or 10 mg/l if expressed as nitrate nitrogen. Since pollution and inorganic nitrogen in the form of fertilizers can gain entrance to underground water supplies it is possible for nitrates to build up to such a level that the water would be

unsuitable for use without costly treatment. This was the case in a number of the wells tested.

Contrary to the frequent occurrence of nitrate ions, phosphate ions were only found in two locations, in Dry Fork below the entrance of Little Dry Fork, and in Meramec spring. This would suggest the possibility of a direct route between Dry Fork and the spring. It is also interesting to note that algae which require both phosphorus and nitrogen for growth were also detected at these points.

The carbonate karst terrain of the study area was characterized by dry stream beds which contained water only during and shortly following heavy rainfall, and other streams which had perennial flow. Much of the water lost to the dry stream beds was thought to resurface somewhere in the immediate area. The effect of subsurface discharges on surface water was first noticed between sampling points 1131 and 1130 on the Dry Fork. The mineral concentration of the water in this stream was found to increase significantly over a distance of approximately 400 feet. Since there were no surface tributaries in the vicinity, the logical explanation was the introduction of groundwater into the stream. Rainfall was also found to have an interesting effect on some water in the area; at certain locations the stream mineralization increased, while at others it decreased following precipitation. It is postulated that the areas above sampling point 1120, where increased mineralization was noted, were receiving subsurface discharges of water

enriched with calcium and magnesium ions. The increase in mineral content was most significant when the sample was collected shortly following a rainfall. The locations having this physical characteristic were classified as effluent stream points. Some of the points showed greater increases than others and this was attributed to the concentration of chemicals in the groundwater and the distance of the sample point from the point of discharge. The mineral content of the Meramec spring water also increased following a rainfall which further indicated that rainwater resulted in a rapid dissolution of underground formations.

The mineralization of the water in the Dry Fork creek decreased following precipitation at sampling points 1115 and 1110. These points were classified as influent or locations where water was lost to the ground. In these cases it was believed that the rain water had a diluting effect and reduced the mineral concentration of the stream.

Crouch (25) recently concluded, on the basis of water elevations in the wells and streams of the general study area, that Dry Fork was effluent above the vicinity where it flows beneath Route 8 and influent below this location to its mouth. The findings of Crouch compare favorably with the results of this investigation with the exception of sampling point 1105 which he reported as influent but which was found to exhibit an increase in mineral content following rainfall. The discharge of Brook spring into Dry Fork immediately above point 1105 might account for this increase. Detailed stream flow measurements beyond the scope

of this thesis would be necessary to confirm the postulation concerning water accretions and losses in Dry Fork creek.

The selection of the field area for the investigation was appropriate because the studies performed in this area enabled an evaluation of the effect of karst terrain on water quality. The present study was concentrated upon the northern part of the field area because Norman, Benton, and the perennial portion of Dry Fork creek were located there. Also, checkpoints on the southern leg of Dry Fork indicated the stream to be dry. During the preparation of this thesis, however, information was received (26) concerning a perennial tributary of Dry Fork, the Spring Branch creek which originates in Salem, Missouri; its water evidently does not contribute to the flow of Dry Fork and, consequently, it must be lost to the karst terrain of the area. Local residents think that the flow from this stream eventually reaches Meramec spring. Valuable information concerning the effect of the terrain on water quality might be obtained by the investigation of this source. Tracers, although not utilized in this study, would be a useful tool for detecting water pathways through the topography.

Norman creek has been described in all available literature as a dry stream which only flows as a result of heavy rainfall. Water was found to flow at one location, however, and although the flow ceased in the late summer, water could be found approximately one foot beneath the surface. This indicated the possibility of flow directly

under the bed of the creek and further investigation at this location would be warranted.

The parameters used in this work were selected to enable the characterization of the water in the study area and evaluation of the effect of the terrain on its quality. Although all of these parameters are important, more intensive sampling with fewer complete analyses might be more beneficial from the standpoint of evaluating the effect of karst terrain. Limiting the parameters to the calcium, magnesium, hardness, alkalinity, nitrate, iron, pH, and bacteriological determinations, which can be run quickly, will provide the opportunity for frequent sample collection and analysis especially after rainfalls. The information obtained from these determinations would indicate water quality changes. Complete analyses of the water should be made periodically, however, and should include all the parameters employed in the present study, along with sulfate ions, which, although not considered to be present in large quantities, would allow a more complete chemical balance. Since the water might be used for irrigation purposes, potassium might also be determined because its presence in agricultural soils is needed for continued productivity (19, p.91). In addition, the use of a galvanic cell oxygen analyser would allow the measurement of dissolved oxygen and water temperature rapidly and accurately. This instrument was not available in this study and the determination of

dissolved oxygen was considered to be of limited accuracy because of the difficulty encountered in sampling. With an analyser these determinations could be incorporated with the group of tests used in the intensive sampling studies.

Finally, it is appropriate to consider the application of water resources found in carbonate karst terrain to some of the major water uses, which are domestic, industrial, agricultural, and recreational. The water found in this terrain can be expected to contain significant amounts of carbonate hardness, caused by approximately equal concentrations of calcium and magnesium (expressed as calcium carbonate). Hardness in water causes high soap consumption, wear and tear on clothing, and scaling in hot-water pipes, heaters, and boilers. This makes it unacceptable from an economic viewpoint. High concentrations of magnesium sometimes have a laxative effect on the consumers. Excess-lime softening would be necessary to reduce hardness, but soda-ash treatment would not be required because of the limited amount of non carbonate hardness present. Tuepker and Hartung (27) of the St. Louis County Water Company in their experience with the treatment of Meramec river water found that it was difficult to stabilize magnesium in softened water and changes in temperature and small changes in pH would cause scaling. They further reported that magnesium can be reduced by softening with lime in the presence of clean, previously precipitated calcium carbonate softening slurry to an amount that will not precipitate at 140° F.,

and will not require recarbonation. Substantial savings in operational expenses can be realized by this method.

Due to the nature of karst topography the possibility of contamination of groundwaters would always exist in this environment and chlorination would be necessary at all times to insure safety. The waters of karst areas are subject to the nitrate problem which is perhaps the most serious disadvantage of groundwater supplies. There is no easy method for nitrate removal (28, p.466), and in some cases the use of these waters could be detrimental to the health of infants. This will not preclude the use of the water, however, because distilled or other bottled water can be used for infants. Iron may also be present in significant concentrations as found in these studies. Although there are no physiological hazards involved, the staining properties of iron in the amounts measured would make treatment necessary. Softening, or use of metaphosphates in concentrations of about 2 mg/l (29) would prevent the precipitation of iron and would be economically feasible.

The water quality requirements of individual industries vary widely, however, many industries require water of a quality equal and sometimes better than that needed for domestic purposes. General statements regarding treatment cannot be made and it would be necessary to consider each industry separately.

The water in karst terrain was of high enough quality for most recreational purposes. The concentration of dis-



solved oxygen in the water was sufficient to support aquatic life, although swimming could be hazardous due to the possibility of direct contamination, especially if the location were near a municipality. Many lakes are constructed for recreational purposes, however, impounding water in karst terrain would be impractical because most of it would be lost to the underlying formations.

## VI. CONCLUSIONS

On the basis of the findings of this study the following conclusions were drawn:

1. The main constituents of water in carbonate karst terrain were calcium and magnesium bicarbonate present at approximately equal concentrations when expressed as equivalent calcium carbonate. The hardness of the well, spring, and surface waters was in the range of 90 to 330, 150 to 240, and 50 to 200 mg/l as equivalent calcium carbonate, respectively.
2. Coliforms were present in significant numbers in surface water. They were also detected in all spring and two well waters. Their presence in groundwater was attributed to contamination through the sinkholes and solution cavities characteristic of karst terrain.
3. The nitrate ion content of surface water was generally low, however, in some well waters nitrates exceeded the 45 mg/l concentration limit established for the protection of infants. Because of the direct access routes available for organic pollution and inorganic nitrogen in the form of fertilizers to reach underground supplies, high nitrate content was considered a characteristic of water in karst regions.

4. Iron which causes stains to porcelain and laundry was found at concentrations in excess of the recommended 0.3 mg/l limit in both surface and underground water.
5. On the basis of changes in the mineral content of Dry Fork water following rainfall, the stream was classified as effluent, or receiving subsurface accretions, above point 1120 (See Figure 2, p.32) and influent, or losing water to the ground, below point 1115.
6. The Meramec spring area, east of Rolla, Missouri, was appropriate for the study conducted on the effect of karst terrain on water quality.
7. Calcium, magnesium, hardness, alkalinity, nitrate ion, iron, pH, temperature, dissolved oxygen, and bacteriological determinations, supplemented with periodic complete chemical characterization, are appropriate parameters for the investigation of the effect of karst terrain on water quality.
8. The main attributes of karst waters whose presence may necessitate treatment prior to use, and which should be considered in evaluating water resources in carbonate karst terrain, are hardness, nitrate ions, and iron content, and the possibility of contamination.

## VII. RECOMMENDATIONS FOR FUTURE RESEARCH

Although the field investigations conducted as part of this thesis were performed in the dry season of the year, it was found that rainfall had a significant effect on the water resources of the area. The extension of the field studies into the rainy season would enable further evaluation of this effect. The dry stream beds encountered throughout the summer in Norman and in portions of Dry Fork creek would undoubtedly have periodic flow during the fall and spring of the year. The quality of this water should be determined, as well as any changes in quality that might occur in the Meramec spring as a result of this flow. The use of tracers in conjunction with the sampling would be beneficial. Spring Branch creek which is a perennial stream in Dent county and is a tributary of Dry Fork, but whose flow is evidently lost to the karst terrain prior to its junction with Dry Fork, should be investigated using both water analysis and tracer studies.

The quality of the water in the wells sampled exhibited little variation throughout the sampling period, however, heavy rains might have changed this quality considerably and additional studies should be undertaken during the wet season. Investigation of well waters in the same mineral formations and at approximately the same depth may provide information on the direction of water flow and the effect of karst terrain on mineralization. A thesis recently written

by Crouch (25) which lists wells in the study area and their static water levels might be helpful in the latter investigation.

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## APPENDICES

## APPENDIX A

Tables XXIII, XXIV, and XXV describe the locations and characteristics of the stream, well, and spring sampling points employed in this study. The location of these points was also shown in Figures 2, 9, and 11 of the text of this thesis.

TABLE XXIII  
LOCATION OF SAMPLING POINTS IN THE STUDY AREA  
STREAM POINTS

DRAINAGE BASIN	SAMPLE POINT	LOCATION	COUNTY
Dry Fork	1105	Sec.26, T.38N., R.6W.	Phelps
Dry Fork	1110	Sec.33, T.38N., R.6W.	Phelps
Dry Fork	1115	Sec.15, T.37N., R.6W.	Phelps
Dry Fork	1120	Sec.18, T.37N., R.6W.	Phelps
Dry Fork	1125	Sec.13, T.37N., R.7W.	Phelps
Dry Fork	1130	Sec.27, T.37N., R.7W.	Phelps
Dry Fork	1131	Sec.27, T.37N., R.7W.	Phelps
Dry Fork	1135	Sec.35, T.37N., R.7W.	Phelps
Dry Fork	1140	Sec.2 , T.36N., R.7W.	Phelps
Dry Fork	1145	Sec.11, T.36N., R.7W.	Phelps
Dry Fork	1160	Sec.31, T.35N., R.6W.	Dent
Little Dry Fork	2105	Sec.10, T.37N., R.7W.	Phelps
Norman	4105	Sec.21, T.37N., R.6W.	Phelps
Norman	4110	Sec.29, T.37N., R.6W.	Phelps
Norman	4115	Sec.8 , T.36N., R.6W.	Phelps
Norman	4120	Sec.27, T.36N., R.6W.	Phelps
Norman	4125	Sec.28, T.36N., R.6W.	Phelps
Benton	7110	Sec.5 , T.36N., R.5W.	Crawford
Benton	7120	Sec.29, T.36N., R.6W.	Crawford
W. Fork Benton	8105	Sec.19, T.36N., R.5W.	Crawford

TABLE XXIV  
 LOCATION OF SAMPLING POINTS IN THE STUDY AREA  
 WELL POINTS

DRAINAGE BASIN	SAMPLE POINT	OWNER	Mo.G.S.* LOG NUMBER	APPROX. DEPTH	APPROX. DISTANCE FROM CREEK	LOCATION	COUNTY
Dry Fork	1305	T.Truesdell	-	285 ft.	600 ft.	Sec.33,T.38N.,R.6W.	Phelps
Dry Fork	1310	Wycoff Bros.	10675	167 ft.	1300 ft.	Sec.16,T.37N.,R.6W.	Phelps
Dry Fork	1320	V.Frank	15234	140 ft.	1000 ft.	Sec.22,T.37N.,R.7W.	Phelps
Dry Fork	1325	A.Hudek	-	130 ft.	1000 ft.	Sec. 3,T.36N.,R.7W.	Phelps
Dry Fork	1330	B.Apperson	-	198 ft.	1000 ft.	Sec.11,T.36N.,R.7W.	Phelps
Dry Fork	1340	C.Fore	-	205 ft.	1000 ft.	Sec.30,T.35N.,R.6W.	Dent
Norman	4315	C.Pelligrini	15439	235 ft.	800 ft.	Sec.32,T.37N.,R.6W.	Phelps
Norman	4320	G.Strickland	-	290 ft.	1200 ft.	Sec. 7,T.36N.,R.6W.	Phelps
Norman	4330	G.Rhinehart	-	164 ft.	1200 ft.	Sec.33,T.36N.,R.6W.	Phelps
Benton	7305	R.Douglas	12708	203 ft.	1500 ft.	Sec.32,T.37N.,R.5W.	Crawford

\* Missouri Geological Survey and Water Resources

TABLE XXV  
 LOCATION OF SAMPLING POINTS IN THE STUDY AREA  
 SPRING POINTS

SAMPLE POINT	OWNER	DRAINAGE AREA	LOCATION	COMMENTS
1210	-	Dry Fork	Sec. 1, T.37N., R.6W.	Meramec spring
1215	-	Dry Fork	Sec.18, T.37N., R.6W.	-
7209	E.Smith	Benton	Sec.29, T.36N., R.5W.	Drinking water
7210	F.Alexander	Benton	Sec.29, T.36N., R.5W.	Drinking water

## VITA

Robert Russell Kilgo was born on December 19, 1935 at Alton, Illinois and received his primary and secondary education there. He enrolled in the University of Detroit in 1953 and after one semester transferred to the University of Missouri School of Mines and Metallurgy where he received a Bachelor of Science degree in Civil Engineering in January, 1958. He was employed by the Illinois Division of Highways until his return to the University of Missouri at Rolla for graduate study in September, 1964. From February, 1965 until August, 1965 he worked as a Research Assistant in Water Resources at the University.

Mr. Kilgo was married to the former Dolores A. Shockley in April, 1960 and they are the parents of one son.

The author is a member of the National Society of Professional Engineers, the Illinois Society of Professional Engineers, the American Society of Civil Engineers, and the American Water Works Association. He is a Registered Professional Engineer in the State of Illinois.