1970

Evaluation and application of dye tracers in Karst terrain for determining aquifer characteristics

Milton Frank Bradley

Recommended Citation

Bradley, Milton Frank, "Evaluation and application of dye tracers in Karst terrain for determining aquifer characteristics" (1970). *Masters Theses*. 5507.
https://scholarsmine.mst.edu/masters_theses/5507

1. aquifers
I. Title

EVALUATION AND APPLICATION OF DYE TRACERS IN KARST TERRAIN FOR DETERMINING AQUIFER CHARACTERISTICS

BY

MILTON FRANK BRADLEY, 1942

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI - ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN GEOLOGY

Rolla, Missouri

1970

Approved by

James C. Maxwell (advisor) TR Beveridge

V.A.C. Gevecker

ABSTRACT

As ground water becomes increasingly important as a source of water in the United States, reliable information on the hydrological characteristics of carbonate aquifers must be obtained in order to develop them intelligently.

Various tracers have been used in the past to determine if two or more points are connected hydrologically. Today there exists a number of excellent dye tracers and tracer methods have been developed in unconsolidated and clastic aquifers for determining hydrological characteristics.

This paper reviews the various dye tracers and methods which might be applied in a carbonate karst terrain using wells as injection and sampling points. Fluorescein, Rhodamine, and Pontacyl Pink are evaluated.

Effective porosities of the Gasconade, Roubidoux, and Jefferson City Formations were determined from field samples to estimate the amount of water which might be stored and transmitted through these rocks. In field investigations, salt, fluorescein, and Rhodamine were used as tracers during pumping tests at three sites. No background fluorescene was detected in any of the well or spring samples. No connection was established between any wells because none of the tracers placed in the injection wells was detected at any of the observation wells. A point dilution curve was obtained for one injection well.

ACKNOWLEDGEMENT

The completion of this thesis depended upon the assistance and cooperation of many persons. Funds for the project were provided by the State of Missouri, through the University of Missouri - Rolla, Office of Water Resources, Department of the Interior, grant number B-004-MO.

The individual who greatly assisted in the completion of this investigation is the writer's advisor and project director, Dr. James C. Maxwell. His knowledge in the field of ground water hydrology was very helpful in providing valuable information and criticism of this manuscript.

A special appreciation is afforded to the staff of the United States Geological Survey, Water Resources Division, Rolla, Missouri, for the use of their fluorometer and for helpful advice given the author.

Finally, the author wishes to express his gratitude to fellow Water Resources Graduate Assistant, William Mattingly, who allowed me the use of his valuable time and who provided valuable information on the wells and karst features of the area. Last but not least, the author is indebted to the residents of the study area for helpful information and their permission to enter and use their property.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF FIGURES

LIST OF TABLES

Tables Page

Chapter I

INTRODUCTION

The availability for use by man of ground water in any area is determined by the hydrologic characteristics of the different aquifers in which it occurs. Reliable information concerning these aquifers is required in order to develop them intelligently. The standard equations developed for homogenous clastic aquifers may not be valid when applied to limestone aquifers because of the slow apparent movement of ground water in limestone and the internal structure through which it flows. Karst areas are unique in that they are being modified continuously by solution and depositional activity and contain a wide variety of flow patterns within them. With the development of tracers, it has become possible to determine directly the effective rate and direction of flow of ground water and compare the results with those obtained in pumping tests.

The objectives of this study were to compare the reported behavior of several dye tracers and the relative effectiveness and disadvantages of each, to establish a method of determining the distance wells should be spaced in order to conduct relatively reliable tests over short periods of time, and to test the feasibility and well spacing method in field trials to determine the hydrologic characteristics of shallow aquifers in the Meramec Spring, Missouri, 15' quadrangle.

The methods involved require the use of fluorescent dye tracers, physical sampling, and laboratory analysis using a fluorometer. The information on many of these methods has been gathered from scattered references in the literature. Additional data have been obtained from preliminary tests conducted in the laboratory and field.

The field area of investigation (fig. 1) lies near the central part of the Missouri Ozarks. Nearly all towns and rural residents of the area obtain their water supply from wells. In this area of uplands and valleys, elevations vary between 800 and 1,100 feet above sea level. The surface water of the area flows almost entirely into the Meramec River which in turn drains to the east to the Mississippi River Near St. Louis. Because of the presence of springs, layers of porous chert, thick residuum, and the lack of topsoil, the streams in the area are relatively clear except during high floods. The lack of topsoil, the abundance of chert over large portions of the area, and the ruggedness of the topography have made the land less desirable for agricultural purposes than that of other Missouri areas outside the Ozarks. This unique situation has created and encouraged the

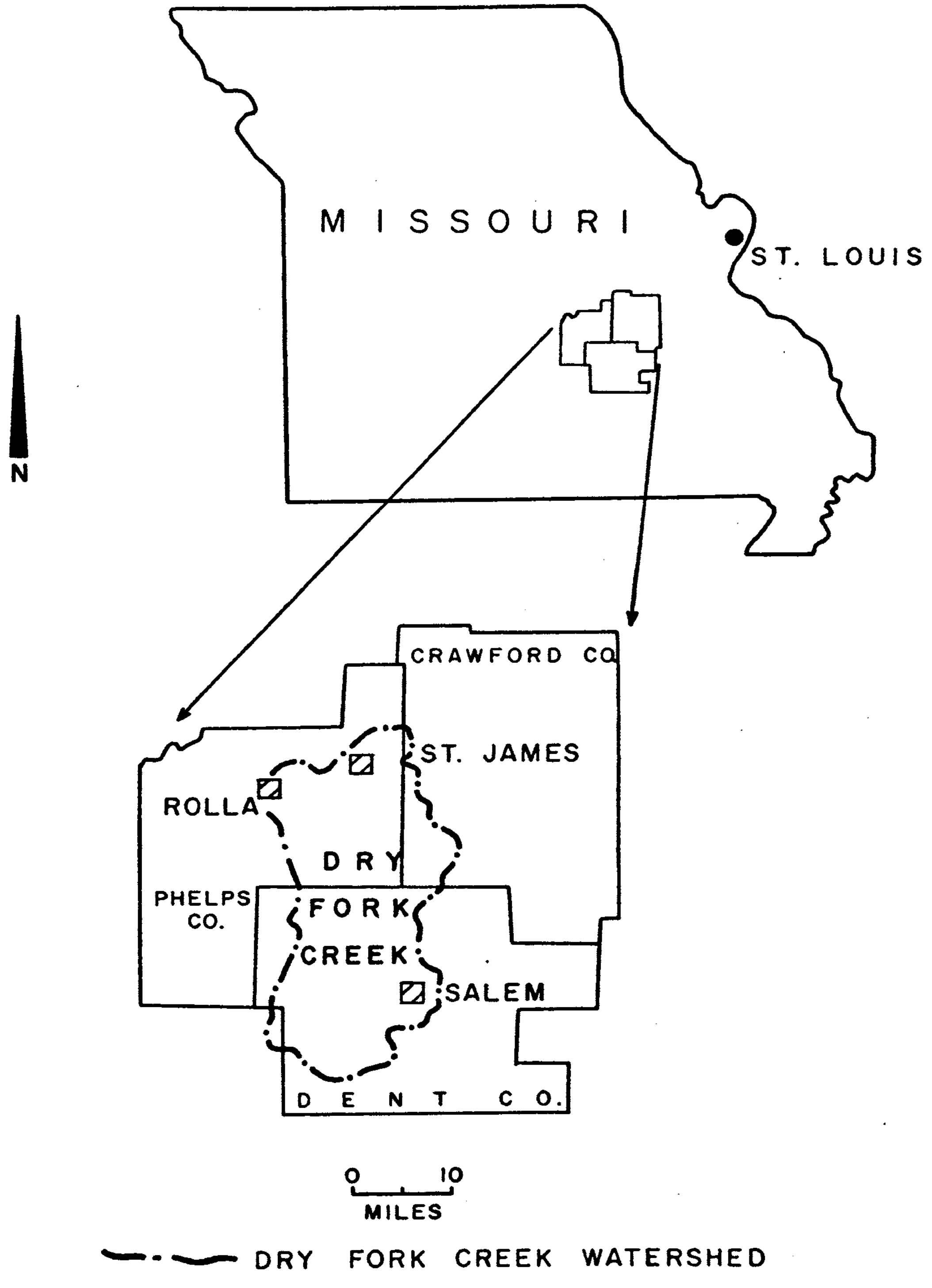


FIG. I LOCATION MAP OF PROJECT AREA

development of hunting, fishing and tourism within the Ozarks by both state and federal agencies thus giving the area a culture and economy all its own.

Chapter II

GEOLOGY

A. Geomorphology

The area under investigation lies within the Salem Plateau which is a subdivision of the Ozark Plateaus. The Salem Plateau takes its name from the city of Salem, Dent County, Missouri where it is typically developed. The topography is developed almost entirely on rocks of Ordovician age, which are predominantly dolomites with lesser amounts of sandstone. The area is dissected by the Meramec, Dry Fork, and Little Dry Fork rivers. The maximum relief in the area is four hundred and fifty feet.

Many geologists consider the upland surface of the Salem Plateau, of which the Meramec Spring Quadrangle is a part, to be a peneplain surface rather than a stripped structural plain and some consider it neither a peneplain nor a stripped structural surface. The widespread distribution of cavernous dolomites in the area and deep dissection by the major streams has led to the development of large springs. The largest and most prominent spring in the area is Meramec Spring with an average discharge of ninety-six million gallons per day.

Bretz (1956, 1965), from his detailed studies of Missouri caves, concluded that most of them were the result of solution by phreatic waters beneath mature topography that preceded development of the Ozark Peneplain. By the time the topography has been reduced in relief to peneplain conditions, circulation of phreatic waters through the caves stagnated to such a degree that most of the caves became filled with clay derived from the deep residual soil on the surface of the Ozark Peneplain. Subsequent uplift of the peneplain resulted in deep dissection of the topography and lowering of the water tables. This brought most of the caves into the zone of vadose waters. Later, partial or complete removal of clay fill took place. In support of this theory, Bretz noted that few cave streams can be traced to sinkhole sources or to engulfment of surface streams into sinks.

B. Hydrogeology of Shallow Aquifers

An abundant supply of potable ground water is found throughout the area with shallow aquifers yielding enough water for small farms and domestic use. The shallow aquifers in the area of investigation include the Gasconade, Roubidoux, and Jefferson City Formations.

These formations are all contained within the Canadian Series of the Ordovician System. All the formations are primarily dolomites except the Roubidoux Formation which includes several sandstone beds within the study area.

The oldest of the aquifers studied, Gasconade Formation, is predominantly a light brownish gray, cherty dolomite. At the base of the formation there is a sandstone unit designated the Gunter Member. This member where present consists of a very pure, light gray to brown, well cemented, usually quartzose sandstone. Its thickness ranges from a few inches to thirty-five feet or more. This sandstone unit where more than a few feet thick will generally yield fifty gallons per minute (Beveridge and Hayes, 1960).

The lower part of the Gasconade Formation above the Gunter Member is a coarsely crystalline unit characterized by large amounts of chert which often exceeds fifty percent of the total volume of the rock. The upper part of the formation is predominantly a finely crystalline dolomite containing relatively smaller amounts of chert. Widespread masses of cryptozoon are present in the formation and are persistent about fifty feet below the contact with the Roubidoux Formation. In the area of the Meramec Spring 15 minute quadrangle, the Gasconade Formation is 250 feet or more thick.

The formation is best exposed where dissection of the topography is a maximum. The karst features of the area are developed predominantly in this formation and to a lesser extent in the overlying Roubidoux Formation where solution of the Gasconade Formation has produced collapse sinkholes in the Roubidoux.

Wells in the Gasconade Formation produce approximately twenty-five gallons per minute from a fifty to seventy-five foot fractured chert zone (Beveridge and Hayes, 1960). This zone is a satisfactory source of water whenever contamination takes place in the overlying Roubidoux Formation.

The Roubidoux Formation consists of lenses of sandstone, dolomite, and chert. The youngest major sandstone unit is at the middle of the formation and is approximately twenty-five feet thick. Another major sandstone unit is at the base of the formation and is generally ten feet thick. These lenses are not widely persistent, but change rapidly from one locality to another, so it has been impossible to trace them over large areas. The sandstone generally consists of medium to coarse grained quartz sand which is often cemented by ferruginous material.

Overlying the Roubidoux Formation is the Smithville, Powell, Cotter, and Jefferson City Formations. They are composed of light brown to brown, medium to finely crystalline, argillaceous dolomite. The Jefferson City and Cotter Formations are the only ones that occur in the study area. A finely crystalline, argillaceous dolomite called "cotton rock" is characteristic of the Jefferson City Formation. The areas of outcrop of the Jefferson City and Cotter Formations are confined essentially to the western and northern sections of the Meramec Spring 15 minute quadrangle. Because they are so shallow and generally above the water table, very little water is produced from these formations in the Rolla area.

C. The Development of Porosity and Permeability

The porosity of a rock is a measure of the contained voids and is expressed as the percentage of the void space to the total volume of the mass. The porosity as determined in the laboratory is a minimum value because it measures only the connected interstitial voids. Large fractures, joints, and bedding planes are not represented in small laboratory test specimens because of their size.

The pores and other openings such as fractures may be characterized by their size, shape, irregularity, and distribution. There are two major divisions of porosity, original porosity which was created by geologic processes governing the origin of the formation, and secondary porosity which develops after the rock has been formed and includes joints, faults, and solution openings.

When water fills all the interstices in an aquifer the aquifer is said to be saturated. Not all this water may be removed because of molecular and surface tension forces that tend to hold a portion of the water in place. The ratio expressed as a percentage of the volume of water which can be drained by gravity from a saturated rock to the total volume of the mass, is known as the specific yield or effective porosity. This value will always be a fraction of the total porosity because of the retained water.

The permeability of an aquifer is its capacity for transmitting fluids. The degree of permeability depends upon the size and shape of the pores, the size and shape of their interconnections, and the extent of the latter. It is measured by the distance which water under a given head can move in a given interval of time. The darcy is a standard unit of permeability and is equivalent to the passage of one cubic centimeter of water of one centipoise viscosity flowing in one second under a pressure differential of one atmosphere through a porous medium having an area of cross-section of one square centimeter and a length of one centimeter. A millidarcy is one one-thousandth of a darcy.

The development of original porosity in limestones is affected by compaction, solution of aragonite and calcite, precipitation of calcite cement, and the formation of the mineral dolomite. The original porosity of most young limestones is relatively high. One of the methods by which porosity is increased is the post-depositional change from calcite to dolomite. If this diagentic change takes place after the rocks are lithified, a 13 percent volume reduction caused by the transformation will be left as void space. The primary porosity of limestones serves as a significant storage space for ground water which is released slowly to the permeable zones.

The permeability of young limestones is generally low except in rocks such as breccias and coquina in which the larger pores are not filled initially with cement. Permeabilities may range from less than one millidarcy for clay-rich, dense limestone to several thousand darcys for partly cemented coarse breccias. Intermediate values of 10 to 500 millidarcys are more common for limestones having some original porosity.

From the standpoint of water production the greatest quantity of aquifer water is probably transmitted by fractures and secondary openings along bedding planes. Hamilton (1948) concludes from his studies that no appreciable quantity of ground water is transmitted through intergranular openings in the limestone. Rather, ground water movement is restricted to openings along joint and bedding planes. Solution along these planes has been effected only to a limited depth below the land surface. He also states that the depth of solution is greater below stream valleys than ridges.

The effective porosity of sandstone may vary from five to thirty percent. The amount of pore space is a function of sorting, grain size, shape, packing, and degree of cementation. The most important factor influencing the effective porosity is the degree of cementation. Case hardening of sandstone near the surface will be very misleading as to the hydraulic characteristics of the formation (Davis and DeWiest, 1966). The variation of permeability within a sandstone is controlled chiefly by grain size and degree of cementation.

D. Effective Porosity of the Shallow Aquifers

During the spring of 1968, a study was made of the effective porosity of samples from formations thought to be shallow aquifers in the vicinity of Rolla, Missouri. The Gasconade, Roubidoux, and Jefferson City Formations were sampled at freshly excavated road cuts, a quarry and a cave. Sample locations are shown on Figure 2. The selection of samples, their size, and the number were critical factors affecting what specimens were tested. Extensive sampling rather than intensive sampling was used because of the heterogeneous character of the formations. Large enough samples were collected to provide several test pieces from each sample in order to check the precision of the method and for averaging values obtained in the different samples.

The samples were sawn into rectangular blocks using a diamond saw and a sliding vise. Care was taken to make sure that all angles between faces were 90 degrees and that all sets of faces were parallel. Samples were cut so that their long axes would be perpendicular to

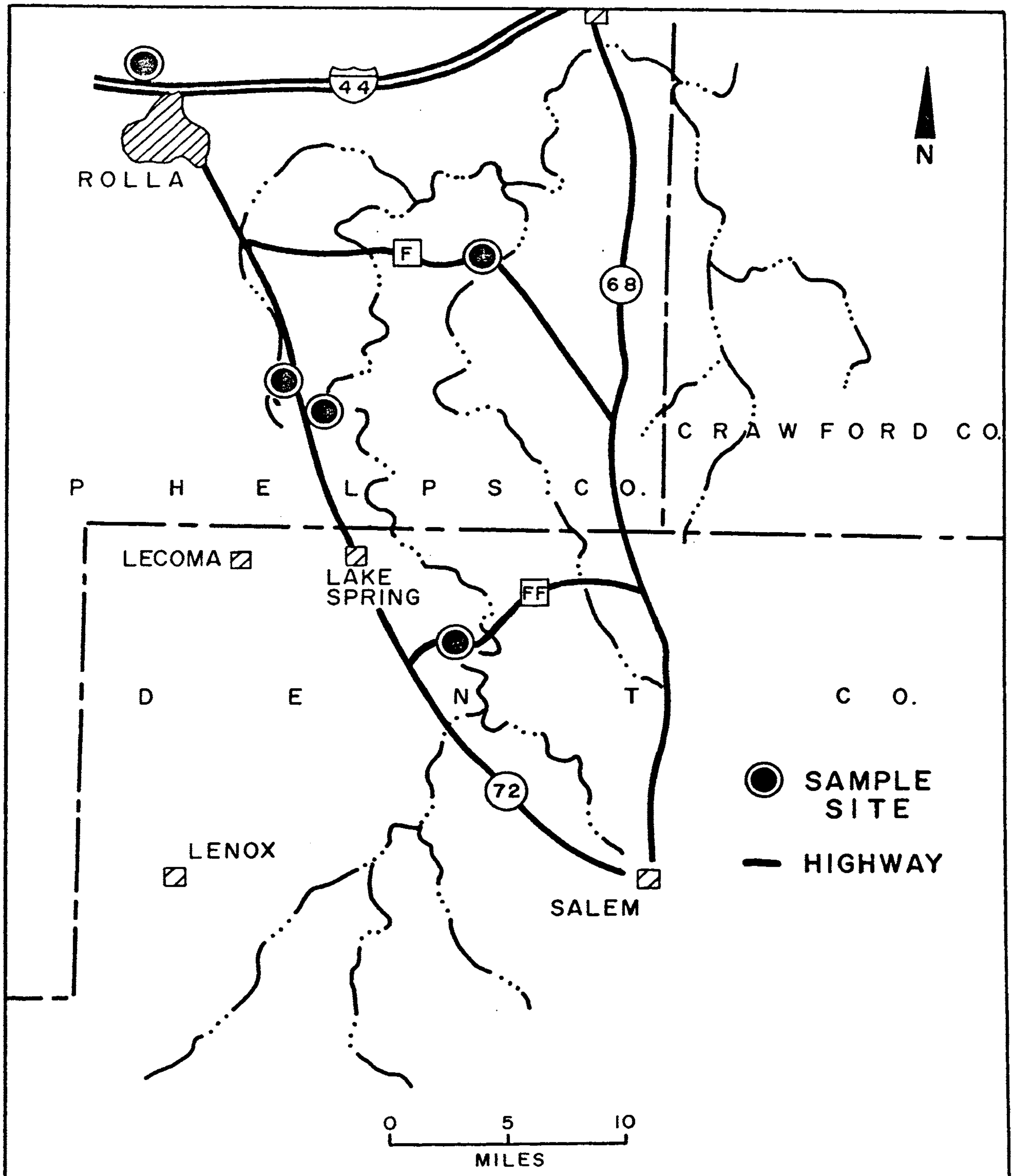


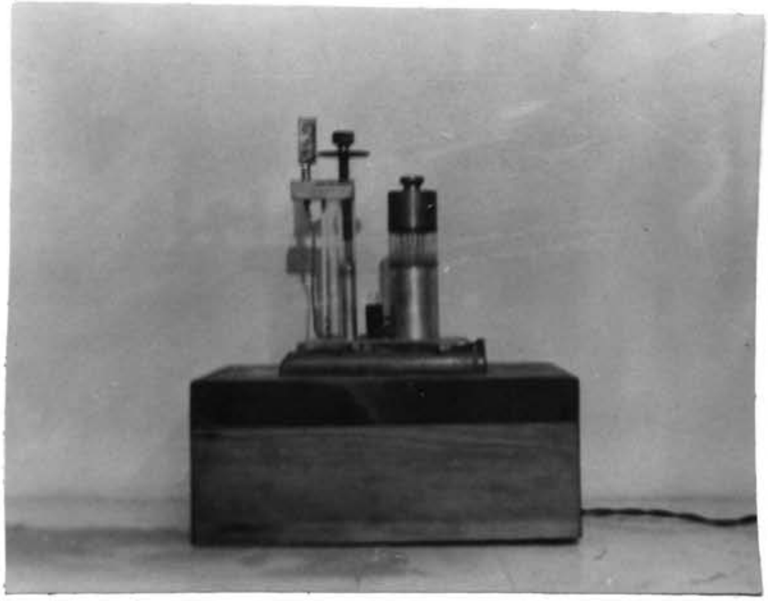
FIG. 2 LOCATION OF EFFECTIVE POROSITY SAMPLES

the bedding. The specimens had to be cut so that the short diagonals in each sample were less than three-quarters of an inch so that they could fit into both the porosimeter and pyncnometer. A water cooled diamond saw was used instead of the oil bath type to minimize contaminating or sealing the rock's small pores.

The volumes were measured by two methods. In the first, the diagonals and heights of each sample were measured to a tenth of a millimeter using a micrometer. The area of the top and bottom of each sample was calculated using the formula $A = ef/2$, where e and f are the diagonals. The volume was then calculated by $V = 1/3h(A_t+A_b+\sqrt{A_tA_b})$ where A_t and A_b are the areas of the top and bottom respectively, and h is the height between the two areas.

The second method uses an electric pyncnometer (fig. 3a) which is essentially an instrument to measure the density of materials but is constructed so that it can measure volumes directly to a high degree of accuracy. The method simply measures the amount of mercury displaced when a sample is added to a known volume of mercury.

The porosity was determined by the use of the Washburn-Bunting method (Krumbein and Pettijohn, 1938), using a McLeod type of porosimeter. The porosimeter (fig. 3b) consists of a sample chamber connected in series to an expansion chamber and to a calibrated



a. ELECTRIC PYCNOMETER

b. MCLEOD TYPE POROSIMETER

FIG. 3 EQUIPMENT USED IN POROSITY STUDIES glass capillary tube and valve. This apparatus is mounted in a fixed position, with the calibrated capillary tube uppermost. The bottom of the sample chamber is connected by a heavy rubber tube to a glass leveling bulb containing mercury. The bulb is attached to a sliding mount next to the glass column so that a comparison of mercury levels can be made when the bulb is raised and lowered.

In this instrument, the air is drawn from the rock pores by means of a mercury piston and is subsequently compressed into the calibrated capillary tube at atmospheric pressure. The volume of air drawn from the sample is read directly from the capillary tube.

The results of this study are presented in Tables 1, 2, and 3, with pictures of a number of the specimens to illustrate the type of porosity present.

Table 1 Effective Porosity of the Gasconade Formation

A: Light grayish brown, very compact, crystalline dolomite. Numberous voids lined with dolomite crystals. (Figure 4a).

Effective porosity........................4.7%

B: Mottled light gray and brownish tan dolomite. Crystalline containing a few small voids that are lined with dolomite crystals. Voids less than a millimeter to almost a half centimeter in diameter.

Effective porosity.......................11.5%

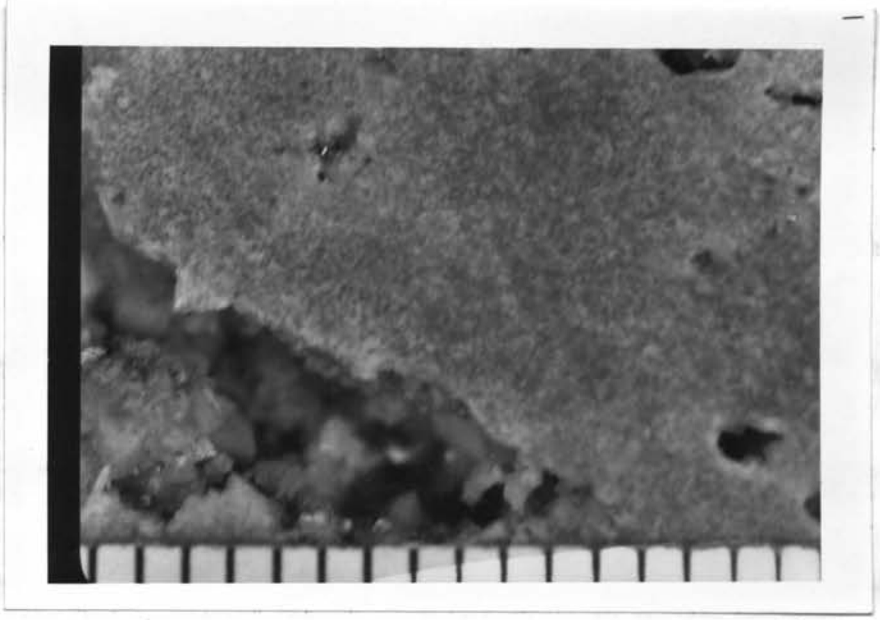
C: Mottled light gray and light brown dolomite with light to medium gray chert. Compact dolomite containing some small voids and a few minute fractures.

Effective porosity........................8.5%

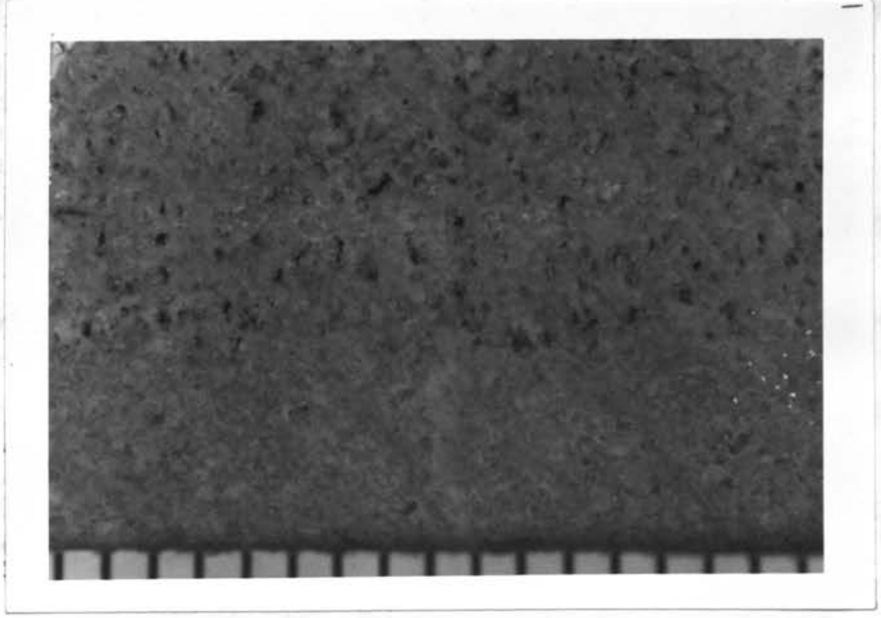
D: Light to medium gray, compact, crystalline dolomite. Color banding parallel to bedding. (Figure 4b).

Effective porosity........................9.1%

Note: All samples were collected from a road cut 1½ miles west of Rolla on access road north of highway 66, Phelps County, Missouri



a. SAMPLE A – GASCONADE FORMATION
1 INCH :: 4.5mm.



b. SAMPLE D - GASCONADE FORMATION
1 INCH :: 4.5mm.

FIG. 4 GASCONADE POROSITY SAMPLES A AND D

Table 2 Effective Porosity of the Roubidoux Formation

A: Shelton Cave, Phelps County, Missouri. Light gray to light brown, compact sandstone. Some bedding apparent and a few small voids from one to two millimeters are present in one layer.

Effective porosity.......................17.3%

B: Shelton Cave, Phelps County, Missouri. Light gray to tannish brown, compact sandstone. Some small bedding fractures are present with some small voids less than two to three millimeters.

Effective porosity.......................24.4%

C: Shelton Cave, Phelps County, Missouri. Light brown, very compact, crystalline dolomite containing small voids lined with dolomite crystals.

Effective porosity.......................11.3%

D: Shelton Cave, Phelps County, Missouri. Light gray to medium tan, sandy dolomite. Fairly compacted, granular to crystalline with one small fracture.

Effective porosity........................7.9%

E: Shelton Cave, Phelps County, Missouri. White to light gray sandstone. Compacted but slightly friable. One void containing clay.

Effective porosity.......................12.5%

F: Junction of highway F and Norman Creek, Phelps County, Missouri. Light Gray to brown, sandy dolomite. Dolomite is dense and compacted. (Figure 5a).

Effective porosity.......................18.6%

G: Highway FF between highways 68 and 72, Dent County, Missouri. White to light gray, dense, compacted sandstone with bands parallel to the bedding planes.

Effective porosity........................10.9%

H: Highway FF between highways 68 and 72, Dent County, Missouri. Gray compacted conglomeratic sandstone with pebbles composed of dolomite. (Figure 5b).

Effective porosity.........................8.2%

I: Highway FF between highways 68 and 72, Dent County, Missouri. Light gray to yellowish brown conglomeratic sandstone. Many voids in the shape of pebbles elongated along the bedding planes. Sandstone is strongly cemented around voids. (Figure 6a).

Effective porosity........................23.4%

J: Highway FF between highways 68 and 72, Dent County, Missouri. Light to medium gray banded chert. Voids along bands lined with quartz crystals. Voids partially to nearly filled. (Figure 6b).

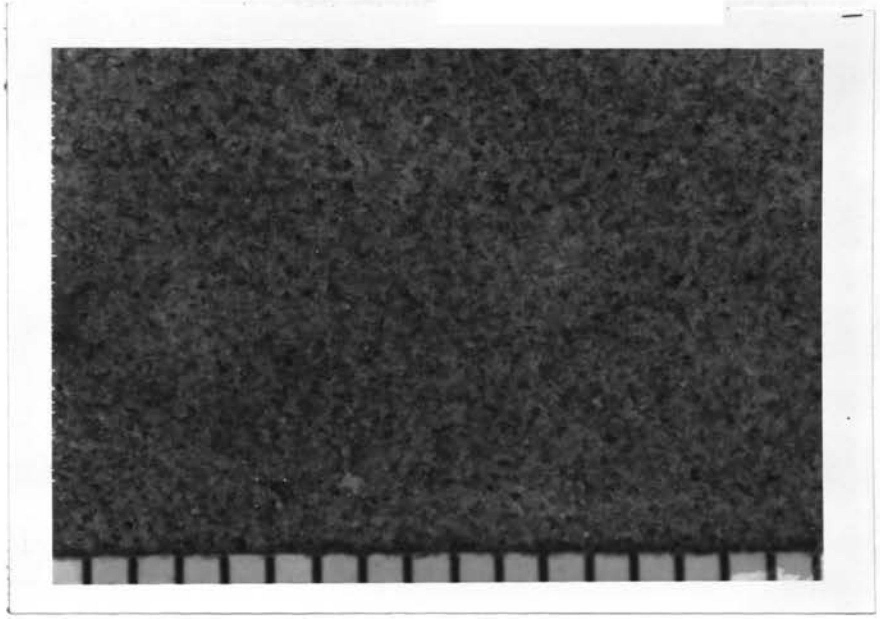
Effective porosity.........................9.7%

K: Highway FF between highways 68 and 72, Dent County, Missouri. Medium gray chert with very irregular texture. Many voids and solution holes with some voids lined with quartz crystals. Many minute fractures some filled, some open.

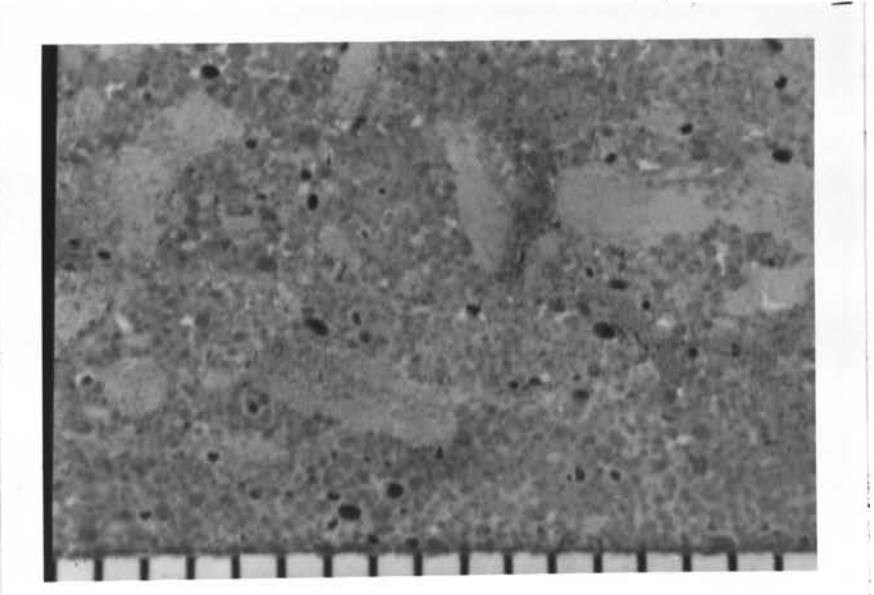
Effective porosity........................11.9%

L: Highway FF between highways 68 and 72, Dent County, Missouri. Tan to light gray, crystalline dolomite. Both large (2-5 mm.) and small (less than 1 mm.) voids. Dolomite crystals partially filled voids. Some fractures are present. (Figure 7).

Effective porosity........................18.0%

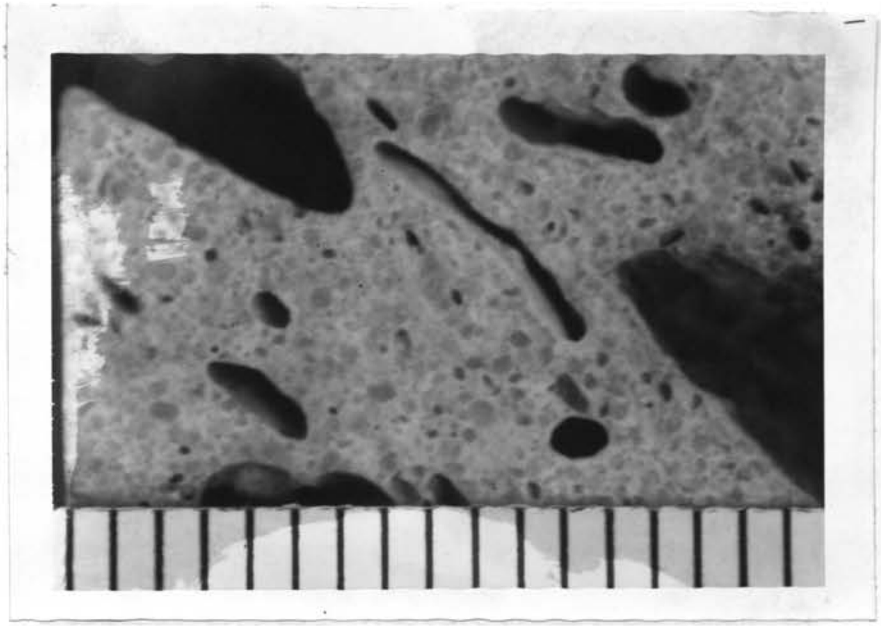


a. SAMPLE F – ROUBIDOUX FORMATION
1 INCH : : 4.5mm.

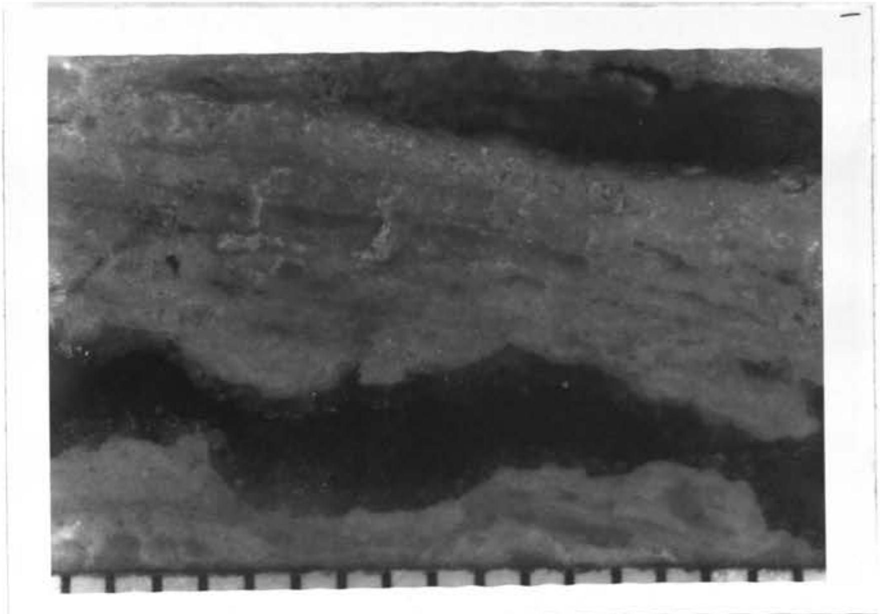


b. SAMPLE H - ROUBIDOUX FORMATION
1 INCH : : 4.5mm.

FIG. 5 ROUBIDOUX POROSITY SAMPLES F AND H

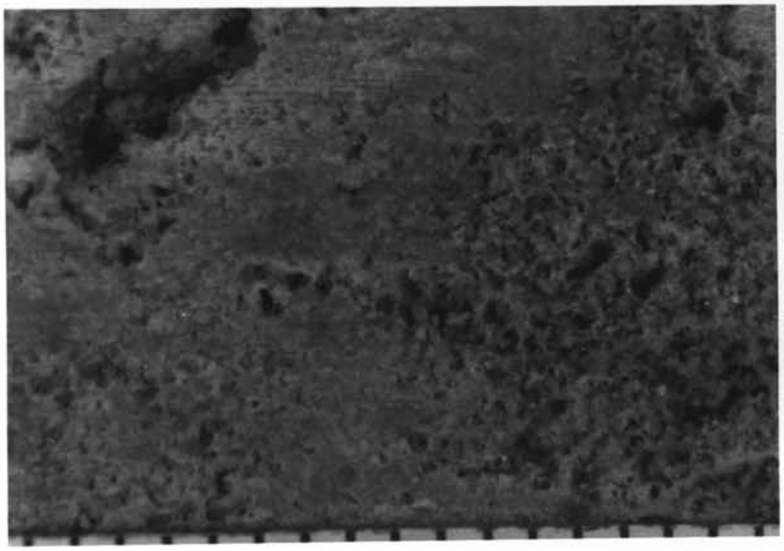


a. SAMPLE I – ROUBIDOUX FORMATION
I INCH : : 4.5mm.



b. SAMPLE J – ROUBIDOUX FORMATION
I INCH : : 4.5mm.

FIG. 6 ROUBIDOUX POROSITY SAMPLES I AND J



SAMPLE L - ROUBIDOUX FORMATION
I INCH :: 4.5mm.

FIG. 7 ROUBIDOUX POROSITY SAMPLE L

Table 3 Effective Porosity of the Jefferson City Formation

A: Light grayish tan, compact, crystalline dolomite. Some small crystals of pyrite are present. Very uniform in color and texture.

Effective porosity........................14.2%

B: Medium gray, very compact, crystalline dolomite. Very uniform in color and texture. Some voids approx. 0.5 mm. in diameter containing quartz crystals are present.

Effective porosity........................16.1%

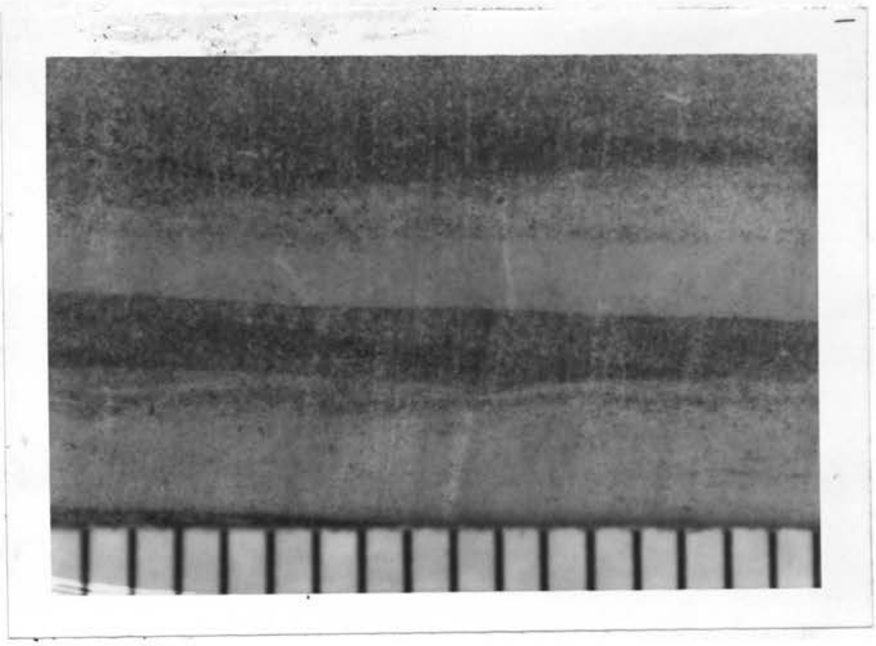
C: Light to dark gray banded dolomite. Layers in the dolomite are cross-bedded. Dense and compact with no voids detectable with naked eye. (Figure 8a)

Effective porosity........................13.5%

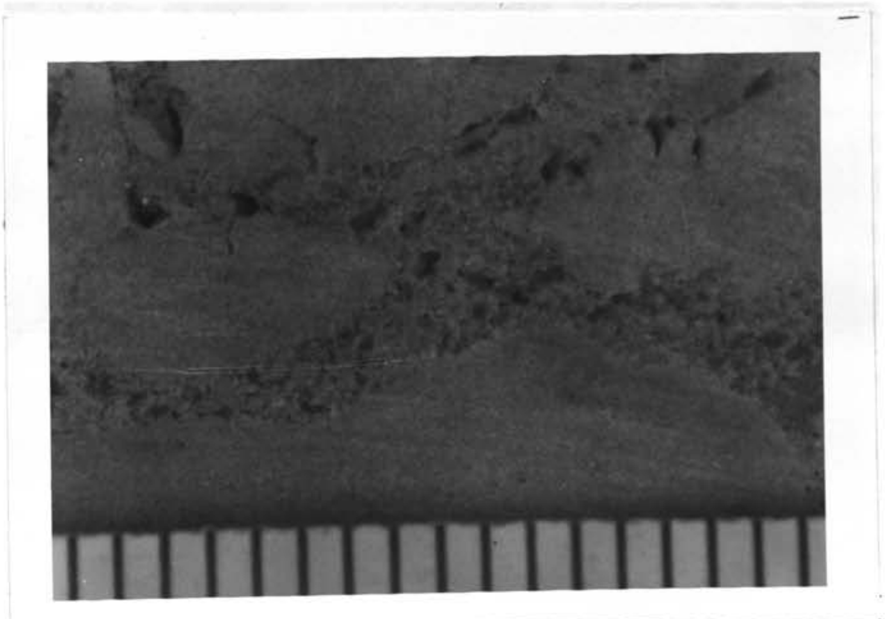
D: Light gray, conglomeratic dolomite. Dolomite has been fractured and recrystallized. Numerous small voids less than 2 mm. in diameter are present. (Figure 8b)

Effective porosity........................13.9%

Note: All samples were collected from a quarry 7 miles south of Rolla on highway 72, Phelps County, Missouri.



a. SAMPLE C – JEFFERSON CITY FORMATION
1 INCH :: 4.5mm.



b. SAMPLE D – JEFFERSON CITY FORMATION
1 INCH :: 4.5mm.

FIG. 8 JEFFERSON CITY POROSITY SAMPLES C AND D

Chapter III

DYES AS GROUND WATER TRACERS

Dye tracers have been used to determine the rate and direction of flow of ground water since the latter part of the nineteenth century. With recent developments in both instruments and fluorescent dyes, it has become possible to determine some quantitative characteristics of aquifers with the aid of tracers. A review of the literature was made in order to select the most suitable dye tracers for use in karst terrain.

A. Selection of Tracers

Carpenter, Morgan, and Parsons (1953) set forth the following requirements for a satisfactory tracer: it must 1) be susceptible of quantitative determination at very low concentration, 2) either be entirely absent or else present only in trace quantities in natural waters, 3) not react with the input or connate water to form a precipitate, 4) not be adsorbed by reservoir rocks, 5) be reasonably water soluble so that the required concentrations may be introduced at input wells, 6) be cheap and readily available. In general the ideal tracer should be easily detected material that correctly describes the velocity variations of the liquid being traced without modifying in any way the transmission characteristics of the system. No single tracer has yet been proven to be an entirely satisfactory tracer of ground water under variable conditions likely to be encountered in subsurface formations.

The organic dyes, including fluorescein, Rhodamine, and Pontacyl Pink come closest to being ideal tracers. Table 4 summarizes the characteristics of these dye tracers.

B. Fluorescein

Fluorescein was used as early as 1877 by a German hydrologist (Dole, 1906), and in 1882 a French medical doctor, Dionis des Carrieres, used fluorescein to prove the origin of contaminated water during a severe typhoid epidemic in France. M. Trillat (1889) conducted elaborate investigations into the sensitivity of certain dyes, including fluorescein, for application as flow indicators and the effect on them of passage through columns of soil. Fluorescein was tested and applied extensively in France by geologists and hydrologists long before its introduction into the literature of the United States (Dole, 1906).

The dye commonly used in tracer experiments has a reddish brown or slightly orange color in powder form. The dye is completely and rapidly soluble in water. In the presence of alkalies its solution is red by transmitted light and bright green by reflected light. The dye solution is a weak acid and represents the type of tracer that can be recognized easily by its color

Table 4. Comparison of Fluorescein, Rhodamine and Pontacyl Pink Dye Tracers

	Fluorescein	Rhodamine B Extra	Rhodamine Ba	Rhodamine Wt	Pontacyl Brilliant Pink
Formula	$C_{20} H_{12} O_5$	$C_{28} H_{31} N_2 Ocl$			$C_{27} H_{24} N_2 O_4 S_2 N_a$
Form	Powder	Powder	40% Solution	20% Solution	Powder
Min. Detect. in Distilled H2O at 20^{o}C	0.000041 Mg/l	0.000046Mg/l	-	-	0.00011 Mg/l
Detectability with naked eye	20-30 ppb	20-30 ppb	20-30ppb	20-30 ppb	---
Effect of PH	Great Reliance on PH	Nearly independent from 5 to 10	--	--	Not effected from 3 to 10
Effect of Temperature	Slight	Great	Great	Great	---
Photochemical Decay Rate	High Rate After two days	Moderately Effected	Moder. Effected	Moderately Effected	Least Effected
Absorption on Suspended Sediments	---	Varies	--	---	No Adsorption

when dissolved in large volumes of water. In diluted solutions of clear water it shows a magnificient yellowish green fluorescence by reflected light and may appear colorless by transmitted light.

Dole (1906) noted that the addition of a small amount of ammonia will excite the fluorescence of fluorescein. Boutari (1940) on investigating this characteristic found that the fluorescent intensity of fluorescein increases with pH, at first moderately rapidly and then more slowly, approximately doubling for a pH rise from 4.6 to about 6, then trebling at pH 7, quadrupling at pH 8 with little change above 8. Ambrose (1921) recommends that if the final sample is acid that the sample be made alkaline before testing so as to develop its full fluorescence. The dye in diluted solutions is not affected by free carbonic acid but its solution is rendered colorless by acetic and mineral acids which are formed by decaying vegetation and decomposition of minerals respectively (Dole, 1906; Austin, 1921; Stabler, 1921; and Plummer, 1945).

Dole (1906) reports that lime, sand, clay, and farm manure exerted no influence on fluorescein but that peat brings about complete decoloration, the degree of influence being proportional to the organic matter present (Dole, 1906; Plummer, 1945). Stabler (1921) also noted that fluorescein had the tendency to lose its color when passing through peaty soils. The dye shows a definite tendency to be removed by adsorption when passing through finely divided soils (Ambrose, 1921; Stabler, 1921). Later studies by Sturm and Johnson (1950) proved that even sand will adsorb fluorescein when the dye is passed through a column and desorption occurs when wetting agents are added. Kaufman and Orlob (1956) in their study of three California soils observed that fluorescein on its arrival through a column of soil exhibited a trailing elution curve so characteristic of strong adsorption. This retardation had been reported elsewhere in the literature (Plummer, 1945; Sturm and Johnson, 1950; Heck, 1954; and Watkins and Mardock, 1954). Heck (1954), Stabler (1921) and others report the loss or failure of fluorescein dye to appear and that it is not known whether the failure of the dye to appear at sampling points was due to its decoloration or too great dilution underground, to faulty methods of conducting the test, or to the fact that the water was actually not migrating from one well to another.

The effect of photochemical decay is extremely high on fluorescein which prohibits its successful use in surface waters.

C. Rhodamine

One of the first references in which the properties of Rhodamine B as a water tracer are discussed was published by Feverstein and Selleck (1963a). They conducted a laboratory investigation of Rhodamine B in order to determine the analytical response of the tracer in surface waters. An excellent description of its properties is given with conclusions as to proper use of the dye. Dunn and Vaupel (1965) reported on the influence of temperature on the determination of fluorescent dyes, including Rhodamine, using a Turner Model-III fluorometer. They developed a procedure for the preparation of correction curves for the effect of compartment and sample temperature for field use of the fluorometer where sample and compartment temperatures cannot be controlled.

Rhodamine B ($C_{28}H_{31}N_2O_3Cl$) is related to the more familiar disodium fluorescein dye in that both are organic dyes and belong to the phenolthalein family of dyes. Among the strongly fluorescent synthetic dyes the rhodamines seem to be the only exceptions which are not phosphorescent in solid solutions at room temperature. The dye may be obtained commercially in solution concentrations of 40 percent by weight in acetic acid (BA), 20 percent solution in methanol (WT), or as a dry powder. Because of Rhodamine's high solubility in methanol, concentrated dye solutions may be adjusted to the same density as that of water.

Rhodamine B is dark brown in powdered form and a vivid red color in diluted solutions. The dye is very soluble in acetic acid, methanol, and water and hence the different forms such as B, BA, and WT behave differently when injected into an aquifer.

Wright and Collings (1964) conclude that with respect to low cost of tagging large volumes of water and to harmlessness by or from light when in diluted solutions, Rhodamine B is very suitable for tracer studies. They compare the adsorption spectra of several naturally occuring substances with that of Rhodamine to show how principal background components might be expected to interfer. Adsorption spectra, fluorometers, and fluorometer filters are discussed briefly.

Wright and Collings (1964) report that the fluorescence of Rhodamine B is not affected by acidity within a pH range of 4.0 to 10.5; at pH value of 2, fluorescence is decreased only 13 percent. Rhodamine B is most independent of pH and can be used when extreme values of pH are encountered.

Wright and Collings (1964) state that the average adsorption rate of Rhodamine was 12 percent when tested on sands in the laboratory. When organic material was used the rate varied from 2 to 28 percent. Practically all the dye adsorbed on the sand could be recovered by washing. Feuerstein and Selleck (1963) also report a 12 percent loss of Rhodamine on suspended sediments of low concentration in fresh water. Adsorption on suspended sediments is the most significant disadvantage to its application in tracer studies.

Feuerstein and Selleck's (1963) tests on the fluorescent dyes indicated that the photochemical decay rate of Rhodamine is one twenty-fifth that of fluorescein. Pritchard and Carpenter (1960) found that the dye in glass bottles, when exposed to fluorescent lighting for eight months, decreased in fluorescence only five percent. When exposed to direct sunlight for two months, however, it decreased forty percent. They suggest that in surface systems, the decomposition by light would be negligible for periods up to two weeks.

D. Pontacyl Brilliant Pink

Pontacyl Pink ($C_{27}H_{24}N_2O_4S_2Na$) is the least well known of the above tracers and may be the best quantitative water tracer with perhaps the exception of Rhodamine WT. Feuerstein and Selleck (1963) state that: 1) It demonstrated no adsorption on suspended sediments, 2) indicated the lowest photochemical decay rate, 3) was least affected by pH, 4) was markedly effected by temperature, and 5) the cost of this dye is much higher, but when considering the overall characteristics of the dye and the total cost of conducting a test, this economic differential might be justified.

E. Movement of Dye Tracers

The movement and concentration of a tracer is governed by the geologic, hydrologic, biologic and cultural environment of the water and varies from time to time and place to place. Marked changes in movement and concentration can, and often do, accompany shifts in hydrologic equilibrium such as variations in recharge and pumping rates. The most common forces that act to mix tracers in ground water are the differences in velocities and pressure as the water passes through material of hetergenous permeability, and to a lesser extent ionic diffusion.

Generally, dye tracers travel more slowly than the water in which they are injected because of their greater density, and tend to migrate to lower places along their path. Hence, large subterranean passages could retain the dye for a short while before an influx of water would flush out the dye. The dye is also retarded by ionic exchange or adsorption which occurs along its route.

Velocities calculated from flow of dye between pairs of wells are generally maximum velocities because the tracer will follow the routes of highest permeability. Such values are too high for the average of the entire section tested as concluded by Wensel (1942). He also states that ground water velocities vary considerably over short distances which requires that tests be made at as many places as possible and over the entire thickness of the aquifer.

F. Dispersion

The dispersion or scattering of the dye as it merges with the untraced liquid may be the result of several phenomena. The degree of frontal dispersion or dilution along the axis of flow is governed by the following criteria as set forth by Kaufman and Todd (1960):

1. Gross or macroscopic variations in permeability may result in channeling, causing very rapid travel of portions of the tracer front, while other portions may actually be retarded. Such channeling may be either longitudinal or transverse to the major direction of flow.

2. Minute, or microscopic variations in permeability, resulting from the differing diameters of adjacent pores, will cause velocity differences from pore to pore, and increase the length of the front.

3. Velocity distribution within a single capillary will cause further longitudinal dispersion with additional lengthening of the front.

4. Molecular diffusion in the direction of flow is probably relatively small, except in cases where the actually linear flow rate is extremely small. However, diffusion transverse to the direction of flow may be a significant factor in determining frontal characteristics.

5. The presence of non-transmitting interstitial cavities connected to water transmitting pores by small openings may permit the interception and retention of a portion of the tracer by diffusion.

G. Adsorption

As a liquid containing a tracer enters a permeable medium having the capacity to adsorp the component, the liquid is supersaturated with respect to the solid and adsorption takes place. The liquid and tracer front will cease to flow at the same velocity. As fresh liquid, free of the tracer component, comes into contact with the tracer-media complex, the liquid is undersaturated and desorption occurs. The ratio of the velocity of the tracer front to that of the liquid has been formulated for organic resins by Vermeulen and Hiester (1952).

Chapter IV

TRACER TECHNIQUES

In recent years a number of new techniques have been developed for determining aquifer characteristics using tracers. Some of the older techniques were qualitative in nature and simply determined the elapsed time and direction of flow. With the development of several new techniques in recent years, it has become possible to determine some quantitative characteristics of aquifers.

A. Time of Travel Method

The usual method of expressing the rate of flow of tracers is in feet per minute or feet per day. This value is calculated by dividing the horizontal distance in a straight line from the point of entry to the point of appearance by the time which elapses. Thus

$$v = D/T$$

where v is the rate of flow in feet per day, D the distance, and T the time in days.

This value will always be less than the actual rate of flow due to the time consumed by the solution soaking through the material separating the ground surface from the strata in which the water circulates. This time lag is eliminated when wells are used for injection. It is also probable that the actual path of travel of the tracer will deviate from a straight line. If we take into account the time consumed in infiltrating through the material separating the surface where the dye was injected to the strata through which the water circulates then the corrected velocity v_1 is calculated by setting

$$v_1 = D/T_2 = D/(T-T_1)$$

where T_1 is the time consumed in infiltrating. The difference between the corrected and uncorrected rate is:

$$v_1-v = D/T-T_1-D/T = DT_1/TT_2$$

where T_2 is equal to $T-T_1$.

The greater the time consumed by the preliminary infiltration the larger will be the error of the uncorrected rate; and the error will vary inversely with the permeability of the soil through which the tracer must pass.

B. Dunn Method

Dunn (1957), using fluorescein, developed a method primarily for tracing ground water in fissured or cavernous areas by using highly adsorbent charcoal as a concentrating agent. The charcoal adsorbs and retains the dye as the dyed water passes through the charcoal suspended in the water at the expected or suspected site of emergence. Highly adsorbent coconut charcoal is enclosed in a piece of window screening and supported in the water by wire and weights. The packets are constructed so that the maximum amount of surface area of the charcoal is exposed to the passage of the dyed water without restricting the circulation of the water through the packet.

A few granules of the charcoal can be removed from the packet at regular time intervals and marked with an appropriate sample number or the packet may be left undisturbed until the fluorescein dye has had sufficient time to reach and pass the site. The former will give data from which to calculate when the dye passes the site. The later will only tell if the dye has passed the site.

To test the charcoal a few granules are placed in a white porcelain dish and a small amount of five percent potassium hydroxide solution in ethyl alcohol is added so that the chemical solution desorbes the dye making it visible on the surface of the charcoal. The intensity of the color is dependent upon the surface area of the charcoal available. As stated by Dunn, the distinctive green color of fluorescein can be seen.

The Dunn method is applicable to quantitative studies of ground water movement through fissured or cavernous strata or over relatively short distances through highly permeable materials having a low organic content. Otherwise, fluorescein will serve only qualitatively in indicating the direction of flow, but not the velocity of ground water.

C. Point Dilution Method

In studying the ground water movement in a limestone terrane it is desirable to determine the coefficient of permeability of fractured and jointed rocks. The low coefficient of permeability and fixed paths in a jointed flow system tend to disperse a tracer injected and limit the adequacy and success of a two well test system.

In the point dilution method of Lewis, Kriz and Burgy (1966) the dye is introduced into a well so that the horizontal movement of water through the penetrated section diminshes the tracer concentration with time. If all tracer dilution is caused by water flowing through the well cross-section, the apparent ground water velocity can be calculated from measurements of tracer concentrations at various times after injection. The apparent velocity, is expressed by

$$v = Q/A$$

where v is the apparent ground water velocity, Q is the flow rate, and A is the gross area of the flow cross-section.

When a two-dimensional flow system with parallel streamlines is assumed, the flow intercepted by a well closely approximates a width equal to twice the well diameter.

Lewis, Kriz, and Burgy (1966) analyzed data from field studies by two methods. The first method was to plot the logarithm of the ratio of tracer concentration at any time to the initial concentration versus time. The slope of the semilogarithmic plot is then evaluated, and a value for the apparent ground water velocity is determined from

$$\log \ (C_0/C) = 1.106 \ vt/d$$

by Filip and Vukmirovic (1964),
after Moser et al (1957) and

$$C/C_0 = \exp. \ (-8vt/\pi d), \qquad \ln \ (C_0/C_n) = 2.55 \ vt/d$$

by Kaufman and Todd (1962)

where v is the apparent ground water velocity, C_0 is the initial tracer concentration, C is the tracer concentration at any time T, and d is the bore hole diameter. The second method employed using pumping tests which were compared, where possible, to the first method using tracers.

Moser et al (1957) listed three conditions that must exist before the tracer dilution equations can be applied to calculate the apparent ground water velocity, these are that 1) steady state conditions must exist during the test, 2) uniform ground water flow and tracer distribution occur, and 3) tracer concentration diminution with time is due only to horizontal ground water flow within the well volume being sampled. The first condition is satisfied if water table fluctuations caused by pumping or sudden water level changes in nearby surface water bodies do not occur. The second condition generally exists when small sections of a well surrounded by nearly uniform porous material are selected. If the water in the well is mixed before sampling, the sample represents an average for the entire vertical section. The third condition is usually satisfied when a well penetrates only one water bearing layer.

Kaufman and Todd (1960) list the following sources of error in well dilution methods: 1) increased rate of dilution due to vertical movement of ground water in the well which in turn increases the apparent velocity; 2) surging and sampling of the well increases dilution with formation water thus causing a high apparent ground water velocity; 3) if the effective well diameter is greater than the borehole diameter, the apparent velocity calculated from the dilution method will be less than the actual ground water velocity.

The following are advantages of the tracer dilution method: 1) the ground water velocity can be determined without knowing the effective pore volume; 2) if Darcy's law is valid, the hydraulic conductivity can be calculated from

$$(K = v/dh/dl)$$

where v is the apparent ground water velocity and dh/dl is the hydraulic gradient; 3) tests require only a single borehole; 4) it can measure several strata within the well if several different depths are sampled; 5) ranges from fractions of an inch to several hundred feet per day can be measured; 6) the method has a very low cost due to the small amount of equipment and personnel needed.

The method involves the addition of a sufficient quantity of dye solution into an injection well to bring the initial concentration within the well to approximately one part per million. Injection is made by lowering a small plastic hose into the water in the well 1/3 from the bottom and raising the tube as the dye solution is mixing with the well water. Sufficient time should be allowed for the solution to mix thoroughly with the well water and for any chemical reactions between the dye and the formation to take place.

An intergrating type of sampler which consists of a thin metal or plastic cylinder weighted at one end and capped at the other should be used when calculating the average velocity for the entire vertical section. The sampler should fill at a constant or nearly constant rate as it is lowered into the well. The combined sample being representative of some average conditions within the well. When sampling at different intervals a "down-the-hole" type of commercial sampler should be used so samples can be collected at desired depths. Sampling intervals should vary from one half hour at the start to daily after the test has run a few days.

D. Multilayered Method

A method for determining the average porosity and the different permeabilities of a multilayered, horizontally stratified aquifer was developed by Mercado and Halevy (1966). In a multilayered aquifer where layers are not separated from each other by confining beds, the different permeabilities and average porosities may be determined by this tracer technique.

In the method three wells are drilled in a line so that one penetrates the upper layer, one the lower layer, and a third penetrates both layers. The only requirement is that the combined layer must be confined both at the top and the bottom by an impervious layer with no confining layer in between.

The tracer is injected into the upper layer of the aquifer. The well that penetrates both layers is then pumped continuously until all the injected tracer is pumped out. The tracer is then injected into the lower layer and the pump is operated until this tracer is pumped out. See Figure 9 for setup of multilayered method.

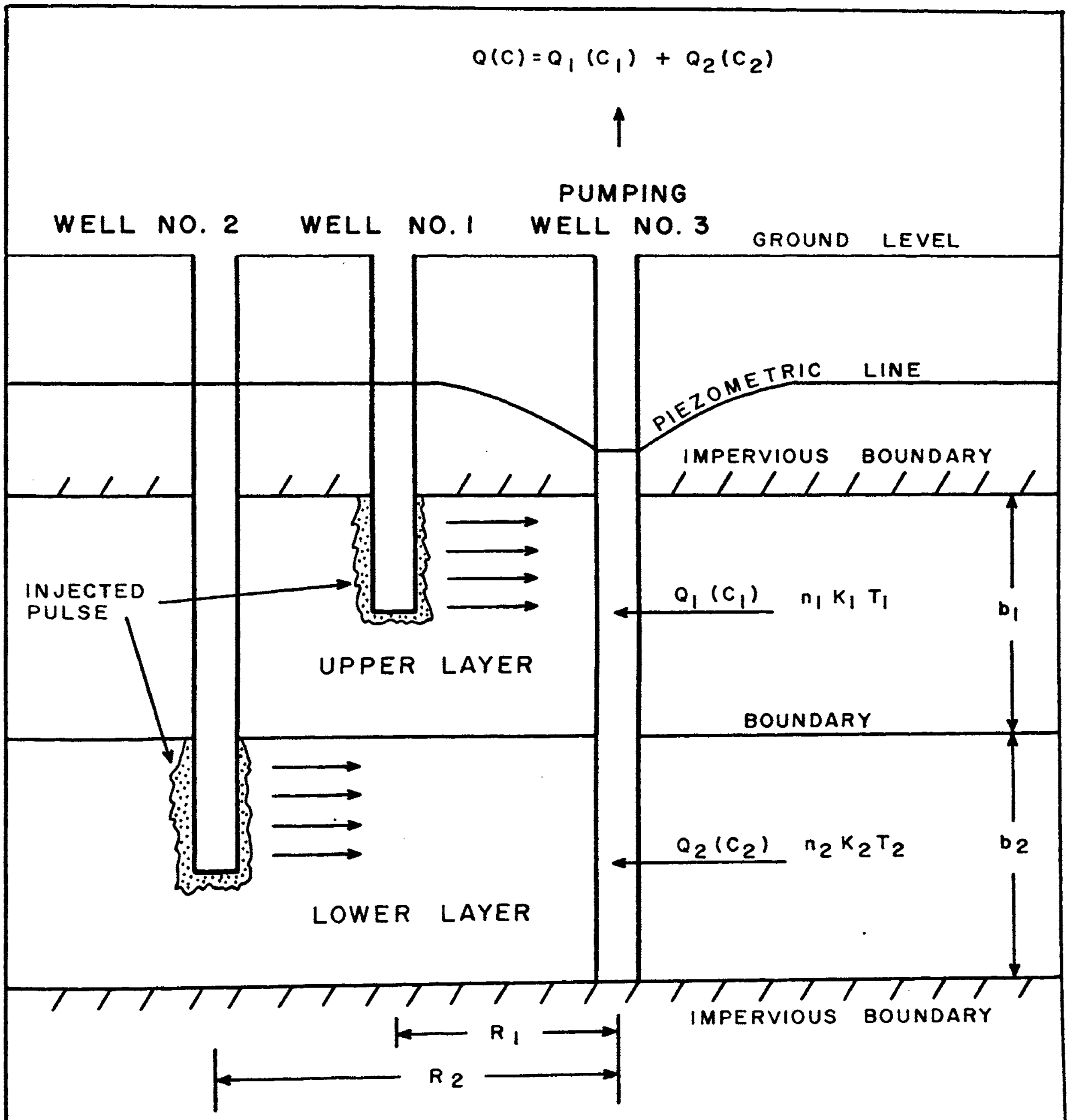


FIG. 9 PUMPING FROM A TWO LAYERED AQUIFER

Thus if R_1 and R_2 are the known radii from the pumped well which penetrates both layers, b_1 and b_2 the layer thicknesses from geologic sections, n_1 and n_2 the porosities of each layer from core analysis, $(V_p)_1$ and $(V_p)_2$ the volume pumped from each layer from experimental tracer results, and T from pumping tests, the values of T_1 and T_2 can be calculated from experimental results. Knowing the values of the transmissivities (T_1 and T_2) and recalling that $T=Kb$ (K being the hydraulic conductivity) it is now possible to calculate the permeability values.

Chapter V

FIELD METHOD OF INVESTIGATION

A comparative study of closely spaced wells and other hydrologic features was made in the Phelps County, Missouri, karst area to determine the feasibility of calculating aquifer characteristics by the aid of tracers.

The location, depth, and condition of several hundred wells was studied in order to select several sets of wells that were close to each other and penetrated the same water bearing horizons. Also several dozen sinkholes, caves and springs were investigated for the possibility of conducting tracer tests at these sites. The following criteria were used in selecting well tracer sites: 1) the wells should be relatively close together, generally less than fifty feet apart, 2) both wells should penetrate the same water bearing horizons, 3) at least one hole should be open to permit the installation of a continuous water level recorder before and after the test and to serve as the injection well during the test, 4) the other well should have a pump of sufficient size and capacity to create a cone of depression of sufficient size to effect the water level in the injection well, 5) the pumped well must have a large enough hole in the well seal to admit the use of a probe to measure water level changes in the pumped well, 6) a constant pumping rate or gradient should be maintainable to reduce the number of variables.

A. Collection of Samples

The sample is usually only an infinitesimal part of the total volume and is therefore representative of the total volume only to the degree that uniformity of dispersion and chemical composition exists within the total volume. Rainwater and Thatcher (1960) conclude that the fact that ground water is subjected to forces that promote mixing and homogeneity is not sufficient cause for assuming that a body of ground water is so well mixed that no attention to sampling techniques is required. Often because of local conditions, a tracer within a body of ground water may not have uniform dispersion with respect to time, direction, and distance. Therefore care should be taken in both collecting the sample and interpreting the significance of it.

Suspended solids or turbidity in samples undergoing analysis can significantly decrease or increase the tracer fluorescence recorded, depending upon the relative concentrations of tracer and turbidity. For accurate measurements, therefore, the samples should be either centrifuged or permitted to stand in order to allow natural sedimentation of the solids prior to analysis. Samples should be collected and tested under controlled conditions to minimize the effects of photochemical decay, temperature, and instrument error. Samples should always be stored in a light proof container to prevent photochemical decay.

B. Background Fluorescence

Almost all natural water contains minerals and organic compounds which are fluorescent to some degree. Background samples therefore should always be taken before conducting a test so that one may differentiate between normal background levels and abnormal levels. The later indicate the arrival of injected dye.

The magnitude and variation of background fluorescence should be determined from several sites within the specific area of study and over several months time in order to determine the variation of background with time. Knochenmus (1967) bases site selection on the following criteria: 1) environments which could be used as monitoring points during the experiment, and 2) sites along an approximately inferred flow line down the piezometric gradient.

Ten background samples were taken within the study area (see Figure 10) and in every case the background count was zero using the most sensitive settings on a Turner Model III fluorometer. If background fluorescence had been encountered the variation of samples might have been significant between different types of

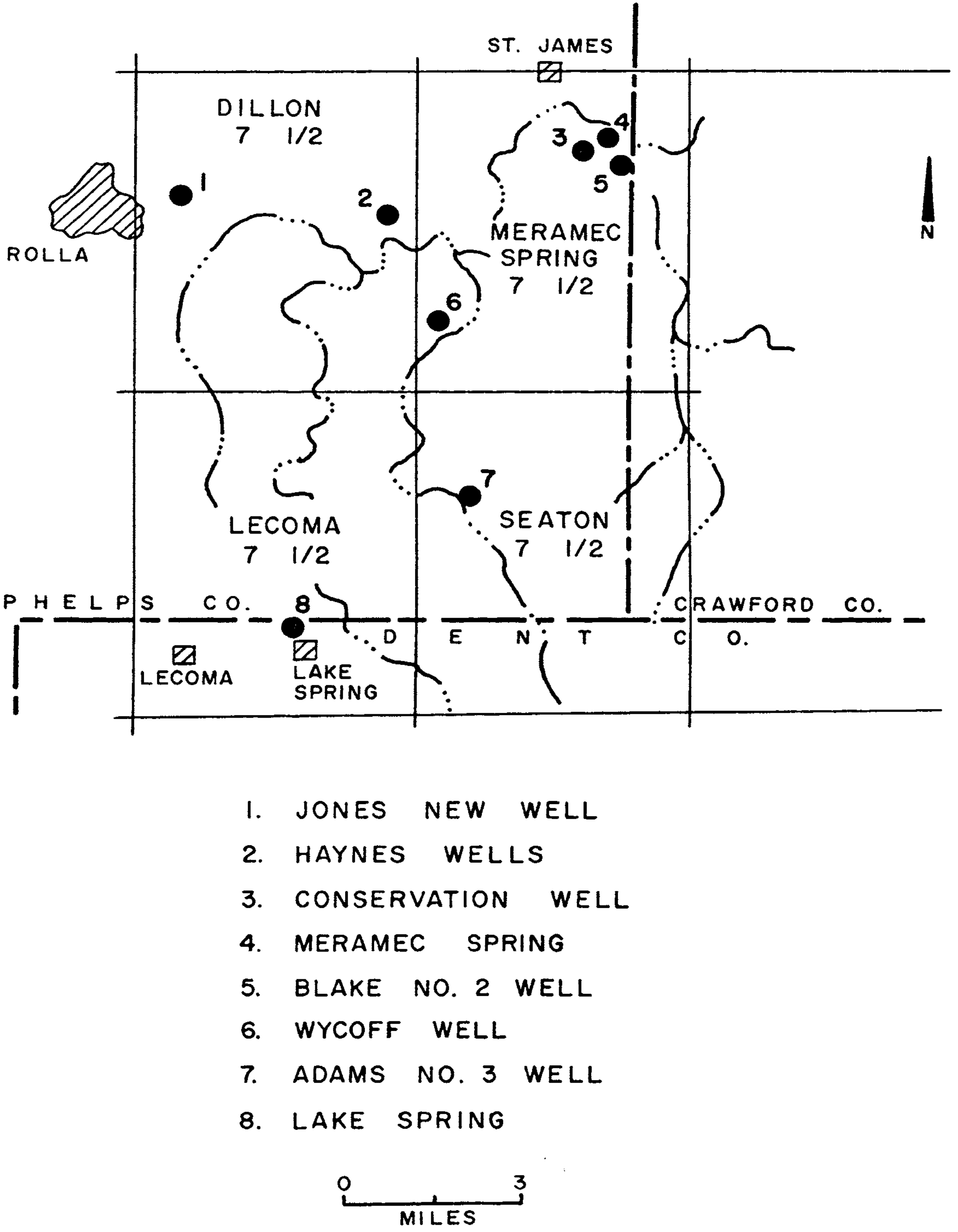


FIG. 10 LOCATION OF BACKGROUND FLUORESCENCE SAMPLES

sites, depending on the amount of organic material present. For instance, background fluorescence is low in ground water and high in streams and lakes.

C. Dose Computations

Detectability is the controlling factor in determining the lower limit on the amount of dye to be injected. The upper limit is arbitrary and is based on safety, upper limit on the quantitative detectibility of the apparatus used, and economy. Dispersion, adsorption, decay, and quenching also effect the concentration of the dyed solution. Dispersion is the primary factor to consider in any dose computations. It could be extremely variable over large areas due to the variability of the composition of the formations transmitting water. This variability is somewhat reduced when closely associated wells are tested.

The question of the amount of dye to be used was not generally resolved. A few grams to one pound should be sufficient for most tests because dyes such as fluorescein and rhodamine may be detected in concentrations less than one part per billion. In all tests in this study, effort was made to keep dye concentrations as low as possible to avoid influencing any water which might eventually be used for human consumption. It is not known whether failure of detection resulted from too low concentration or from other factors.

D. Field Studies

1. The Blake Test Site

Figure 11 shows a generalized east-west cross section of the Blake test site. The site consists of three wells drilled in a straight line. The horizontal distance from well number one to well number three is 383.1 feet. The distance from well number two to well number three is 128.1 feet. The total difference in elevation of the ground surface between well number one and well number two is 73 feet. Figure 12 shows pumping in well number three which was the injection well during the tracer test.

All three wells penetrate the lower part of the Gasconade Formation and insoluble residues studies conducted by the Missouri Geological Survey indicate an approximate composition of 50 percent dolomite and 50 percent chert.

In February, 1967, a pumping test was conducted (Nawrocki, 1967) for three days with the pump in well number two. After twelve hours of pumping, a fifty pound quantity of salt was diluted with one hundred and fifty gallons of fresh water and added to well number three. Samples were collected periodically during the test and for a two month period afterward with no results.

The samples were tested for salt using the electrical conductivity method and checked by titrating

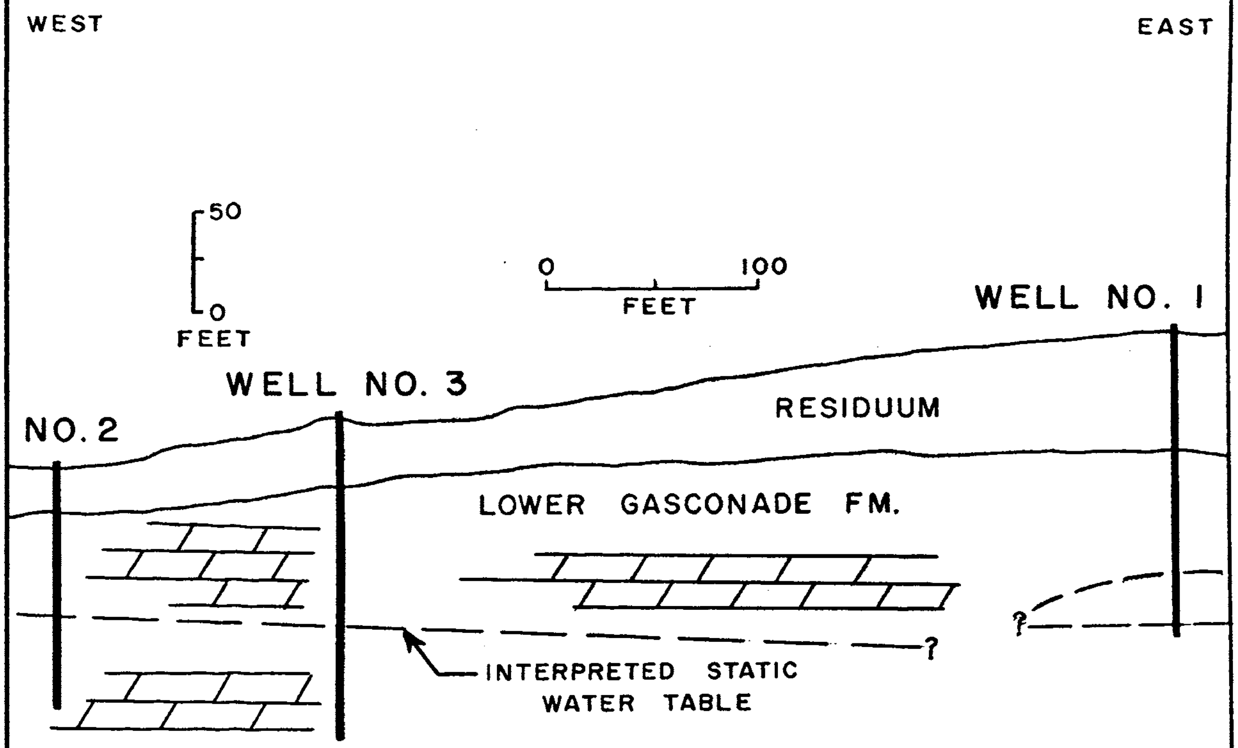


FIG. II GENERALIZED CROSS-SECTION OF BLAKE TEST SITE (AFTER NAWROCKI, 1967)

FIG. 12 BLAKE TEST SITE WELL NO. 3

with a silver nitrate solution. The results of all tests were negative.

It is believed that several factors could have been responsible for the negative results. 1) The permeability of the Gasconade formation between the wells was so low that the time of travel of the salt solution between the wells might be measured in months and years instead of days and weeks. 2) That a density separation could have taken place dropping the heavier salt solution well below the bottom elevation of the pumped well. 3) That clay minerals along the path of travel removed the salt by ion-exchange reactions.

Any combination of these factors could have contributed to absence of the tracer at the sampling well during the experiment.

Salt was used in this first experiment to test both salt as a tracer and the electrical conductivity method of detecting the tracer. Although the results were negative the tracer and method might be applied successfully in more permeable zones and over shorter distances.

2. The Haynes Test Site

The Haynes site is located seven miles east of Rolla on Highway BB. The site consists of a new well and an old unused well. The old well is located in a shed just west of the house and the new well is twenty-six feet to the northwest of the old well. The top of the new well is buried approximately two feet under a lawn. (See Figure 13 for a generalized cross-section.)

A Leopold and Stevens type F water level recorder was installed at the old well several months prior to the tracer test in order to determine water level variations. (See Figure 14.) The new well was temporarily uncovered and a vent tube (Figure 15) was installed to allow the measurement of water levels using an electric probe (Figure 15). To measure the amount of water pumped, a water meter was installed in the main line leading from the new well to the household storage tank.

In December, 1967, a week before the tracer test was to begin, a ten minute drawdown test was performed in order to determine how rapidly the old well responded to drawdowns in the new well. Electronic water level probes were placed in both wells to measure the variations in water level during the drawdown and recovery of the pumping well. The water level in the new well was lowered twenty feet and then allowed to recover. Figures 19 and 20 show the draw-

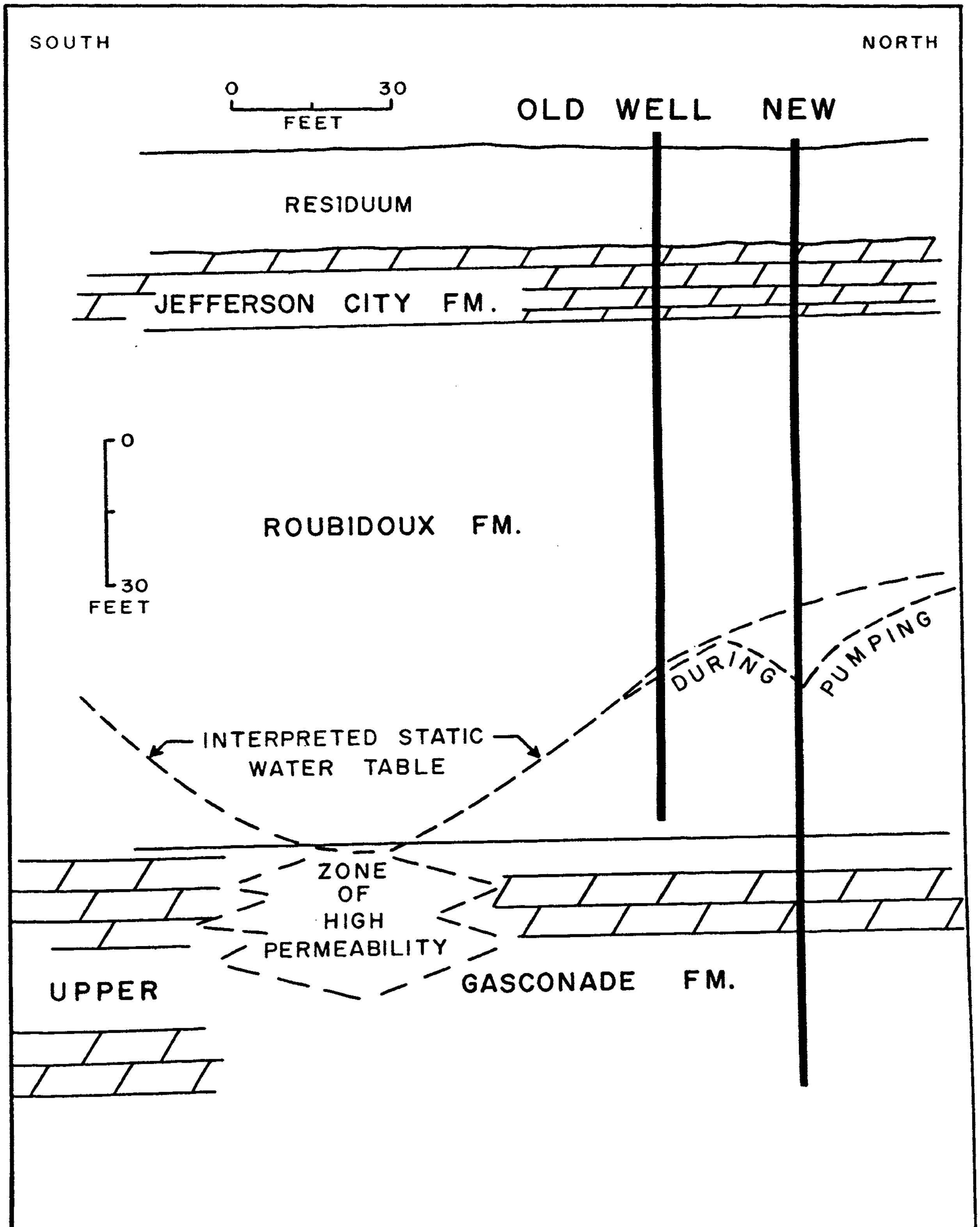


FIG. 13 HYPOTHETICAL CROSS-SECTION OF THE HAYNES SITE

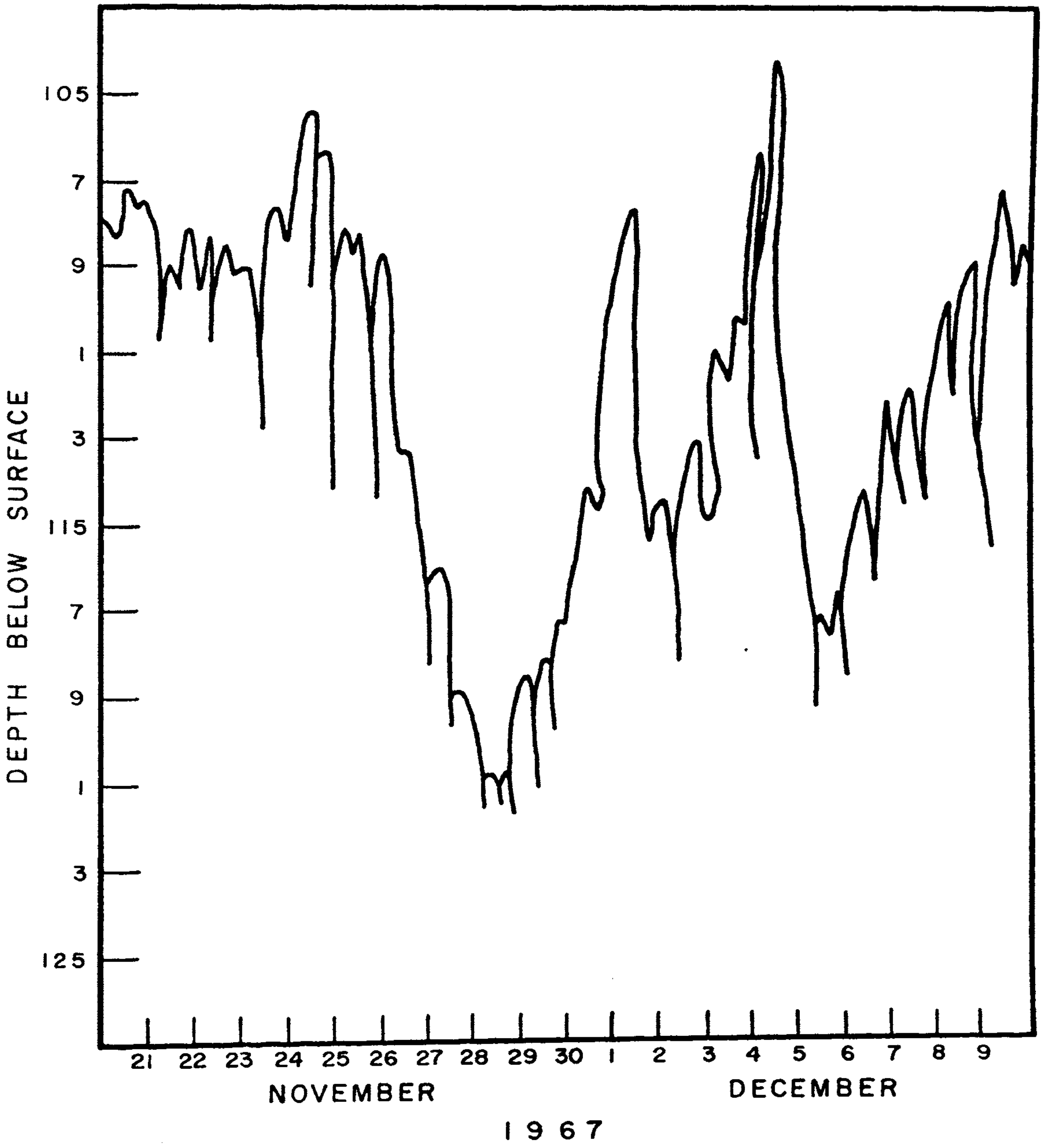


FIG. 14 WATER LEVEL VARIATION IN HAYNES OLD WELL NOVEMBER THRU DECEMBER 1967

a. HAYNES TEST SITE

b. ELECTRIC WATER PROBE

FIG. 15 HAYNES TEST SITE AND ELECTRIC WATER PROBE down and recovery curves obtained during the ten minute test in the new well. The "two level" curve in Figure 19 is the result of using a domestic well with an on-off cycle to maintain a "constant" discharge.

The old well responded almost instantaneously to the drawdown in the new well. Figure 14 shows a period between November and December in 1967 in which a recorder was placed on the old well. The long, nearly vertical downward line of the figure represents periods in which large amounts of water were used by the Haynes family. The larger trend represents longer periods of fluctuations of the piezometric head. The upward trends represent periods of recharge and the downward ones periods of discharge of the aquifer.

During the ten minute test, it was discovered that the water level in the old well was ten feet lower than in the new well. Several checks of these measurements were made over a two month period and the water levels in both wells remained the same with respect to one another.

When the tracer test was started the water level in the new well was pumped down below the level in the old well to reverse the normal gradient. The pumping lasted for two days and represented two weeks of normal pumping in the new well. The volume of water pumped was measured using a flume (Figure 16).

The hour after the start of the test two thousand milliliters of one part per million of Rhodamine B dye were injected into the old well and mixed by lowering and raising the injection bailer (Figure 17a) through the column of water for three minutes. An initial sample was taken from both wells. Periodically throughout the test samples were collected from the old well using a weighted sampler (Figure 17b). Samples were taken periodically from the expected site of emergence (pumped well) during the test. Samples from the injection well were taken to plot a time dilution curve (see Figure 18). The dye was never detected in the new well.

From the time dilution curve it is possible to determine the apparent groundwater velocity by using Filip and Vukmirovic's formula (see page 41), where:

$$\log (Co/_{cn}) = 1.106\ vt/d$$

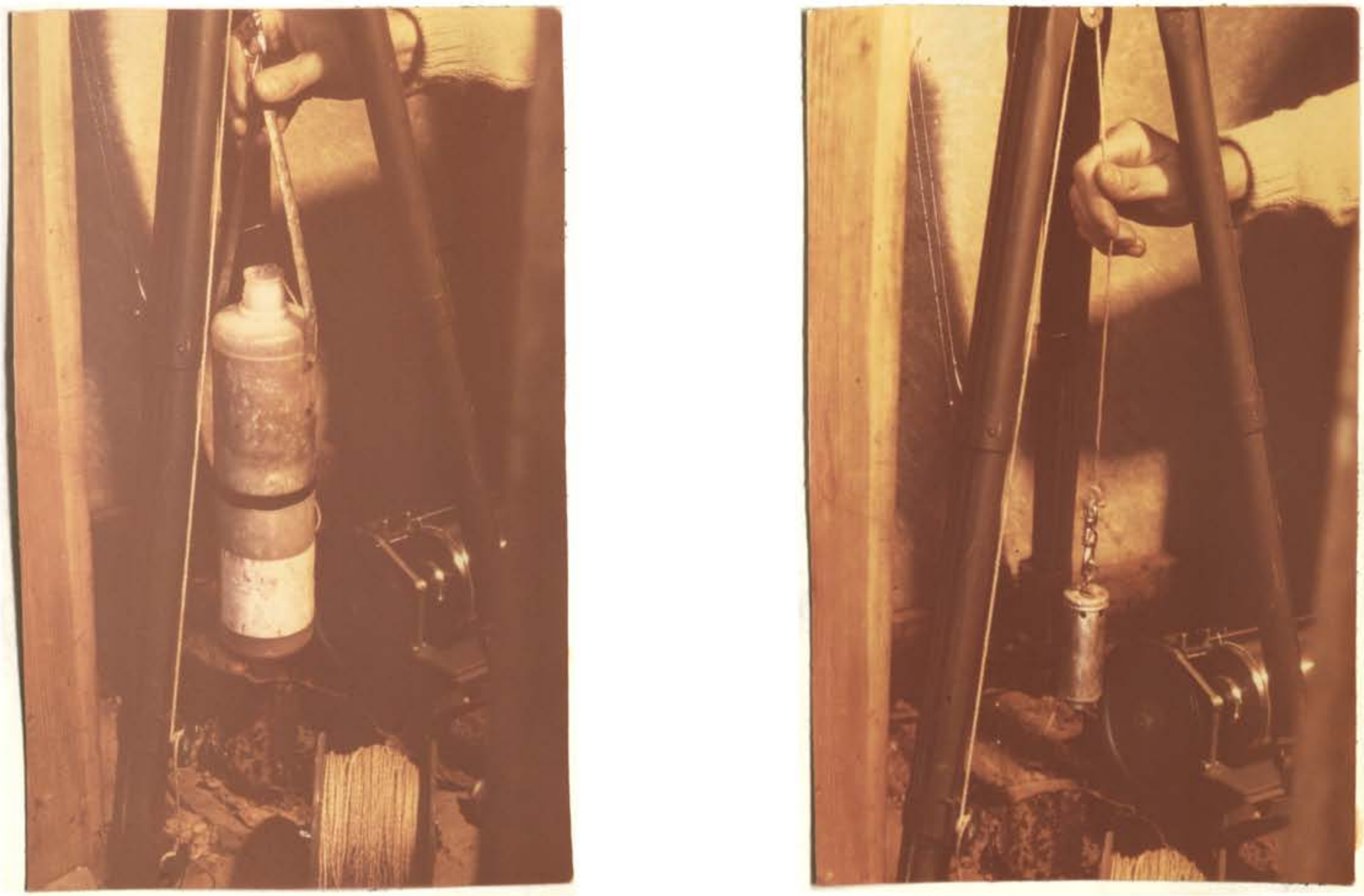
Where C_o is 2500 ppb, the initial concentration; Cn is 335 ppb, the concentration after 8.3 hours (T); and d is 7.5 inches, the well diameter.

$$\log (2500/335) = 1.106v(8.3\text{ hrs.})/7.5\text{ inches}$$

$$v = 0.11\text{ inches/hour}$$

$v = 2.64$ ft./day (The Apparent Groundwater Velocity

FIG. 16 FLUME SETUP AT HAYNES TEST SITE



a. INJECTION BAILER

b. SAMPLING DEVICE

FIG. 17 INJECTION AND SAMPLING DEVICES

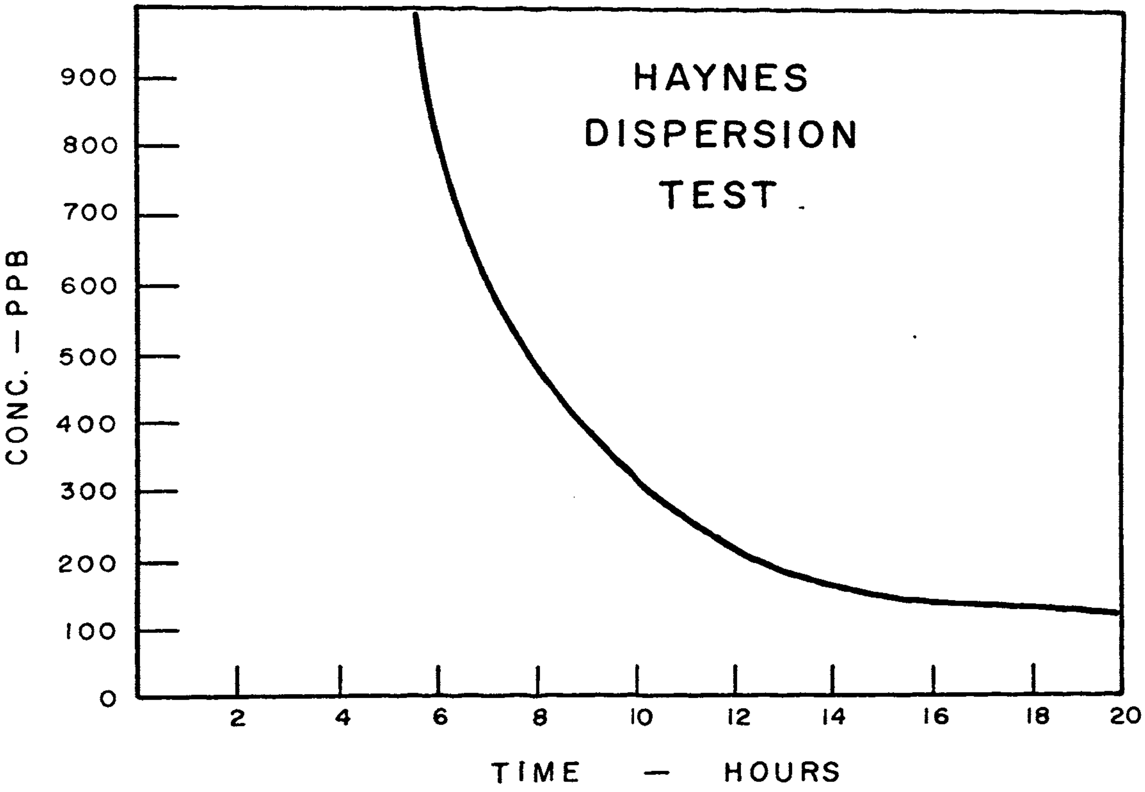


FIG. 18 TIME-DILUTION CURVE FOR HAYNES INJECTION WELL

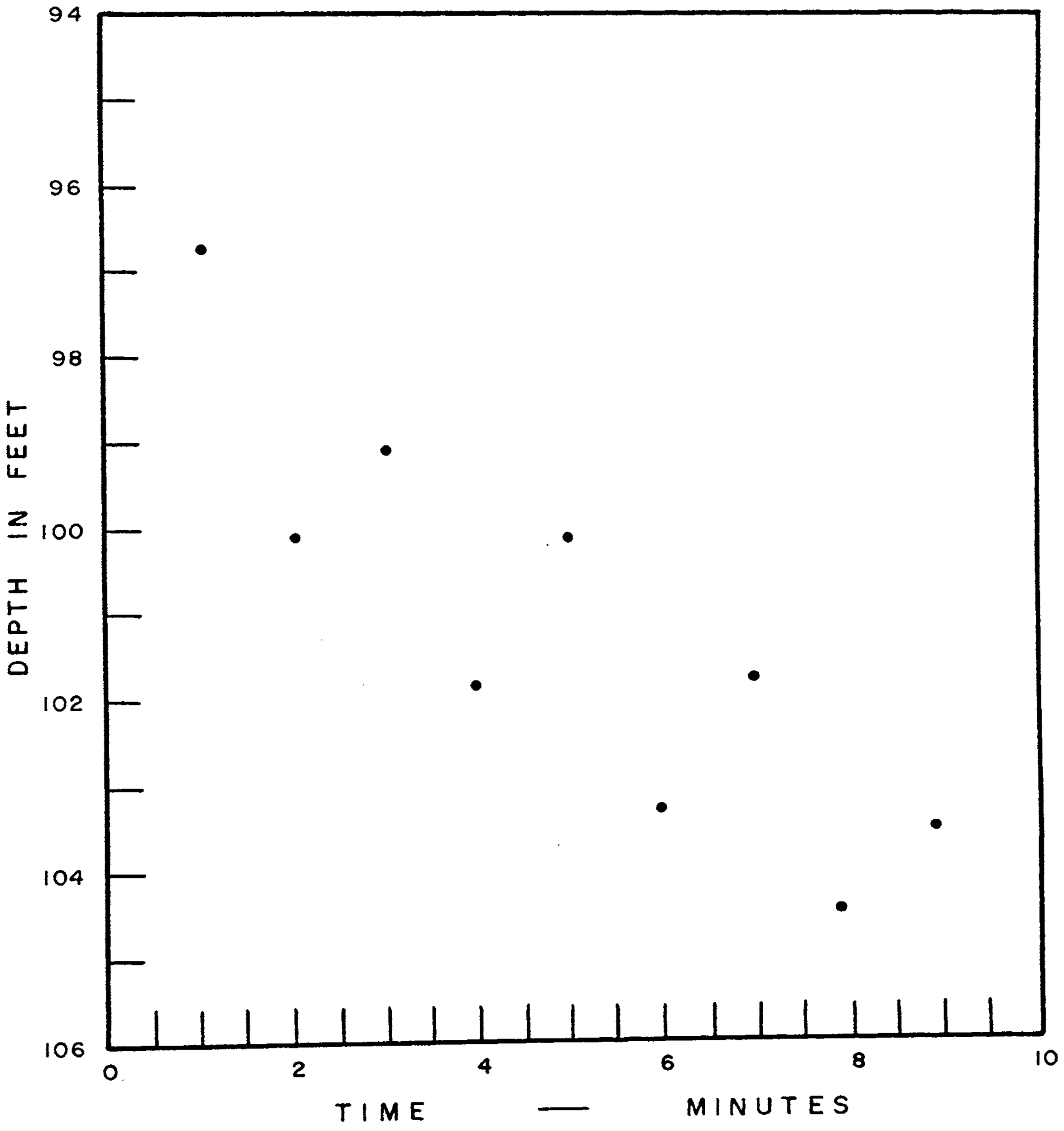


FIG. 19 DRAWDOWN CURVE FOR HAYNES PUMP TEST

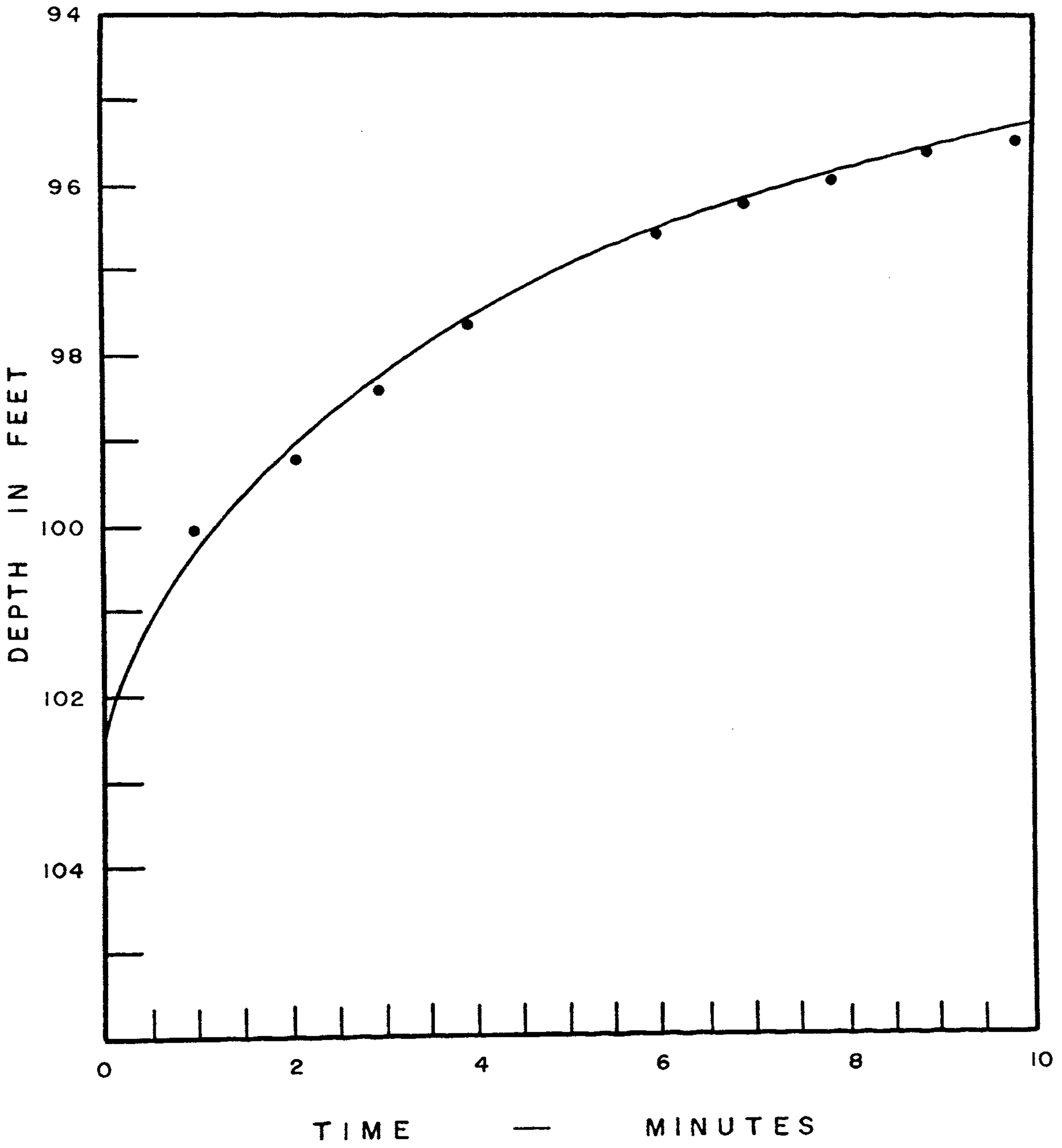


FIG. 20 RECOVERY CURVE FOR HAYNES PUMP TEST

3. The Jones Test Site

The Jones site like the Haynes site consisted of two domestic wells (See Figure 21). One of these was first used as a water supply and was later found inadequate and was abandoned when a second well was drilled deeper a short distance away. The two Jones' wells are only twelve feet apart. The old well was drilled to a depth of 177 feet while the depth of the new well is 280 feet. The new well has twenty-four feet of six and one-quarter inch diameter casing.

A pumping test was conducted at the new well in order to determine if the two wells were connected hydraulically. The new well was pumped at the rate of three gallons per minute for three hours with no discernible effect on the water level in the old well (See Figure 22).

The lack of connection may be attributed to several factors: 1) the main water table is below well number one and the water standing in that well is perched with respect to the main water table; 2) the rock between the wells is so dense that it will not permit the flow of water between; and 3) the rate of pumping in the new well was not sufficient to cause a drawdown in the old well over a three hour period.

Although no tracer test was conducted at this time because of the lack of connection between the two wells, a later test might be made possible by deepening the old well.

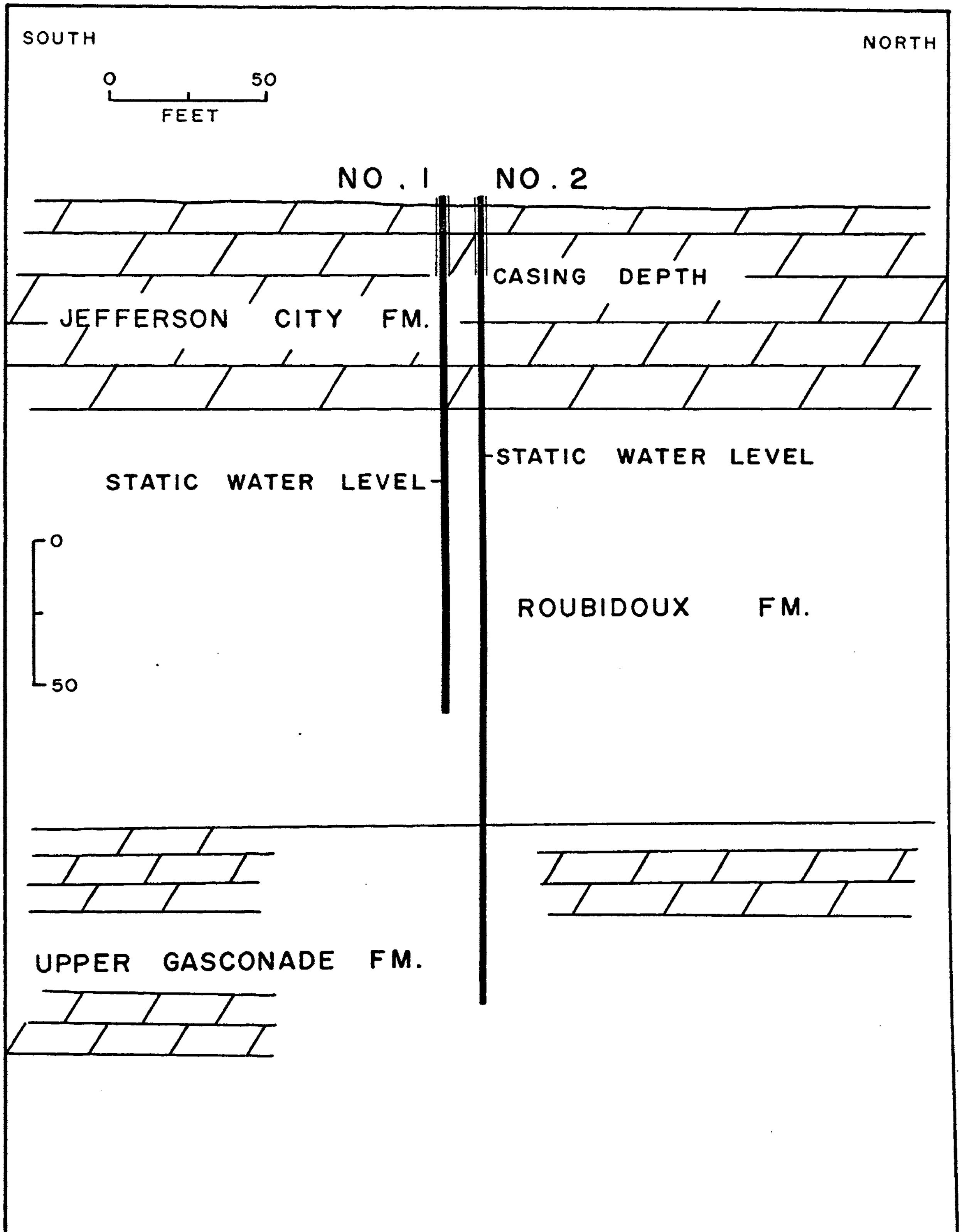
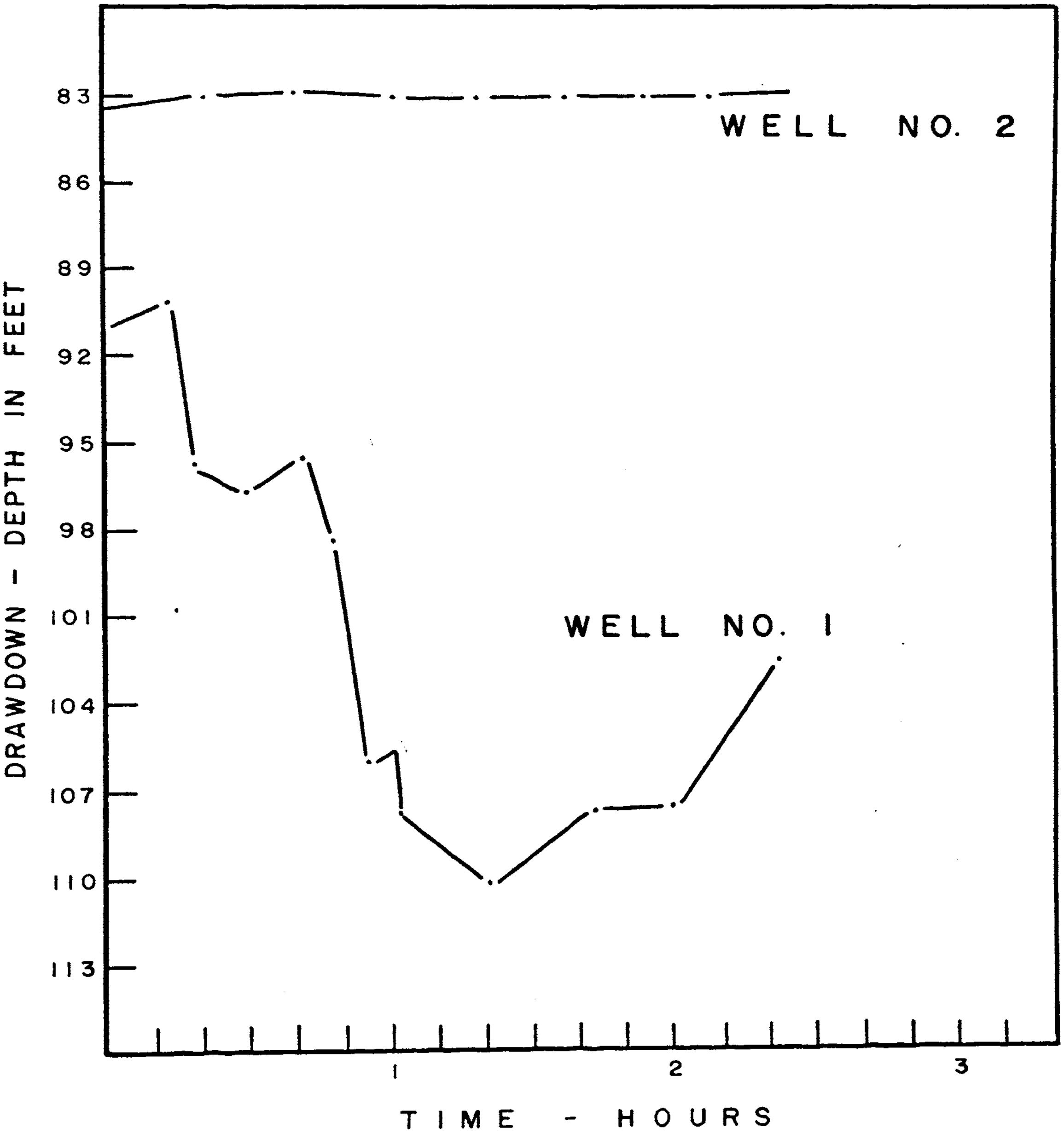


FIG. 21 GENERALIZED CROSS-SECTION OF THE JONES SITE



JONES — SITE

FIG. 22 DRAWDOWN CURVES FOR JONES PUMP TEST

Chapter VI

DISCUSSION AND CONCLUSIONS

A. Tracers

Although none of the three dye tracers reviewed could be termed an ideal tracer, Pontacyl Pink appears to be the most suitable quantitative tracer for applications in natural water. The overall reactions of Pontacyl Pink to various intrinsic characteristics of natural waters are markedly less than those of other tracers. It does not adsorb on suspended sediments and it shows the lowest photochemical decay rate. The cost of Pontacyl Pink is higher than Rhodamine but, considering the much greater overall cost involved in conducting a tracer test and the necessity for obtaining meaningful results, this economic differential might be easily justified and, in some cases, required. At the present time Rhodamine is probably the most widely used quantitative tracer of those discussed. Because of its relatively low cost fluorescein should be considered useful as a qualitative tracer for short term studies where the effect of sunlight is a minimum.

The success of a dye test is fundamentally based upon the proper introduction of the dye into the formation through which the water flows; mechanical and other means for insuring this result can probably be developed. The well where the dye is expected should be pumped at a rate high enough to draw the dyed water toward it.

Tests giving negative results may be due to decoloration of the dye or too great a dilution underground, to faulty methods of conducting the test, or to the fact that water was not actually migrating from one well to the other.

B. Methods

The point dilution method can be used in connection with all the other tests where a well is used as an injection site. The greatest advantage of the method is that it requires only one well. Since only a measurement of dilution with time is required a very small quantity of dye is needed. Individual zones within the aquifer can be tested by casing out all the other zones. The times required is relatively small, usually a few days in which meaningful results may be obtained. It can be used where permeabilities are low and where the distance between existing wells would prohibit the use of the other methods. The greatest disadvantage of the point dilution method is that a representative sample must be obtained over the entire section tested. This may be overcome if an intergrating "down-the-hole" type of sampler is used. The dye may be adsorbed by material lining the well hole and not actually diluted by the flow of water through the cross-sectional area of the well. This error can be avoided by waiting a short time after the dye has been injected before sampling is begun.

The Dunn method has been used with great success in determining if two or more sites are connected hydraulically and has the further advantage that the suspected site is continuously monitored by the charcoal packets. The method is also suitable for use in the other well methods when large time-intervals of sampling occur. The method concentrates the dye and hence would increase the sensitivity of detecting the dye in minute concentrations. The Dunn method has the disadvantage of being semi-quantitative in nature when samples are tested at large time intervals.

The multilayered method as it imples may be used to test several zones simultaneously. Its greatest application would be in testing the Roubidoux formation where several sandstone layers may be present between relatively impervious dolomite layers.

The time of travel method is the most frequently used semi-quantitative method and given velocities and connecting points.

C. Well Spacing

The most important consideration when conducting a tracer test between wells in a particular formation or unit is the distance between the injection point and the sites of emergence. The following is a discussion of well spacing as applied to the different tracing methods:

The point dilution method when used by itself eliminates any spacing at all because only one well is involved in the experiment.

The Dunn method was employed specifically to determine whether two wells were connected hydraulically. The wells may be spaced a considerable distance apart since the water is continuously monitored by the charcoal packets so that the packets need only to be tested at large intervals. This distance is highly dependent on the type and degree of permeability of the rock. If the packets are incorporated within one of the other methods, the spacing is then controlled by the limitations of that method.

When using the multilayered method in a karst terrain the distance between the injection well and sampling wells should be in the order of a few tens of feet whereas the distance between the sampling wells should be less than ten feet.

Once the dyed water has proven the interconnection of two or more wells during a pumping test over a short period of time, the next step is to rerun the test using the natural gradient between the wells.

When testing is begun with any of the methods discussed one should first run tests over distances less than fifty feet unless knowledge of the geologic and hydrological characteristics of the aquifer will permit longer distances.

Chapter VII

RECOMMENDATIONS FOR FUTURE RESEARCH

On the basis of the findings of this investigation the following recommendations are made:

1. That larger quantities of dye, up to one pound, should be used at each site to avoid losing the dye to extensive adsorption and dilution.
2. That the Jones' old well be deepened to the depth of the new well for the purpose of conducting a pumping and tracer test simultaneously.
3. That a new well should be drilled at the Haynes site, so as to form a triangle with the existing wells, first to the depth of the old well and later to the depth of the new one. This third well should be drilled up gradient from the two existing wells and should be used as the injection well during the test.
4. That several point-dilution tests should be conducted within the several formations throughout the study area since the test requires only one well.

BIBLIOGRAPHY

AMBROSE, A.W. (1921) Use of detectors for tracing movement of underground water, U.S. Bureau of Mines, Bull. 195. Pet. Tech., 62, pp. 106-120.

AUSTIN, A.W. (1921) Use of detectors for tracing movement of underground water, Underground conditions in oil fields, U.S. Bureau of Mines, Bull. 195.

BEVERIDGE, T.R., and HAYES, W.C. (1960) Guidebook to the geology of the Rolla area emphasing solution phenomena, Missouri Geological Survey and Water Resources, Prepared for the fifth annual midwest groundwater conference field trip.

BOUTARI, A., and ROY, M. (1939) Fluorescence and pH of solution of uranine, Compt. rend., vol. 209. p. 162-164, Chem. Abst., vol. 34, Cal. 1915, 1940.

BRETZ, H.J. (1953) Genetic relations of caves to peneplains and big springs in the Ozarks, American Jour. Sci., vol. 251, p. 1-24.

______________ (1956) Caves of Missouri, Missouri Geological Survey, vol. XXXIX, Second Series, 490 p.

______________ (1965) Geomorphic history of the Ozarks of Missouri, Missouri Geological Survey, vol. XLI, Second Series, 147 p.

BUCHANAN, T.J. (1964) Time travel of soluble contaminants in streams, Am. Soc. of Civil Eng., vol. 90, No. SA3, 12 p.

CARPENTER, P.G.; MORGAN, T.D.; and PARSONS, F.D. (1953) Boron compounds used as water-flood tracers, World Oil, April.

COBB, E.D. and BAILEY, J.F. (1965) Measurement of discharge by dye-dilution methods, Surface Water Techniques, Book 1, Chapter 14, U.S.G.S. Report, 27 p.

CORNING GLASS WORKS (1962) Glass color filters, catalog, Corning, N.Y., 25 p.

CROUCH, J. (1965) Piezometric levels and shallow aquifers, Dillon and Meramec Spring quadrangles, Missouri, Thesis, Missouri School of Mines.

DAVIS, S.N., and DEWIEST, R.J.M. (1966) Hydrogeology, John Wiley and Sons, Inc., New York, p. 346-374.

DES CARRIERES, D. (1882) Etiologie de l'epidemic typhoide qui a eclate a auxerre en septembre 1882, Soc. mid des Hopitaux de Paris, Bul. et Mem., 2d series, vol. 19, p. 277-286.

DOLE, R.B. (1906) Use of fluorescein in the study of underground water, U.S. Geological Survey, Water Supply Paper 160, p. 73-86.

DUNN, B., and VAUPEL, D.E. (1965) Effects of sample and fluorometer-compartment temperatures on fluorometer readings, U.S. Geological Survey Prof. Paper 525-d, p. 225-227.

DUNN J.R. (1957) Stream tracing, Mid-Appalachian Bull. No. 2, M.A.R. Region, Natl. Speleological Soc., p. 7, Nov. 1957.

FEUERSTEIN, D.L. and SELLECK, R.E. (1963a) Tracers for dispersion measurements in surface streams, Univ. of Calif., SERL Report No. 63-1, 69 p.

_______________ (1963b) Fluorescent tracers for dispersion measurements, Am. Soc. Civil Eng. Proc., vol. 89, No. SA4, Paper 3586, p. 1-21.

G. K. TURNER ASSOCIATES (1964) Operating and Service Manual, Model 111 Fluorometer, Palo Alto, Calif., 27 p.

HAAS, JOHN L. JR. (1959) Evaluation of ground water tracing methods used in speleology, Natl. Speleological Soc. Bull., vol. 21, Part 2, July 1959.

HALEVY, E. and NIR, A. (1962) The determination of aquifer parameters with the aid of radioactive tracers, Jour. Geophy. Research, vol. 67, No. 6, p. 2403-2409.

HAMILTON, D.K. (1948) Some solution features of the limestone near Lexington, Kentucky, Econ. Geology, vol. 43, No. 1, p. 39-52.

HECK, E.T. (1954) Tracing fluids between wells, Producers Monthly, July 1954, p. 31-33.

HEM, J.D. (1959) Study and interpretation of the chemical characteristics of natural water, U.S. Geological Survey Water Supply Paper 1473, 269 p.

HOWARD, ALAN D. (1963) The development od karst features, Natl. Speleological Soc. Bull., vol. 25, part 2.

JOYCE, R.J. (1963) Fluorometric procedures, Procedures Manual 1217, Beckman Instruments, Inc. 17 p.

KAUFMAN, W.J. and ORLOB, G.T. (1956a) Measuring ground water movement with radioactive and chemical tracers, Amer. Water Works Assn. vol. 481, May 1956, p. 559-572.

_______________ (1956b) An evaluation of ground water tracers, Transactions, Amer. Geophy. Union, vol. 37, No. 3, June 1956.

KAUFMAN, W.J. and TODD, D.K. (1960) Application of tritium tracer to canal seepage measurements, Sanitary Engineering Research Laboratory, University of California, Berkeley.

KENT, D.F. (1950) Techniques used in mine-water problems of the East Tenn. zinc district, U.S. Geological Survey Circular 71, 9 p.

KNOCHENMUS, D.D. (1967) Tracer studies and background fluorescence of ground water in the Ocala, Florida Area, U.S. Geological Survey Open File Report, November 1967, 35 p.

KRUMBEIN, W.C., and PETTIJOHN, F.J. (1938) Manual of sedimentary petrography, Appleton-Century-Crofts, Inc., New York, p. 503-517.

LEWIS, D.C.; KRIZ, G.J. and BURGY, R.H. (1966) Tracer dilution sampling technique to determine hydraulic conductivity of fractured rock, Water Resources Research, vol. 2, No. 3, p. 533-542.

MARTIN, J.A.; KNIGHT, R.D.; HAYES, W.C. (1961) Ordovician System-Canadian Series, In Koenig, J.W., The Stratigraphic succession of Missouri, Missouri Geol. Survey vol. XL, second series, p. 20-24.

MERCADO, A. and HALEVY, E. (1966) Determining the average porosity and permeability of a stratified aquifer with the aid of radioactive tracers, Water Resources Research, vol. 2, No. 3, p. 525-531.

MOSER, H.; NEUMAIER, F.; and RAVERT, W. Die Anwendung Radioaktiver Isotopen in der Hydrologie II. Ein Verfahren Zur Ermittlung Der Ergiebigkeit von Grundwasserstromungen, Atomkernenergie, 2 (6), 225-231, June 1957.

MUELLER, H.E. (1950) Geology of the north half of the Meramec Spring 15' quadrangle, Thesis 1949, Missouri School of Mines.

NAWROCKI, MICHAEL A. (1967) Hydrologic characteristics of shallow bedrock aquifers in the vicinity of Norman Creek, Central Phelps County, Missouri, Thesis, University of Missouri - Rolla.

PALMER, ARTHUR N. (1965) The occurrence of ground water in limestone, The Compass, vol. 42, No. 4, p. 264-255.

PLUMMER, F.B. (1945) Tracing flow of fluids and gas beneath ground, Oil and Gas Journal, 44, 141.

PRITCHARD, D.W. and CARPENTER, J.H. (1960) Measurement of turbulent diffusion in estuarine and inshore waters, Internat. Assoc. of Scientific Hydrology Bull., No. 20, p. 37-50.

RAINWATER, R.H. and THATCHER, L.L. (1960) Methods for the collection and analysis of water samples, U.S. Geological Survey Water Supply Paper 1454, 297 p.

SLICHTER, C.S. (1902) The motions of underground waters, U.S. Geological Survey Water Supply Paper 67, p. 46-51.

_______________ (1905) Field measure of the rate of movement of underground water, U.S. Geological Survey Water Supply Paper 140, p. 9-85.

STABLER, H. (1921) Fluorescein an aid to tracing waters underground, U.S. Bureau of Reclamation, The Reclamation Record, vol. 12, No. 3, p. 122-123.

STURM, P.W. and JOHNSON, W.E. (1950) Field experiments with chemical tracers in flood waters, Producers Monthly, December 1950.

THORNBURY, W.D. (1965) Regional Geomorphology of the United States, John Wiley and Sons, Inc., New York, p. 267-268.

TODD, D.K. (1967) Ground water hydrology, John Wiley and Sons, Inc., New York, p. 346-374.

TRILLAT, A. (1889) Sur l'emploi des matieres color antas pour la recherche de l'origine de sources et des eaux d' infiltration, Acad. Sci, Paris Comptes Rendus, vol. 128, p. 698-700.

U.S. GEOLOGICAL SURVEY, MISSOURI GEOLOGICAL SURVEY, and others (1967) Mineral and Water Resources of Missouri, Senate Document 19, U.S. Government Printing Office, Washington, D.C.

VERMEULEN, T. and HIESTER, N.K. (1952) Ion Exchange Chromotography of Trace elements, Ind. Eng. Chem., 44: 636.

WALLICK, G.C. and JENKINS, R. (1954) Analysis of short time tracer injection in underground formations, Jour. of Applied Physics, vol. 25, no. 12, p. 1491-1496.

WATKINS, W.J. and MARDOCK, E.S. (1954) Use of radioactive iodine as a tracer in water flooding operations, Journal of Petro. Tech., Sept. 1954.

WENZEL, L.K. (1942) Methods for determining permeability of water bearing materials, U.S. Geological Survey Water Supply Paper 887, pp. 71-74.

WEYL, P.K. (1960) Porosity through dolomitization conservation-of-mass requirements, Jour. Sed. Pet., vol. 30, No. 1.

WRIGHT, R.R. and COLLINGS, M.R. (1964) Fluorescent tracing techniques and applications to hydrologic studies, Amer. Water Works Assn. Jour., vol. 56, No. 6, pp. 748-754.

YORSTON, H.H. (1954) Geology of the south half of the Meramec Spring quadrangle, Thesis, Missouri School of Mines, 109 p.

ZOTTER, H. (1963) Stream tracing techniques and results: Pocahontas and Greenbrier Counties, Va., Natl. Speleological Soc. News, vol. 21, No. 10.

______________ (1965) Stream tracing techniques and results: Pocahontas and Greenbrier Cos., Va., Natl. Speleological Soc. News, Vol. 23, No. 12.

APPENDIX A

Fluorometry Turner Model 111 Fluorometer

Fluorescence occurs because some substances have the ability of discharging energy obtained when they absorb light, by re-emitting light of a longer wavelength. The intensity of selected portion of this re-emitted light is measured proportional to the amount of exciting light. The efficiency of this process may be anywhere from a fraction of a percent to 100 percent. The intensity of light emitted at low concentrations may be considered proportional to the concentration and to the intensity of the exciting light. In practice, therefore, the dial reading of the fluorometer is linear with the concentration of the sample. The range between the lowest detectable concentration and the point where significant nonlinearity occurs is normally a factor of 10^4 - 10^5 in concentration.

The proportionality of the fluorescence and concentration are maintained even when the exciting light and measured fluorescent light are far removed from the peaks. See Figure 24 for peak values of Rhodamine B, Rhodamine WT and Pontacyl Pink. To obtain the greatest sensitivity possible the excitation line of mercury should be closest to the major absorption peak of the substance.

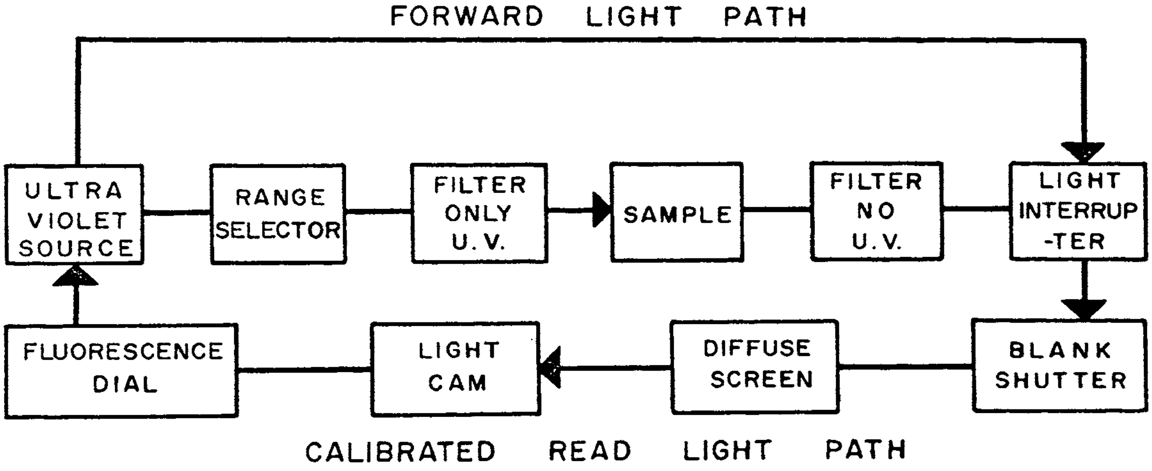


FIG. 23 OPTICAL SYSTEM OF THE TURNER MODEL III FLUOROMETER

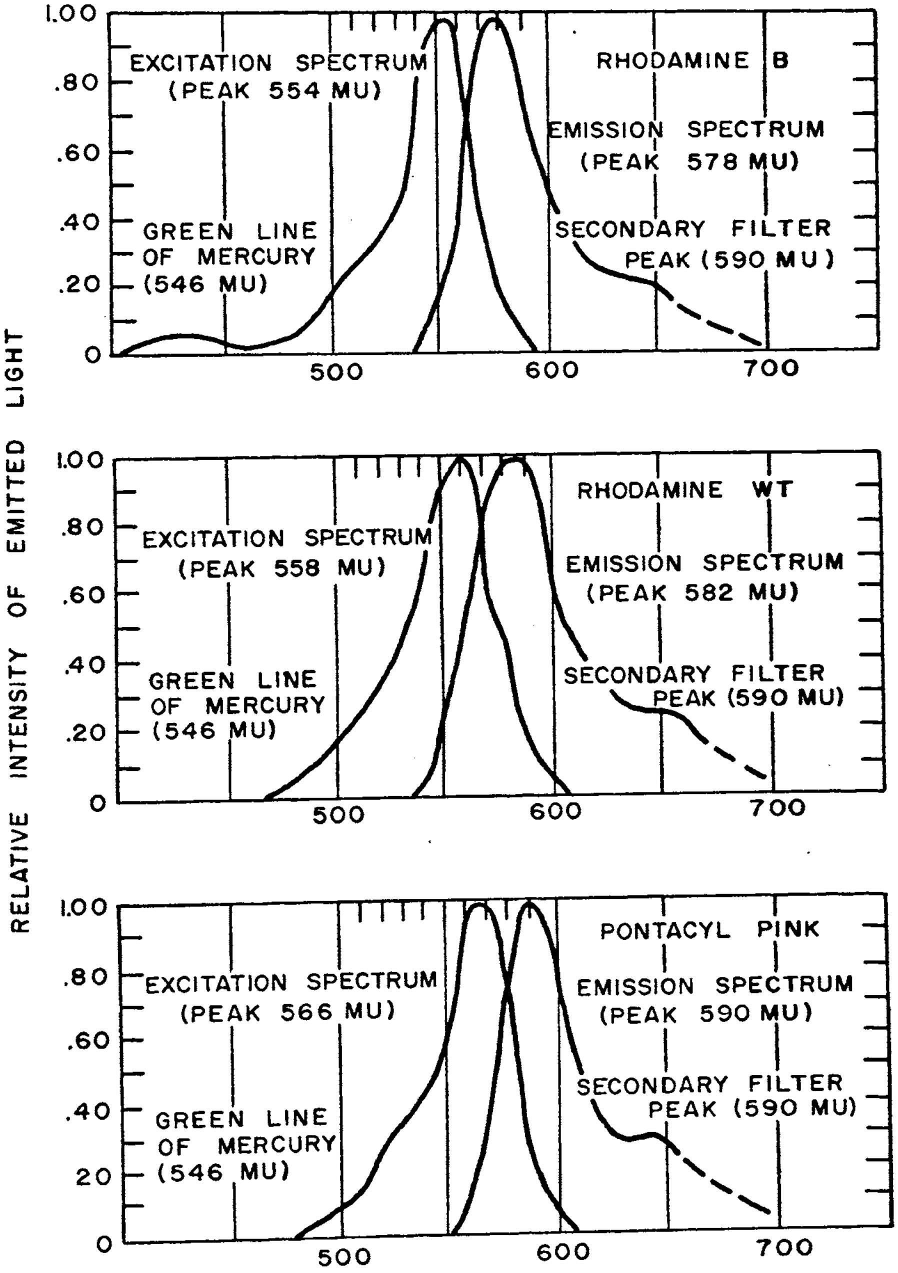


FIG. 24 EXCITATION AND EMISSION SPECTRA OF RHODAMINE B, RHODAMINE WT, AND PONTACYL PINK

The fluorometer is basically an optical bridge (see Figure 23) which measures the differences between light emitted by the sample and that from a calibrated rear light path. A single light photomultiplier tube surrounded by a mechanical light interrupter sees light alternately from the sample and from the rear light path. The quantity of light required in the rear light path to balance that from the sample is indicated by the fluorescence dial. The instrument itself has four operating ranges to give it a large range of sensitivity. Each range is determined by the size of the aperture emitting light to the sample from the light source. One of its unique properties is that of giving repeatable readings over long periods of time due to the inherent stability of the optical bridge.

VITA

Milton Frank Bradley was born on January 22, 1942 in Bridgeport, Connecticut. He received his primary and secondary education in Stratford, Connecticut. In June, 1960 he graduated from Stratford High School.

He graduated from the University of Missouri at Rolla with the degree of Bachelor of Science in Geology in May, 1965. Following graduation, the author enrolled as a graduate student at the University of Missouri - Rolla and was appointed as a Research Assistant in Water Resources in September, 1967.

During the summers of 1965 and 1966 he was employed as a consulting geologist for Manley Sand Division of Martin Marietta. In September, 1968 the author joined Cominco American Inc. as a mine geologist and has served in this capacity continuously to date.

He has been a member of the C. L. Dake Geological Society, Sigma Gamma Epsilon, and American Institute of Mining, Metallurigical, and Petroleum Engineers (A.I.M.E.).