

**THE INFLUENCE OF A DEEP-STORAGE RESERVOIR AND AN  
UNDERGROUND RESERVOIR ON THE PHYSICOCHEMICAL  
LIMNOLOGY OF A PERMANENT RIVER IN  
CENTRAL TEXAS**

**THESIS**

**Presented to the Graduate Council of  
Southwest Texas State University  
in Partial Fulfillment of  
the Requirements**

**For the Degree of  
MASTER OF SCIENCE**

**By**

**Larry David Broz, B.S.  
(Hooks, Texas)**

**San Marcos, Texas**

**December, 1974**

## ACKNOWLEDGEMENTS

I wish to express my gratitude to many persons for help and understanding in the course of this study.

Dr. H. H. Hannan helped design the project. He also spent valuable time in helping with the writing of this paper. His help and suggestions throughout the study were gratefully appreciated.

Acknowledgement also goes to Dr. W. C. Young and to Dr. A. O. Parks for critically reading the manuscript and to Dr. Huffman for statistical assistance. I wish also to thank Corky Roberts, Buddy Wiegand, and Donald Baker of the Southwest Texas State University Maintenance Department in the timely installing of new equipment upon arrival at the laboratory.

My final thanks are given to my wife, Judy, and our children Todd, Gretchen, Kim, Lisa, and Bart for their love and support through the trials they withstood during the period of the writing of this paper.

## TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION . . . . .	1
II. DESCRIPTION OF THE STUDY AREA. . . . .	2
A. General Description. . . . .	2
B. Description of Stations. . . . .	3
III. METHODS AND MATERIALS. . . . .	6
IV. RESULTS AND DISCUSSION . . . . .	9
A. Limnological Conditions. . . . .	9
B. Nutrients. . . . .	19
C. Cations. . . . .	24
V. SUMMARY. . . . .	35
BIBLIOGRAPHY . . . . .	37

## LIST OF TABLES

Table		Page
I	AVERAGE FLOW IN CUBIC METERS PER MINUTE. . . . .	10
II	NITRATE NITROGEN FOR AQUATIC ECOSYSTEMS IN TEXAS . . . . .	20
III	TOTAL PHOSPHORUS FOR AQUATIC ECOSYSTEMS IN TEXAS . . . . .	23
IV	CATION PROGRESSION FOR AQUATIC ECOSYSTEMS IN TEXAS . . . . .	25
V	ANNUAL CHANGES IN PHYSICOCHEMICAL CONDITIONS BETWEEN STATIONS . . . . .	36

TABLE OF FIGURES

Figure		Page
1	MAP OF THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	4
2	BICARBONATE ALKALINITY IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	14
3	pH IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	15
4	SPECIFIC CONDUCTANCE IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	17
5	NITRATE NITROGEN IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	21
6	DISSOLVED CALCIUM IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	27
7	DISSOLVED MAGNESIUM IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	29
8	DISSOLVED SODIUM IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	30
9	DISSOLVED POTASSIUM IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	32
10	DISSOLVED IRON IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS . . . . .	33

## CHAPTER I

### INTRODUCTION

Most published studies on the physicochemical limnology of deep-storage reservoirs located in central Texas have been restricted to determining conditions within the impoundment (Fruh and Davis, 1969; Higgins and Fruh, 1968; Huang, Mase, and Fruh, 1973). Only in the study by Hannan and Young (1974) on Canyon Reservoir has reference been made to the influence of the impoundment on the parent river; this study was restricted to such basic limnological parameters as dissolved oxygen, nutrients, conductivity, alkalinity, and pH. Several workers have discussed the limnological conditions of spring runs (Odum, 1957; Tilly, 1968; Brunskill, 1969 and Trogdon, 1953). Published limnological studies of spring runs in central Texas have been limited to the upper San Marcos River (Hannan and Dorris, 1970).

This study differed from these previous works in that the influence of an underground reservoir - spring run complex and a bottom-draining deep-storage reservoir on the physicochemical limnology of the parent river were studied.

CHAPTER II  
DESCRIPTION OF THE STUDY AREA

General Description

The study area is located along a 98-km stretch of the Guadalupe River and the 5-km Comal River in Comal County, Texas. The Guadalupe and Comal rivers receive their waters from precipitation on the Edwards Plateau. The Edwards Plateau is the recharge area of the Edwards Underground Reservoir which covers 16,577 sq km. Throughout most of the region the plateau rises from about 305 m elevation to 820 m above sea level along its northern edge. Edwards limestone covers most of the surface throughout the Edwards Plateau (U.S. Army Corps of Engineers, 1964).

Canyon Reservoir is a deep-storage bottom-draining reservoir with a variable depth measuring 37 to 40 m in the inundated riverbed approximately 100 m from the dam. The geology of the area is primarily Glen Rose limestone. Drainage area of the basin above Canyon Dam is 3961 sq km (Rawson, 1968). The conservation pool covers 3300 hectares and has a volume of 500 million cubic meters (U.S. Army Corps of Engineers, 1966).

The Edwards Underground Reservoir is a limestone aquifer that stretches about 282 km across south-central Texas and varies in width from eight to 65 km. It is estimated that approximately 3.5 billion cubic meters of water is in storage in this underground reservoir (U.S. Army Corps of Engineers, 1964).

The Comal River, about five km in length, has its origin in Comal Springs and flows to the Guadalupe River (U.S. Army Corps of Engineers, 1964). It is the shortest river in Texas and also the shortest river in the United States carrying an equivalent amount of water (A. H. Belo Corp., 1973). Nearly all of the water that it carries is supplied by Comal Springs (George, Breeding, and Hastings, 1952). Dominant macrophytes in abundance in the Comal River include Cabomba, Elodea, Ludwigia, Myriophyllum, Potamogeton, and Sagittaria.

Hueco Springs, between stations 2 and 3, is an outflow of the Edwards Underground Reservoir that empties into the Guadalupe River about four km north of Comal Springs (U.S. Army Corps of Engineers, 1964). The water from Hueco Springs was slightly turbid after heavy rains. The temperature of the water was 1.8 to 3.6 C lower than Comal Springs. Hueco Springs had an average flow of approximately 1.7 cubic meters per second (cms) (George, Breeding, and Hastings, 1952).

#### Description of Stations

Station 1 was located approximately 55 km upstream from Canyon Dam in the Guadalupe River to determine the water quality entering the reservoir. Water depth varied from 1.0 to 3.5 m over a substrate of mud and gravel.

Station 2 was located in the tailrace of Canyon Dam to study the water quality being released from the reservoir. Depth varied

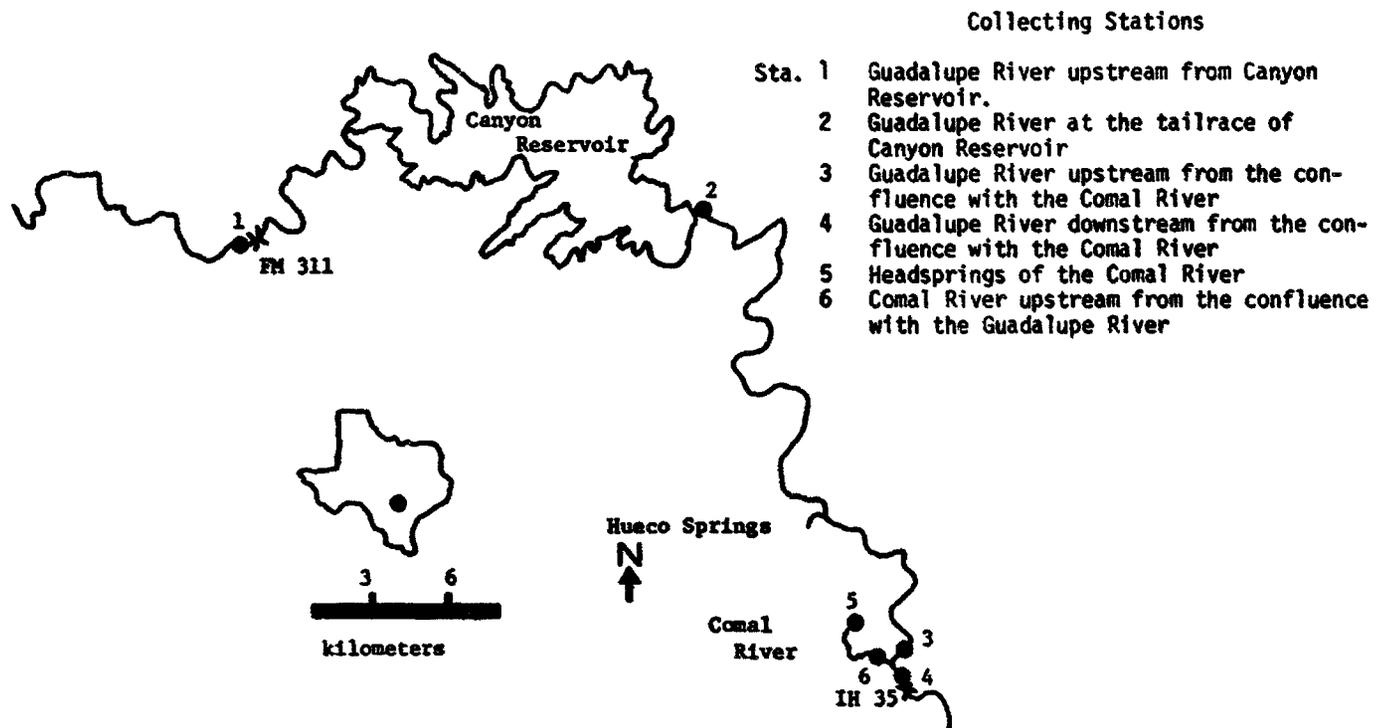


Figure 1 MAP OF THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS

from 1.5 to 4.0 m over a substrate of limestone and clay.

Station 3 was located approximately two river km above the confluence of the Guadalupe and the Comal rivers to determine what changes in water quality of the Guadalupe River occurred below station 2 prior to combining with the Comal River. Water depth ranged from 2.6 to 4.1 m with a mud and gravel substrate.

Station 4 was approximately one km below the confluence of the Comal and Guadalupe rivers. Water depth ranged from 2.5 to 4.0 m with a gravel and mud substrate which supported Ludwigia in the littoral zones. This location was chosen to determine the influence of the Comal River on the water quality of the Guadalupe River.

Station 5 was located at the head springs of the Comal River in New Braunfels, Texas to determine the water quality of the aquifer. The springs are an outflow of the Edwards Underground Reservoir and provide the source for the Comal River. Comal Springs are the largest springs in the Southwest (George, Breeding, and Hastings, 1952).

Station 6 was located on the Comal River approximately 0.1 km upstream from the confluence of the Guadalupe and Comal rivers. This location was chosen to determine if the water quality of the Comal River had changed before mixing with the Guadalupe River. Water depth ranged from 2.3 to 3.8 m with a mud and gravel substrate which supported scattered growths of Ludwigia, Cabomba, and Myriophyllum.

### CHAPTER III

#### METHODS AND MATERIALS

The study began in March, 1973, and continued through February, 1974. Stations were sampled at about 30-day intervals for physicochemical parameters and chlorophyll a. All parameters were sampled just below the surface. Dissolved oxygen samples were taken with a 2.0-l Kemmerer sampler. Water for chlorophyll a, alkalinity, turbidity, nitrates, pH, specific conductance, phosphorus, and metal analyses was taken by submerging a polyethylene bottle beneath the surface until filled.

Air and water temperatures were measured with a mercury thermometer. Specific conductance was measured with a temperature compensated (25 C) Beckman RB3 Solubridge conductivity meter, pH was measured with a Portomatic model 175 portable pH meter, and turbidity was measured as percent transmittance on a Bausch and Lomb Spectronic 20 colorimeter at 450 m $\mu$  and converted to Jackson Turbidity Units.

Dissolved oxygen was determined by the Alsterberg-azide modification of the Winkler method (American Public Health Association, 1971), and oxygen saturation values were determined from a nomograph (Reid, 1961). Samples for phenolphthalein and methyl orange alkalinity were titrated with 0.02 N sulfuric acid (American Public Health Association, 1971).

Chlorophyll a was determined by the trichromatic method of Richards and Thompson (1952). Five hundred-ml aliquots of water were filtered through a thin layer of magnesium carbonate on a 0.45  $\mu$  Millipore filter. The filter was ground in three ml of 90 percent acetone in a glass homogenizer at about 500 rpm. The total volume was adjusted to 10 ml with 90 percent acetone and kept 10 minutes in the dark at room temperature. Optical densities were determined at 750, 663, 645, and 630  $\mu$  against an acetone-solution blank with a Beckman Model DU spectrophotometer. Calculations were based on the trichromatic equation of the United Nations Educational, Scientific and Cultural Organization (1966).

Dissolved nitrate was determined using the method of Jenkins and Medsker (1964). The sample was filtered through a 0.45  $\mu$  Millipore filter. This method is based on the reaction of nitrate with sulfuric acid and brucine-sulfanilic acid solutions under controlled temperatures to produce a yellow color.

Two forms of phosphorus were determined by the method of Murphy and Riley (1962). This method involves formation of phosphomolybdic acid which is subsequently reduced by ascorbic acid to the molybdenum-blue color. Total phosphate was determined from samples digested until a final volume of 10 ml was reached prior to addition of the color developing reagent. Samples for the determination of dissolved inorganic phosphate were filtered through 0.22  $\mu$  Millipore filters before the mixed reagent was added.

Inorganic phosphate determined by this method included orthophosphates and dissolved polyphosphates.

Magnesium, potassium, sodium, calcium, copper, and iron were determined by atomic absorption spectrophotometry. The Perkin-Elmer Atomic Absorption Spectrophotometer model 305 was used following the methods described by Brown, Skougstad, and Fishman (1970). All samples were filtered through 0.45  $\mu$  Millipore filters and preserved with 1:1 redistilled nitric acid and kept at 4 C. Copper and iron were chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl iso-butyl ketone (MIBK) prior to aspiration into the flame of the spectrophotometer.

The nonparametric Wilcoxon matched-pairs signed ranks was used to determine significant differences in concentrations (Siegel, 1956). References to significance for each parameter are at the two-tailed 0.01 alpha level for the twelve month sampling period.

CHAPTER IV  
RESULTS AND DISCUSSION

Limnological Conditions

Flow--Flow data for the study area are given in Table I.

Flow at station 1 peaked in July, 1973, at 3432 cubic meters per minute (cmm) and in October, 1973, at 2562 cmm with the minimum flow in February, 1974, at 402 cmm. Flow at station 2, which is dependent upon discharge controlled by the U.S. Army Corps of Engineers at Canyon Reservoir, peaked in July, 1973, at 3432 cmm and in November, 1973, at 1998 cmm with a minimum flow in June, 1973, at 564 cmm. Discharge from the Edwards Underground Reservoir at station 5 ranged from 570 cmm during May, 1973, to 906 cmm in October, 1973. Record flow for Comal Springs was 714 cmm before January, 1973. This record was exceeded four times during this study.

Water temperature--Water temperature ranged from 10.6 C at station 2 in March, 1973, to 26.3 C at station 1 in June, 1973. Seasonal water temperature correlated with seasonal ambient temperature except at station 5. Water temperature at station 5 ranged from 23.3 C in December, 1973, to 24.5 C in July, 1973, exhibiting little fluctuation. This constancy of temperature has also been reported in San Marcos Springs (Hannan and Dorris, 1970). The Comal and San Marcos springs are both formed by fissures of the Balcones Fault Zone. Water temperature at station 2 reached a high of 23.0 C in September, 1973, in contrast to a high of 18.5 C in July reported at the same station

TABLE I  
AVERAGE FLOW IN CUBIC METERS PER MINUTE

Month	+Spring Branch, above Canyon Reservoir	+Sattler, below Canyon Reservoir	@Comal Springs
1973			
January	378	360	546
February	570	498	546
March	618	732	588
April	642	780	618
May	474	1020	570
June	858	564	636
July	3432	3432	774*
August	918	1656	654
September	738	948	798*
October	2562	1614	906*
November	1068	1998	756
December	624	1158	750
1974			
January	492	780	708
February	402	786#	684

\*record high

#average through 13 February

+Flow data from USGS

@Flow data from the Edwards Bulletin

(Hannan and Young, 1974). This increase in temperature could possibly be attributed to an unusually large outflow of hypolimnetic water during the summer of 1973 (Table I).

A 16 percent increase in annual mean water temperature was observed between stations 2 and 3. This significant increase was attributed to Hueco Springs and solar radiation along the 40-km segment of river. The 5-km spring run of the Comal River showed no significant difference in water temperature due to the effect of relatively cool water from the hypolimnion of Canyon Reservoir being offset by the relatively warm water of the Edwards Underground Reservoir.

A temperature profile was taken in Canyon Reservoir approximately 100 m out from the dam over the inundated river bed on November 2, 1973. The isothermal profile indicated that the fall overturn had occurred.

Dissolved oxygen and percent saturation--Dissolved oxygen (DO) ranged from 3.5 mg/l at station 5 in July, 1973, to 10.6 mg/l at station 2 in March, 1973. Oxygen saturation ranged from 40 percent at station 5 in July, 1973, to 105 percent at station 6 in March, 1973. Oxygen saturation at station 2 ranged from 89 percent during thermal stratification to 101 percent during the period of greatest turbulence and flow. A six percent increase in annual mean percent saturation occurred between stations 1 and 2. This significant increase was due to turbulence at the tailrace. There was no significant difference

in percent saturation between stations 2 and 3. There was a 16 percent increase in annual mean water temperature and a seven percent decrease in annual mean DO. The significant decrease in DO was due to seasonal ambient temperatures and Hueco Springs. There was no significant difference in DO between stations 3 and 4. An 89 percent increase in annual mean percent saturation and annual mean DO occurred between stations 5 and 6. Since there was a significant increase between stations 5 and 6, the differences between stations 3 and 4 can not be entirely attributed to the underground reservoir, but more to the spring run. An eight percent increase in annual mean DO occurred between stations 1 and 4. This significant increase was due to the increase at the tailrace and the confluence of the Guadalupe and Comal rivers.

Chlorophyll a--The method used to determine chlorophyll a is limited in that not all types of phytoplankton respond equally well to acetone extraction. If caution is used, however, chlorophyll a can be indicative of the relative number of photosynthetic organisms present in an aquatic ecosystem (Vollenweider, 1968).

There was a significant difference in chlorophyll a between stations 5 and 6 only. Since there was a significant increase between stations 5 and 6, the non-significant difference in concentrations between stations 3 and 4 can be attributed to the 5 km spring run of the Comal River. No significant difference in chlorophyll a was observed between stations 1 and 4.

Alkalinity--Alkalinity was due to bicarbonate ions which ranged from 167 mg/l at station 2 in March, 1973, to 257 mg/l at station 1 in October, 1973 (Figure 2). Annual mean alkalinity at station 2 increased four percent during the time of thermal stratification in the reservoir. This increase is attributed to the increase of carbon dioxide in the hypolimnion during anoxic conditions. Between stations 1 and 2 alkalinity decreased by 20 to 30 percent except for a 10 percent increase in September. Hannan and Young (1974) reported a decrease in alkalinity in the range of 10 to 50 percent for the same stretch of the river. This significant decrease was attributed to autotrophic assimilation of the bicarbonate ion and possible sedimentation due to decreasing velocity as the water entered the impoundment. A six percent increase in annual mean alkalinity occurred between stations 2 and 3. This significant increase was attributed primarily to the influence of Hueco Springs. A six percent increase in annual mean alkalinity occurred between stations 3 and 4. This significant increase was attributed to the higher alkalinity from the Edwards Underground Reservoir. There was no significant increase in alkalinity between stations 5 and 6. A 12 percent decrease in annual mean alkalinity occurred between stations 1 and 4. This significant decrease was due to the uncompensatable loss of alkalinity from Canyon Reservoir.

Hydrogen ions--The pH ranged from 7.4 at station 5 to 8.4 at stations 1 and 2 (Figure 3). A two percent decrease in annual





mean pH occurred between stations 1 and 2. This significant decrease was the result of decomposition of organic matter in Canyon Reservoir which increased the carbon dioxide thereby decreasing the pH. A four percent decrease in pH occurred at the tailrace in September and October, 1973, during thermal stratification. This significant decrease was also the result of increased carbon dioxide from decomposition of organic matter in the hypolimnion. There was no significant difference in pH between stations 2 and 3. A one percent decrease in annual mean pH occurred between stations 3 and 4. This significant decrease was attributed to the lower pH from the water of the Edwards Underground Reservoir. A 12 percent increase in annual mean pH occurred between stations 5 and 6. This significant increase was attributed to the release of carbon dioxide to the atmosphere as the water emerged from Comal Springs and to autotrophic assimilation as water flowed over the profuse growth of aquatic macrophytes in the Comal River. A two percent decrease in annual mean pH occurred between stations 1 and 4. This significant decrease was due to impoundment of water in Canyon Reservoir and the confluence with the water from the Comal River.

Specific conductance--Specific conductance in the study area ranged from 245  $\mu\text{mhos/cm}$  at station 2 in August, 1973, to 610 at station 6 in April, 1974 (Figure 4). Specific conductance decreased 34 percent between stations 1 and 2, which is similar to the 30 percent decrease reported by Hannan and Young (1974) for the study area. Their

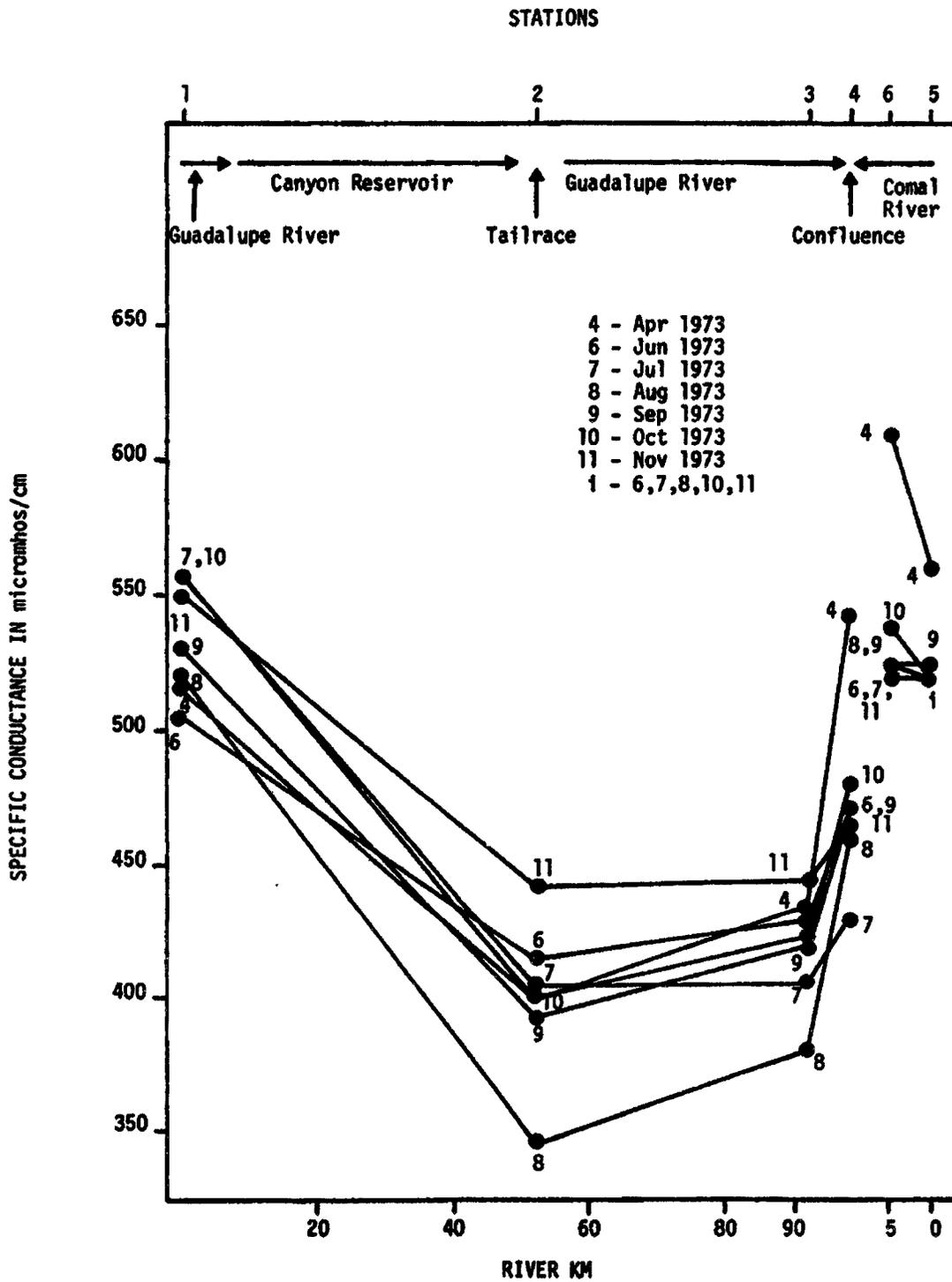


Figure 4 SPECIFIC CONDUCTANCE IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS

stations in the riverine reach of Canyon Reservoir showed a marked increase in chlorophyll a. This increase in autotrophic assimilation depleted carbon dioxide causing the autotrophs to utilize bicarbonate as a carbon source thereby reducing the alkalinity, increasing the pH, and decreasing the specific conductance (Hannan and Young, 1974). A six percent increase in annual mean specific conductance was observed between stations 2 and 3. This significant increase was attributed to Hueco Springs. A 10 percent increase in annual mean specific conductance occurred between stations 3 and 4. This significant increase was attributed to the high specific conductance from the Edwards Underground Reservoir. A 10 percent decrease in annual mean specific conductance occurred between stations 1 and 4. This significant decrease was attributed to the uncompensatable loss from Canyon Reservoir.

Turbidity--Turbidity, in Jackson Units, ranged from zero at stations 2, 5, and 6 to 40 at station 1. A 20 percent decrease in annual mean turbidity occurred between stations 3 and 4. This significant decrease was due to the mixing of clear spring water from the Edwards Underground Reservoir with the more turbid Guadalupe River water. The five km stretch between stations 5 and 6 showed a significant increase in turbidity. The annual mean for station 5 was zero JTU and the annual mean for station 6 was two JTU, showing a minimal increase. There was no significant difference in turbidity between stations 1 and 2, 2 and 3, and 1 and 4.

## Nutrients

Dissolved nitrate nitrogen--Dissolved nitrate nitrogen concentrations are compared with concentrations reported for other aquatic ecosystems in Texas in Table II. The Edwards Underground Reservoir shows a consistently higher concentration than any other lentic system. Lakes Dunlap, McQueeney, and Gonzales are on the Guadalupe River below station 4. They receive additional nitrogen from the effluents of the New Braunfels and Seguin sewage treatment plants (Hannan and Young, 1973).

Dissolved nitrate nitrogen ranged from less than 0.10 mg/l at station 2 in September, 1973 to 1.62 mg/l at stations 5 and 6 in January, 1974 (Figure 5). A significant decrease in nitrate nitrogen was observed between stations 1 and 2. This decrease was the result of a longer retention time of water permitting phytoplankton in the reservoir to assimilate nitrate nitrogen. Another factor causing the decrease in nitrate nitrogen at station 2 was anaerobic metabolism of nitrate by bacteria in the anoxic hypolimnion during thermal stratification. There was a significant increase in nitrate nitrogen at station 4 due to the high concentration of nitrate nitrogen (Figure 5) and the consistently high discharge (Table II) from Comal Springs.

The annual mean of nitrate nitrogen at station 2 was 0.36 mg/l compared to 1.03 mg/l at station 1. The annual mean at station 3 was 0.44 mg/l compared to 0.83 mg/l at station 4. Canyon Reservoir retained 65 percent of the nitrate nitrogen received from the influent

TABLE II  
NITRATE NITROGEN FOR AQUATIC ECOSYSTEMS IN TEXAS

Ecosystem	Reference	Nitrate Nitrogen mg/l
Lake Waco	Kimmel, 1969	0.20 - 0.40
Lake Travis	Higgins & Fruh, 1968	0.01 - 0.55
Lake Dunlap	Hannan, et al, 1973	0.20 - 1.39
Lake McQueeney	Hannan, et al, 1973	0.02 - 1.40
Lake Gonzales	Hannan, et al, 1973	0.50 - 1.90
Canyon Reservoir	Hannan, et al, 1974	0.02 - 0.61
Lake Bridgeport	Harris & Silvey, 1940	0.00 - 0.20
Eagle Mountain Lake	Harris & Silvey, 1940	0.00 - 0.08
Lake Worth	Harris & Silvey, 1940	0.00 - 0.01
Lake Dallas	Harris & Silvey, 1940	0.00 - 0.44
Lake Travis	Huang, et al, 1973	0.01 - 0.03
Lake Austin	Huang, et al, 1973	0.01 - 0.05
Decker Lake	Huang, et al, 1973	0.01 - 0.08
Lake Livingston	Huang, et al, 1973	0.01 - 0.70
Massey Lake	Harrel, 1973	1.00 - 5.80
Lake Meredith	Cooper, et al, 1971	0.02 - 0.06
San Marcos River	Hannan & Dorris, 1970	0.64 - 1.66
Edwards Underground Reservoir	This Study	1.25 - 1.62
Comal River	This Study	1.25 - 1.62
Guadalupe River, upstream from Canyon Reservoir	Hannan, et al, 1974 This Study	0.16 - 1.36 0.80 - 1.28
Guadalupe River, tailrace of Canyon Dam	This Study	0.01 - 0.61

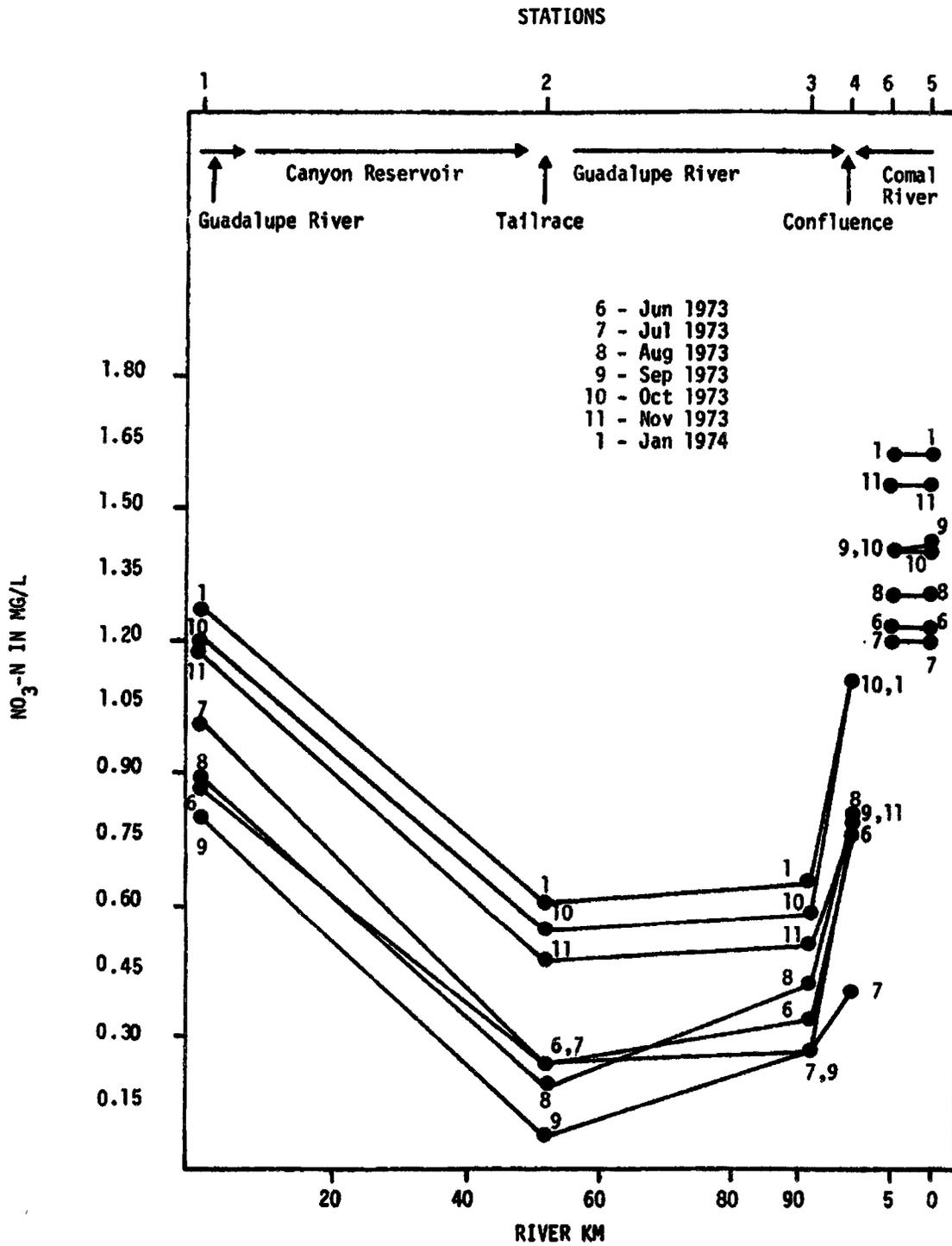


Figure 5 NITRATE NITROGEN IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS

of the Guadalupe River and the Edwards Underground Reservoir replaced 42 percent of that loss. It is apparent that increased retention time, thermal stratification and increased standing crops of autotrophic organisms cause deep-storage reservoirs to become nitrate nitrogen sinks.

The concentration of nitrate nitrogen in rainwater over the study area ranges from about 0.1 to 0.4 mg/l (Junge, 1958). It is interesting to note that the watershed increased the nitrate nitrogen concentration about 400 percent by the time the water reached station 1.

Total phosphate phosphorus--Total phosphate phosphorus concentrations measured in this study were compared with concentrations for other aquatic ecosystems in Texas (Table III). In general, the annual mean of total phosphate phosphorus was less in the study area than in other Texas waters.

Total phosphate phosphorus ranged from less than 0.01 mg/l at stations 2, 3, 4, 5, and 6 to 0.40 mg/l at station 1 in June, 1973. The annual mean for stations on the Guadalupe River was less than 0.02 mg/l, while the annual mean for stations on the Comal River was less than 0.01 mg/l. Neither impoundment nor thermal stratification had an influence on total phosphate phosphorus as is expected for older impoundments. There was no significant difference in total phosphate phosphorus among all the stations.

Dissolved orthophosphate phosphorus--Dissolved orthophosphate phosphorus ranged from less than 0.01 mg/l at all stations to 0.02 mg/l

**TABLE III**  
**TOTAL PHOSPHORUS FOR AQUATIC ECOSYSTEMS IN TEXAS**

Ecosystem	Reference	Total Phosphorus mg/l
Lake Waco	Kimmel, 1969	0.00 - 7.20
Lake Dunlap	Hannan, et al, 1973	0.05 - 0.24
Lake McQueeney	Hannan, et al, 1973	0.05 - 0.15
Lake Gonzales	Hannan, et al, 1973	0.05 - 0.21
Canyon Reservoir	Hannan, et al, 1974	0.02 - 0.03
Lake Meredith	Cooper, et al, 1971	0.11 - 0.60
Lake Bridgeport	Harris & Silvey, 1940	0.07 - 0.02
Eagle Mountain	Harris & Silvey, 1940	0.06 - 0.10
Lake Worth	Harris & Silvey, 1940	0.04 - 0.12
Lake Dallas	Harris & Silvey, 1940	0.05 - 0.30
Massey Lake	Harrel, 1973	0.03 - 0.91
Lake Travis	Higgins & Fruh, 1968	0.00 - 0.57
Lake Travis	Huang, et al, 1973	0.01 - 0.02
Lake Austin	Huang, et al, 1973	0.01 - 0.02
Town Lake	Huang, et al, 1973	0.01 - 0.02
Decker Lake	Huang, et al, 1973	0.01 - 0.08
Lake Livingston	Huang, et al, 1973	0.06 - 0.30
Guadalupe River, New Braunfels to Gonzales	Hannan, et al, 1973	0.02 - 0.24
Guadalupe River, upstream from Canyon Reservoir	Hannan & Young, 1974 This Study	0.02 - 0.03 0.02 - 0.03
Guadalupe River, tailrace of Canyon Dam to New Braunfels	This Study	0.01 - 0.03
Edwards Underground Reservoir	This Study	0.01 - 0.01

at station 2. Mean orthophosphate phosphorus for each station was less than 0.01 mg/l. However, at station 2 orthophosphate phosphorus was at a maximum during November, 1973, which corresponds with one of two peak flows (Table I). This maximum at station 2 was attributed to increased discharge from Canyon Reservoir, which stirred the bottom sediments in the reservoir releasing orthophosphate phosphorus to the water. Neither impoundment nor thermal stratification had an appreciable influence on the concentrations of dissolved orthophosphate phosphorus. The classical pattern of an increase in phosphorus in the hypolimnion after oxygen depletion was not evident in Canyon Reservoir. Hannan and Young (1974) attributed a similar lack of increase in phosphorus to Canyon Reservoir being a young bottom-draining reservoir. There was no significant difference in orthophosphate phosphorus among all the stations.

#### Cations

Hutchinson (1957) has stated that in the more concentrated waters of open river systems there is a tendency for  $Ca > Mg > Na > K$ , and that it is reasonable to suppose that all fresh waters moving through rivers and lakes are gradually tending to such a composition. Table IV shows that the concentration of these cations in the study area and other aquatic ecosystems in Texas generally follow Hutchinson's progression. The Wichita River system had a greater amount of sodium than calcium. This larger amount of sodium was due to the oil fields in the area using surface pits

TABLE IV  
 CATION PROGRESSION FOR AQUATIC  
 ECOSYSTEMS IN TEXAS

Ecosystem	Reference	Progression
Nueces River south-central Texas	Reeves, et al, 1972	Ca > Mg > Na > K
Medina River south-central Texas	Reeves, et al, 1972	Ca > Mg > Na > K
San Marcos River central Texas	Hannan & Dorris, 1970	Ca > Mg > Na > K
Reservoirs on the Trinity River northeast Texas	Harris & Silvey, 1940	Ca > Mg > Na > K
Lake Meredith on the Canadian R. Texas panhandle	Cooper, et al, 1973	Na & K > Ca > Mg
Springs in the Wichita River north Texas	Trogdon, 1953	Na > Ca > Mg
Guadalupe River central Texas	This Study	Ca > Mg > Na > K
Comal River central Texas	This Study	Ca > Mg > Na > K
Edwards Underground Reservoir south-central Texas	This Study	Ca > Mg > Na > K

for brine disposal and the groundwater level often being less than three meters deep (Trogdon, 1953). Lake Meredith in Texas panhandle had a greater amount of sodium and potassium than calcium (Cooper, 1971). No explanation was given for this anomaly.

Calcium ions--Calcium ions in the study area ranged from 54 mg/l at station 2 in March and August, 1973, to 91 mg/l at station 1 in July, 1973 (Figure 6). A 25 percent decrease in annual mean calcium occurred between stations 1 and 2. This significant decrease in calcium corresponds with a significant decrease in specific conductance (Figure 4). An earlier study by Hannan and Young (1974) showed that autotrophic assimilation in Canyon Reservoir caused a decrease in specific conductance and alkalinity and an increase in pH thereby reducing the alkalinity and increasing the pH. These factors could result in the precipitation of calcium carbonate thereby causing the decrease in calcium ions between stations 1 and 2. Stratification did not appear to influence the concentration of calcium. A 10 percent increase in the annual mean of calcium occurred between stations 2 and 3. This significant increase was attributed to Hueco Springs. An eight percent increase in the annual mean of calcium occurred between stations 3 and 4. This significant increase was due to the high concentration of calcium from the Edwards Underground Reservoir. There was no significant difference in calcium between stations 5 and 6. An 11 percent decrease in the annual mean of calcium occurred between stations 1 and 4. This significant decrease is due to the



uncompensatable loss from Canyon Reservoir.

Magnesium ions--Magnesium ions in the study area ranged from 12 mg/l at stations 2 and 3 in August, 1973, to 23 mg/l at station 1 in December, 1973 (Figure 7). A 23 percent decrease in the annual mean of magnesium occurred between stations 1 and 2. Hannan and Young (1974) observed an increase in chlorophyll a in Canyon Reservoir. Since magnesium is a component of the chlorophyll molecule, the significant decrease in magnesium in Canyon Reservoir was attributed to an increase in chlorophyll a. A 40 percent decrease in magnesium between stations 1 and 2 was observed during thermal stratification in Canyon Reservoir. There was no significant difference in magnesium between stations 2 and 3, 3 and 4, and 5 and 6. An 18 percent decrease in the annual mean of magnesium occurred between stations 1 and 4. This significant decrease is due to the uncompensatable loss from Canyon Reservoir.

Sodium ion--Sodium ions in the study area ranged from 6.0 mg/l at stations 2 and 3 in August and October, 1973, to 11.6 mg/l at station 1 in May, 1973 (Figure 8). A 20 percent decrease in the annual mean of sodium occurred between stations 1 and 2, which was significant. An additional 39 percent decrease in concentration occurred during thermal stratification. A nine percent increase in the annual mean of sodium occurred between stations 3 and 4. This significant increase was attributed to the higher concentration of sodium in the Comal River mixing with lower concentrations from the Guadalupe River. There was no significant difference in sodium





between stations 2 and 3, and 5 and 6. A 17 percent decrease in sodium occurred between stations 1 and 4. This significant decrease was attributed to the uncompensatable loss from Canyon Reservoir.

Potassium ion--Potassium ions in the study area ranged from 1.3 mg/l at station 6 in April, May and August, 1973, to 2.4 mg/l at station 2 in October, 1973 (Figure 9). A 31 percent increase in the annual mean of potassium occurred between stations 1 and 2. This significant increase could be attributed to decaying vegetation and/or fertilization of farmland in the watershed. Barrett (1957) studied the fate of potassium in lakes before and after artificial fertilization. The results showed that potassium went into solution in proportion to the amount of fertilizer added and gradually subsided from epilimnial waters while increasing in hypolimnial waters. This type of settling phenomena could partially account for the increased potassium at station 2. There was no significant difference in potassium between stations 2 and 3, and 5 and 6. A 10 percent decrease in the annual mean of potassium occurred between stations 3 and 4. This significant decrease was attributed to the relatively low concentration of potassium in the Edwards Underground Reservoir. A 12 percent decrease in the annual mean of potassium occurred between stations 1 and 4. This significant decrease was attributed to the uncompensatable loss from Canyon Reservoir.

Iron--Iron in the study area ranged from 0.001 mg/l at station 4 in May, 1973, to 0.101 mg/l at station 2 in September, 1973 (Figure 10).

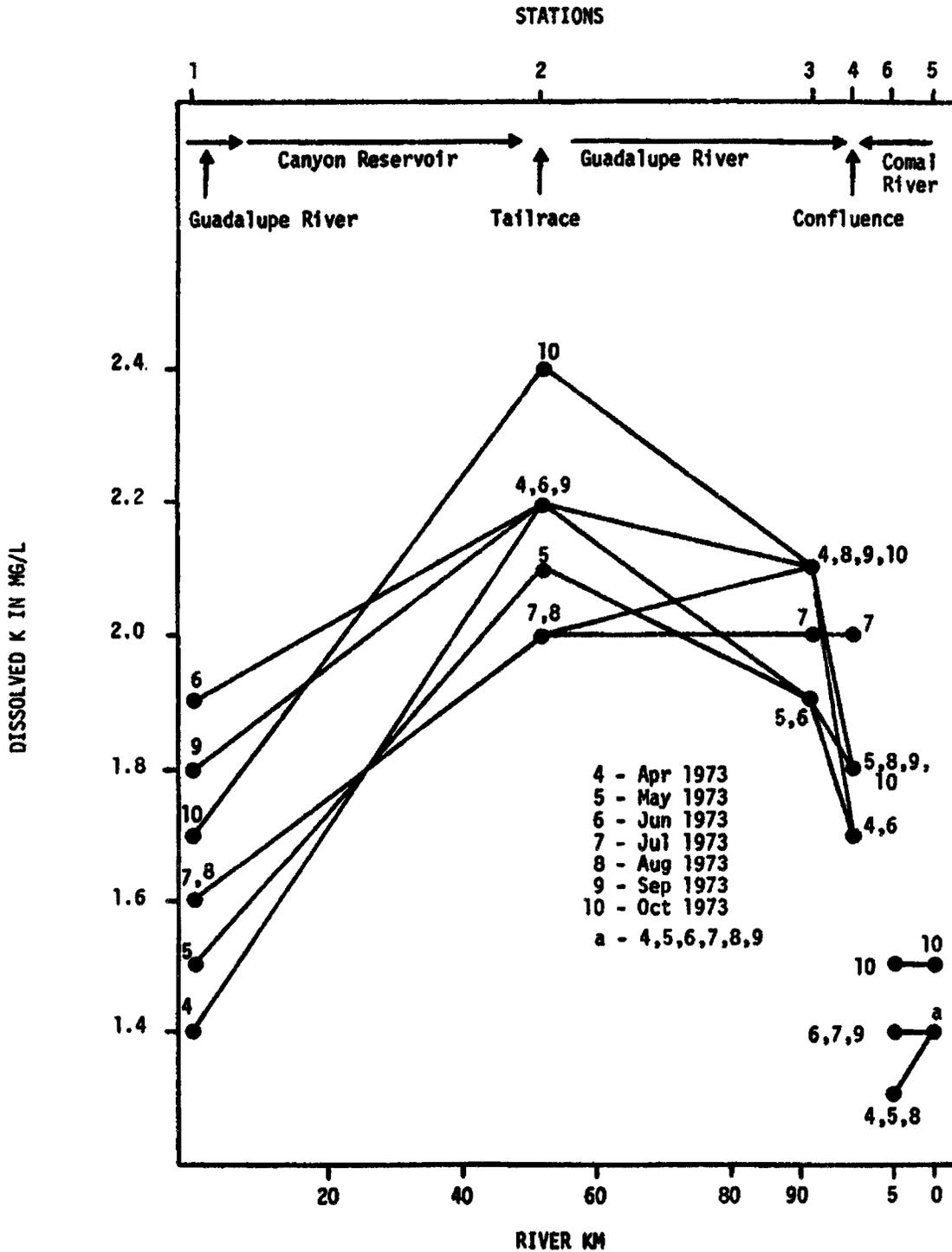


Figure 9 DISSOLVED POTASSIUM IN THE GUADALUPE AND COMAL RIVERS IN COMAL COUNTY, TEXAS



There was no significant difference in iron between stations 1 and 2, other than during thermal stratification in August and September, 1973, when iron increased 1800 percent between these stations. Studies by Hannan and Young (1974) have shown that an oxygen deficit occurs near the bottom of the deeper portions of Canyon Reservoir throughout most of the year, and during four months of the year the hypolimnion is anoxic.

High carbon dioxide, near neutral or acid conditions, the absence of oxygen, and the presence of reducing substances of organic origin occur when the hypolimnion is anoxic (Reid, 1961). These conditions caused the insoluble ferric form of iron to be reduced to the soluble ferrous form thereby causing the 1800 percent increase at station 2 during August and September, 1973.

A 25 percent decrease in the annual mean of iron occurred between stations 3 and 4. This significant decrease was attributed to the low concentration of iron in the Comal River diluting the Guadalupe River. There was no significant difference in iron between stations 2 and 3, 5 and 6, and 1 and 4.

Copper ions--Copper ions in the study area ranged from 0.002 mg/l at stations 2, 3, 4, 5, and 6 to 0.013 mg/l at station 1. There was no significant difference between any of the stations.

## CHAPTER V

### SUMMARY

The study was conducted to determine the influence of a deep-storage reservoir and an underground reservoir on the physico-chemical limnology of a 98-km segment of a permanent river in central Texas. The parameters sampled were total phosphate phosphorus, dissolved orthophosphate phosphorus, dissolved nitrate nitrogen, chlorophyll a, DO, percent saturation of oxygen, pH, total alkalinity, turbidity, specific conductance, water temperature, calcium, magnesium, sodium, potassium, iron, and copper.

The presence of thermal stratification in the deep-storage reservoir decreased nitrate nitrogen, pH, water temperature, DO, magnesium, and sodium, and increased alkalinity and iron. The annual effect of the deep-storage reservoir decreased nitrate nitrogen, pH, alkalinity, specific conductance, calcium, magnesium, and sodium, and increased DO, potassium, and percent saturation. The underground reservoir decreased pH, turbidity, potassium, and iron, and increased nitrate nitrogen, percent saturation, alkalinity, specific conductance, water temperature, calcium, and sodium. The influence of the deep-storage reservoir and the underground reservoir with their corresponding river reaches decreased nitrate nitrogen, pH, alkalinity, specific conductance, calcium, magnesium, and sodium, and increased percent saturation and potassium. A summary of the study is given in Table V.

TABLE V  
ANNUAL CHANGES IN PHYSICOCHEMICAL CONDITIONS BETWEEN STATIONS

Parameter	Stations				
	1 & 2	2 & 3	3 & 4	5 & 6	1 & 4
H <sub>2</sub> O	NS	+S	+S	NS	NS
D.O.	+S	-S	NS	+S	NS
% Sat.	+S	NS	+S	+S	+S
Chl. a	NS	NS	NS	+S	NS
Alk.	-S	+S	+S	NS	-S
pH	-S	NS	-S	+S	-S
S.C.	-S	+S	+S	NS	-S
Turbidity	NS	NS	-S	+S	NS
Diss. NO <sub>3</sub> -N	-S	+S	+S	NS	-S
Total PO <sub>4</sub> -P	NS	NS	NS	NS	NS
Diss. ortho PO <sub>4</sub> -P	NS	NS	NS	NS	NS
Diss. Ca	-S	+S	+S	NS	-S
Diss. Mg	-S	NS	NS	NS	-S
Diss. Na	-S	NS	+S	NS	-S
Diss. K	+S	NS	-S	NS	+S
Diss. Cu	NS	NS	NS	NS	NS
Diss. Fe	NS	NS	-S	NS	NS

+S Significant increase  
 -S Significant decrease  
 NS No significant change

## BIBLIOGRAPHY

- A.H. Belo Corp. 1973. Texas almanac and state industrial guide, 1974-1975. 704 p.
- American Public Health Assoc. 1971. Standard methods for the determination of water and wastewater. Washington, D. C. 874 p.
- Barrett, P. H. 1957. Potassium concentrations in fertilized trout lakes. *Limnol. and Oceanogr.* 11:287-294.
- Bischoff, J. L., R. E. Greer, and A. O. Luistro. 1970. Composition of interstitial waters of marine sediments: Temperature of squeezing effect. *Science.* 167:1245-1246.
- Brown, E., M. W. Skougstad, and M. J. Fishman. 1970. Techniques of water-resources investigations of the United States Geological Survey: Chapter A1, method for collection and analysis of water samples for dissolved minerals and gases. U. S. Government Printing Office. Washington, D. C. 160 p.
- Brunskill, G. J. and S. D. Ludlam. 1969. Fayetteville Green Lake. New York I. Physical and chemical limnology. *Limnol. and Oceanogr.* 14:817-829.
- Cooper, W. A., R. S. Hestand, III, and C. E. Newton. 1971. Chemical limnology of a developing reservoir (Lake Meredith) in the Texas Panhandle. *Tex. J. Sci.* 23:241-251.
- Fruh, F. G. and E. M. Davis. 1969. Limnological investigations of Texas impoundments for water quality management purposes: Limnological and water quality data for the Highland Lakes, 1968. Center for Research in Water Resources Rep. 40, Univ. of Tex., Austin, Texas. 187 p.
- George, W. O., S. D. Breeding, and W. H. Hastings. 1952. Geology and ground-water resources of Comal County, Texas. Geological Survey water-supply paper 1138. U. S. Government Printing Office, Washington, D. C. 126 p.
- Hannan, H. H. and T. C. Dorris. 1970. Succession of a macrophyte community in a constant temperature river. *Limnol. and Oceanogr.* 15:442-453.

- Hannan, H. H., W. C. Young, and J. J. Mayhew. 1973. Nitrogen and phosphorus in a stretch of the Guadalupe River, Texas, with five main-stream impoundments. *Hydrobiologia*. 43:419-441.
- Hannan, H. H. and W. J. Young. 1974. The influence of a deep-storage reservoir on the physicochemical limnology of a central Texas river. *Hydrobiologia*. 44:177-209.
- Harrel, R. C. 1973. Southeast Texas meander scar lake. *Tex. J. Sci.* 24:517:533.
- Harris, B. B. and J. K. G. Silvey, 1940. Limnological investigations on Texas reservoir lakes. *Ecol. Monogr.* 10:111-143.
- Higgins, R. B. and E. G. Fruh. 1968. Relationship between the chemical limnology and raw water quality of subtropical Texas impoundments. *Tex. J. Sci.* 20:13-32.
- Huang, V. H., J. R. Mase, and E. G. Fruh. 1973. Nutrient studies in Texas impoundments. *J. Water Pollution Control Fed.* 45:105-118.
- Hutchinson, G. E. 1957. A treatise on limnology. John Wiley and Sons, New York. 1015 p.
- Jenkins, D., and L. L. Medsker. 1964. Brucine method for determination of nitrate in ocean, estuarine and fresh water. *Anal. Chem.* 36:610-612.
- Junge, C. E. 1958. The distribution of ammonia and nitrate in rain water over the United States. *Trans. Amer. Geophys. Union* 39:241-248.
- Junge, C. E. and R. T. Werby. 1958. The concentration of chloride, sodium, potassium, calcium and sulfate in rainwater over the United States. *J. of Meteor.* 15:417-425.
- Kimmel, B. L. 1969. Phytoplankton production in a central Texas reservoir. Unpublished Master's thesis, Baylor University, Waco, Texas. 113 p.
- Murphy, J. and J. P. Riley, 1962. A modified single method for the determination of phosphorus in natural waters. *Analytica Chemica Acta* 27:31-36.
- Odum, H. T. 1957. Trophic structure and productivity of Silver Springs, Florida. *Ecol. Monogr.* 27:55-112.

- Rawson, J. 1968. Reconnaissance of the chemical quality of surface waters of the Guadalupe River basin, Texas, Rep. no. 88, U. S. Geol. Surv., Austin, Texas. 36 p.
- Reeves, R. D., J. Rawson, and J. F. Blakey. 1972. Chemical and bacteriological quality of water at selected sites in the San Antonio Area, Texas, August 1968 - April, 1972. Edwards Underground Water District, U. S. Geol. Surv. and Tex. Water Development Board, San Antonio, Texas. 63 p.
- Reid, G. K. 1961. Ecology of inland waters and estuaries, Reinhold Corp., New York. 375 p.
- Richards, F. A. and T. G. Thompson. 1952. The estimation and characterization of plankton populations by pigment analyses. J. Mar. Res. 11:156-172.
- Siegel, S. 1956. Nonparametric statistics for the behavioral sciences. McGraw-Hill Book Co., New York. 312 p.
- Tilly, L. J. 1968. The structure dynamics of Cone Spring. Ecol. Monogr. 38:169-197.
- Trogdon, W. O. 1953. Quality of water in the Wichita River system of Texas. Tex. J. Sci. 5:416-423.
- United Nations Educational, Scientific and Cultural Organization (UNESCO). 1966. Determination of photosynthetic pigments in sea-water. Mon. Oceanog. Methodology. 69 p.
- United States Army Corps of Engineers. 1964. Survey report on Edwards Underground Reservoir: Guadalupe, San Antonio and Nueces Rivers and tributaries, Texas, Main report. Fort Worth, Texas. 198 p.
- United States Army Corps of Engineers. 1966. Map of Canyon Reservoir.
- Vollenweider, R. A. 1968. Scientific fundamentals of eutrophication of lakes and flowing water with particular reference to nitrogen and phosphorus as factors in eutrophication, Water Manag. Res.