

CHEMICAL EQUILIBRIA AND DYNAMICS

OF

KEYSTONE RESERVOIR

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PREFACE

This study was made to formulate an adequate experimental and theoretical description of the chemistry of the natural waters of Keystone Reservoir. Chemical equilibria and transport phenomena were the bases of theoretical models formulated for the system.

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CHAPTER I

INTRODUCTION

Adequate experimental and theoretical descriptions of the chemistry of natural water systems are difficult to formulate. The chemical compositions of the waters differ and they change continually. However, the systems can partially be understood when the environmental history of the waters are considered and when well-known and well-established principles of chemistry are applied.

Natural waters acquire their chemical constituents by direct reactions with the solid, liquid, and gas phases that they come into contact with during the various parts of their hydrological cycle. The final compositions are generally the result of a large number and a wide variety of chemical, physical, and biological interactions. These interactions are so complicated that they can seldom be adequately evaluated.

Chemical equilibrium models, which retain the essential features of the real systems, have allowed simplified idealized situations to be abstracted from the complexity of nature. These are based on the principles of classical chemical thermodynamics and are formulated by assuming that the various components which make up the system are in chemical equilibrium. Comparing the models with the real systems has provided a means for the generalization of the

chemical data and has aided in the interpretation of the observed facts. The models have helped isolate some of the principal regulatory processes which determine the composition of natural waters and some of the sources of the dissolved constituents. The deviations from equilibrium can sometimes be explained by well-defined processes, but normally they emphasize where further studies are needed. For example, the deviations may indicate where different equilibria need to be incorporated into the model to duplicate the real system.

Natural water systems are normally dynamic systems so that the equilibrium models can only provide boundary conditions. The models may be oversimplified or be too general to describe the real systems in the desired detail. Dynamic models and models that describe the spatial distributions of the constituents in the system would provide a more exact picture.

Fundamental mathematical expressions which describe the concentration of a constituent at any point in the system are available. However, these require a detailed knowledge of the system and are difficult to solve mathematically. For example, knowledge about the flow rates of material and energy, types and rates of the controlling reactions, complex transport and mixing processes, and the biological phenomena are required.

Keystone Reservoir is representative of a reservoir receiving waters drained from semiarid plains containing numerous sources of inorganic salts. The net result is that the reservoir receives waters with high concentrations of dissolved solids and waters which vary in both quality and quantity. The impoundment of these waters

results in many unusual chemical, physical and biological interactions not commonly observed in impoundments.

In this study, the chemical and physical properties of Keystone Reservoir were observed periodically from May, 1966, to May, 1967, and monthly from May, 1967, to June, 1968. The chemical analysis gives a complete analytical description of the major dissolved inorganic constituents. It includes the total analytical concentrations and the concentrations of the free ions and the known complex bound species. The activities were also calculated. The expression of the chemical composition in this manner allows a more rigorous thermodynamic treatment of the data and expresses the results in a form more consistent with present theories of solutions. Physical and chemical properties of sediment and suspended solids samples were also measured.

Chemical equilibrium models involving the major dissolved inorganic components were formulated for Keystone Reservoir and were compared to the actual system. The models were used to abstract an idealized situation, used as a means to present and generalize the chemical data, and used as an aid in explaining the observed facts. The application of equilibrium models to this type of reservoir appears to be unique.

In an attempt to develop a more detailed picture of the system, a model for the spatial distributions of the major constituents was also suggested. In its simplified form, it was assumed that the distribution of the major conservative constituents were determined by the convective processes.

As far as was possible, the models developed are realistic,

contain precisely formulated hypotheses, and are descriptive of the whole reservoir rather than isolated parts. Although they are simplified, they represent a significant first step toward the ultimate objective to develop a chemical-physical-mathematical model of the reservoir which would be useful for water quality definition and control in the reservoir and the downstream area. The models quantitatively approximate the processes which determine the concentrations of the major inorganic conservative constituents as well as approximate the chemical behavior of these chemical constituents as various stresses, such as changes in carbon dioxide concentration, pressure, and temperature, are applied.

CHAPTER II

DESCRIPTION OF AREA

General Description

Keystone Reservoir is located on the Arkansas River in north central Oklahoma with the dam 15 miles upstream from Tulsa at river mile 538.8 (Figure 1). The dam was built by the U.S. Corps of Engineers for flood control, peak load hydroelectric power, recreation, and navigation purposes. Construction of the dam was completed in the fall of 1964, and the reservoir was filled to power pool level in April, 1965. At the top of the power pool (elevation 723 MSL), the reservoir has a surface area of 26,300 acres, a gross storage capacity of 663,000 acre-feet, and 330 miles of shoreline. At flood stage (754 MSL), the maximum storage capacity is 1,879,000 acre-feet. Water can be released from the reservoir through the tainter or flood gates, the sluice gates, or the power penstocks which are 1.2, 20.1, and 21.5 meters below the power pool level.

The two chief tributaries to the reservoir are the Arkansas and Cimarron Rivers which converge about two miles above the dam to form the two main arms of the reservoir (Figure 2). The total drainage area is 74,500 square miles which extends from the Rocky Mountains in Colorado across southern Kansas and northern Oklahoma (Figure 1). The average volume of water flowing past Tulsa is about 4.5 million

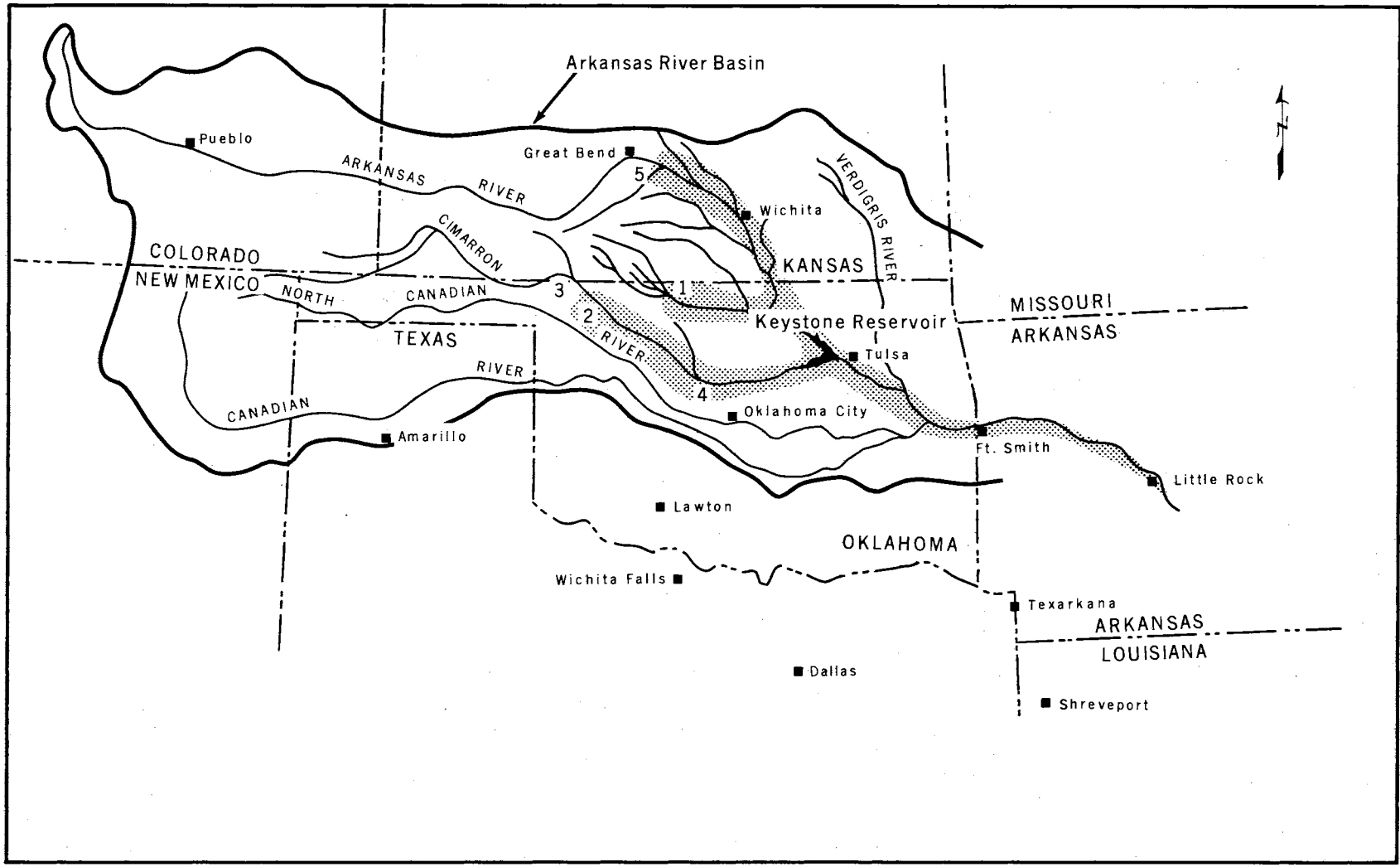


Figure 1. Map of Arkansas River Drainage Basin Showing the Location of Keystone Reservoir, Natural Brine Emissions, and Brine Affected Streams. Numbers indicate areas of natural brine emission and are identified in Table I. Shaded areas indicate brine affected streams.

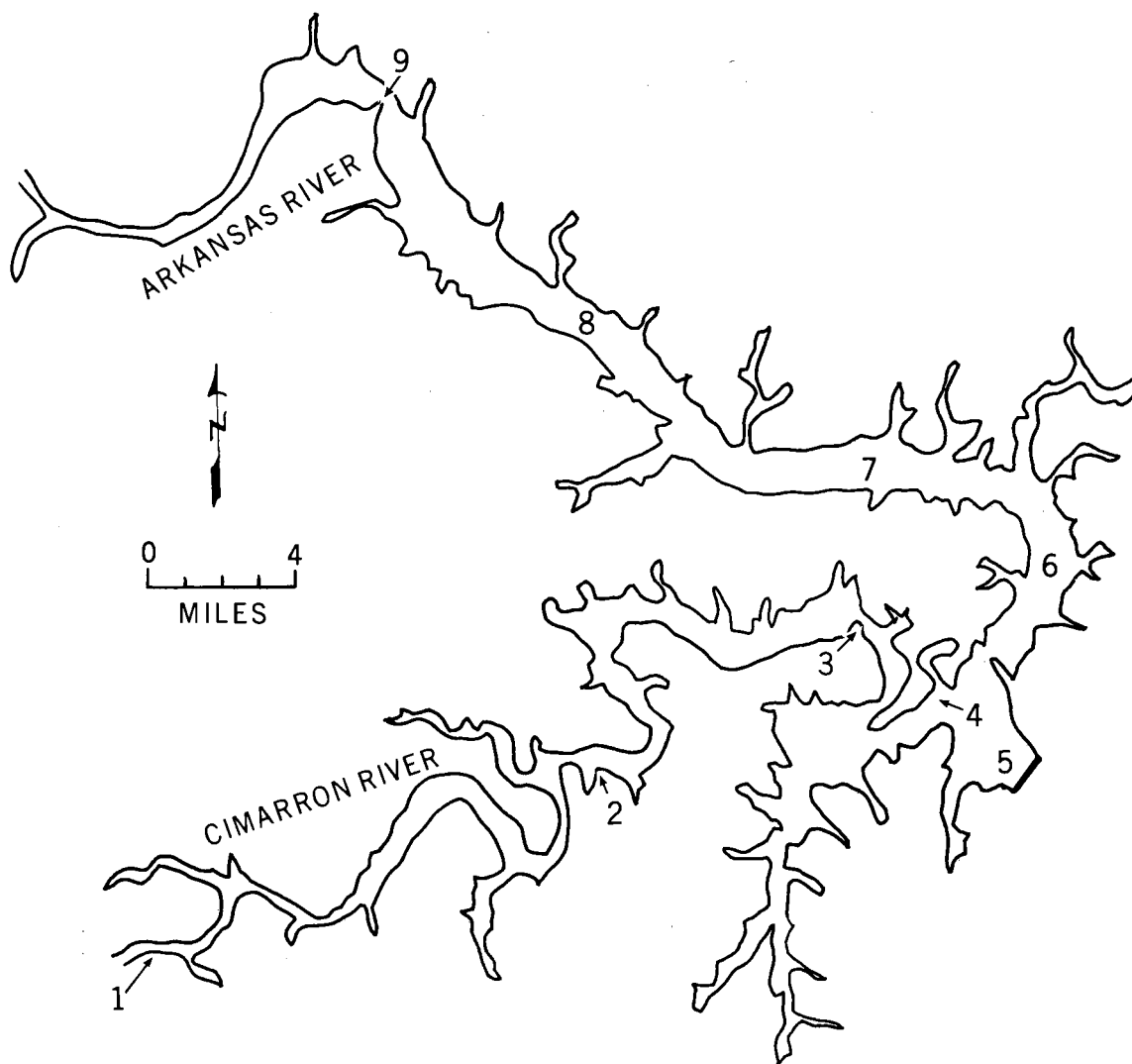


Figure 2. Keystone Reservoir, Oklahoma, and Collection Stations. Numbers indicate locations of sampling stations.

acre-feet per year.¹

The drainage area is in the path of warm, moist air masses moving northward from the Gulf of Mexico and of cold, dry air masses that move southward from the continental interior.^{2,3} The influence of air from the Gulf of Mexico is common, but the climate is essentially continental. During the winter months in Tulsa, low temperatures occasionally fall below zero but last only a short time. Temperatures of 100° F. or higher are frequently experienced from the latter part of July to early September in most of the area. Temperature changes are often rapid which is indicative of a continental climate. The air currents from the Gulf of Mexico bring most of the water supply. The western part of the drainage area receives some of its moisture from the Pacific Ocean, but its total annual rainfall in the west is lower. Spring is the wettest season with an abundance of rain in the form of showers and thunderstorms. Summers are generally dry and drought conditions are not uncommon. In the fall, the rains are generally more steady. The average rainfall varies from less than 16 inches in the west to over 30 inches in the east. There are notable variations in seasonal and annual rainfall.

The quality of the waters originating above Great Bend, Kansas, on the Arkansas River and the Kansas-Oklahoma state line on the Cimarron River is, in general, good. However, from these points to Keystone Reservoir, numerous sources of natural brine occur. The waters of the two rivers are degraded by these natural pollutants to such an extent that they are unsuitable for general municipal, industrial, and agricultural use.¹ This is a detriment to the

to the economic growth of the area and the need for control will become more acute as future water demands develop.

Surveys by the U.S. Public Health Service, U.S. Geological Survey, and U.S. Corps of Engineers have recently been focused on this area because of the adverse effect of the saline waters on the water supply of Oklahoma.^{4,5,6,7,8,9,10,11}

In northwest Oklahoma and central Kansas, rocks of the Permian age outcrop.¹² The geological sequence of the Permian strata consists of basal marine carbonate and shale overlain by four evaporite sequences which are separated by red shale, siltstone, and sandstone. The lower three evaporites consists of halite, anhydrite, and dolomite. Halite clearly dominates in parts of these sections and occurs in as much as 2,000 feet of strata. Some is almost pure rock salt 1,000 feet thick. The upper evaporite consists primarily of gypsum or gypsiferous shales.

Gypsum is frequently found at the surface or at shallow depths beneath shales. It also forms resistant cap-rocks which are conspicuous features in the area. Halite occurs at shallow depths below the surface as isolated crystals, in discontinuous shaley lenses, and in thin layers. Pure halite has been obtained from less than 30 feet below the surface from cores from the Flowerpot shale (Permian) at Big Salt Plain in northwestern Oklahoma.⁵ Numerous salt water springs containing as much as 200,000 ppm chloride, which appear to be saturated with halite,⁷ salt plains, salt water seeps, and salt marshes occur in these areas.

Gypsum is relatively soluble and is readily available to surface and ground waters. Under favorable geological conditions,

fresh water circulates downward through the salt-bearing beds and dissolves large quantities of the halite as well as gypsum. Ground water can circulate to depths greater than 1,000 feet, and they can flow many miles laterally and ultimately emerge as salt springs.¹³ However, in much of this area, a shallow, local hydraulic system appears to control the springs.⁷

Salt waters flowing from these springs saturate the valley alluvium along the rivers and streams, and evaporation from the surface during dry weather produces a thin crust of salt. This produces salt plains. These dissolve during rains but quickly reform after the rains stop. Numerous sinkholes in these areas have been attributed to the solution of halite and gypsum beneath the surface by groundwater and then the subsidence of the overlying rocks.

The major local sources of dissolved solids entering the two rivers have been identified by the combined study of the Corps of Engineers, the Public Health Service, and the Geological Survey. Of the natural pollutants that flow past Tulsa, about 70% originate from five major sources. These are illustrated in Table I and Figure 1.

There is major oil and gas production in this area, and it has drawn considerable attention as a probable source of pollution. There are instances of severe oil-field brine pollution. For example, in the vicinity of Seminole County, Oklahoma, near the area considered in this study, about 26 million barrels of oil-field brine were dumped into the Little River in 1956.¹ This often made the river more salty than sea water. However, pollution control agencies in Oklahoma and Kansas have been quoted as reporting that about 95% of

TABLE I
LOCATION OF AREAS OF NATURAL BRINE EMISSION

Map Index ^a	Location Name	Description
1	Great Salt Plains, Okla.	10,000-acre salt flat immediately above Great Salt Plains Reservoir; saturated brine about 1½ ft. below ground surface at edge of salt flat. Brine may flow on surface at edges of reservoir and into reservoir underwater.
2	Big Salt Plains, Okla.	About 4-mi. stretch of Cimarron River (1 mi. along Buffalo Creek). Densely encrusted salt plains up to 2-mi. wide. Numerous small springs and seeps (less than 5 gpm). Substantial surface flows of brine at lower end of area.
3	Little Salt Plains, Okla.	Similar to Area 2. Plain about 2-mi. long, and up to 1-mi. wide.
4	Salt Creek, Okla.	Numerous small brine springs at base of 300-ft. canyon at upper end of creek.
5	Rattlesnake Creek, Kan.	Numerous small seeps into two salt water marshes and along bed of Rattlesnake Creek.

^aSee Figure 1

the brine resulting from petroleum production is injected into producing formations.¹⁰ Apparently, man-made pollutants can have a drastic influence in localized areas; but the rocks and minerals that the waters come into contact with appear to be the dominant factor which determines the overall composition of these waters.

The average volume of water from the Cimarron River is generally less than 1/5 that of the Arkansas River, but it is more than four times as concentrated with dissolved solids.¹ The Arkansas River water is more dilute since the waters it drains from the geographic area of the Permian outcrop are more diluted by relatively good quality water from Colorado and western Kansas. The waters entering Keystone Reservoir from both rivers vary in both quantity and quality. For example, during a flood on May 21, 1957, prior to construction of the dam, 235,000 cubic feet per second (cfs) flows occurred at Tulsa. Less than a year earlier, on October 12, 1956, a flow of 27 cfs was recorded.¹ The dissolved solids in the Arkansas River near Tulsa before the dam was built varied from less than 250 parts per million (ppm) to over 13,500 ppm.¹⁴

Previous Studies of Keystone Reservoir

Since June, 1965, the Reservoir Research Center of Oklahoma State University has maintained an active research program centered on the effect of industrial and domestic effluents on the biology of Keystone Reservoir. Their studies, including physicochemical measurements such as temperature, conductivity, pH alkalinity, carbon dioxide, oxygen, turbidity, and light penetration at one or two meter depth intervals from top to bottom at four stations along the Cimarron arm,

are available.¹⁵ The U.S. Geological Survey made surveys at about 30 transects which included both arms during 1965-66.¹⁶ Their data included temperature, specific conductivity, hardness, turbidity, dissolved solids, and the concentrations of oxygen, silica, iron, manganese, sodium, bicarbonate, carbonate, sulfate, chloride, nitrate, and phosphate.

Until June, 1965, water was released primarily from the lower layers of the reservoir. Due to the bad odor of this water, surface water was released from June, 1965, until July, 1966, except during floods. During this time, the more saline, dense water from the Cimarron River underflowed the stored fresher water originating primarily from the Arkansas River, sank to its stable density level, and flowed as a density current considerable distances through the reservoir with a minimum amount of mixing.¹⁵ The dense waters accumulated in the bottom of the reservoir and backed up both arms. The resulting stratified system was maintained during all seasons except during floods in June and September, 1965, which flushed the reservoir. The stratification was quickly re-established after each flood.

The dense water which accumulated in the bottom of the reservoir was shut off from the atmosphere and became anoxic. The organic matter was oxidized anaerobically by the reduction of sulfate to sulfide; and high concentrations of carbon dioxide, hydrogen sulfide, organic matter, and probably other biologically active elements such as nitrogen and phosphorus accumulated in the stagnant bottom waters. The most severe conditions developed in July, 1966, when water as shallow as six meters became anoxic and numerous fish began dying.

Because of the severe buildup of stagnant water, a program to drain the hypolimnion was initiated in July, 1966. During the summer of 1966, waters discharged from the reservoir through the sluice gates contained high concentrations of hydrogen sulfide. This caused obnoxious odors, resulting in adverse public reaction, and caused discoloration of buildings and construction equipment. Sporadic fish kills were reported and were attributed to waters of high pH and waters containing high concentrations of ammonia. The high pH values were a result of the release of carbon dioxide and hydrogen sulfide from the aerated waters.

CHAPTER III

LITERATURE REVIEW

Relation of Impoundment to Water Quality

The effect of impoundment on the quality of natural water was recently treated in a comprehensive literature review by Symons, Weibel, and Robeck.¹⁷ Their treatment includes a systematic evaluation of the present research needs.

Impoundment may reduce turbidity, color, and coliform bacteria and even out sharp variations of flow and other properties. However, it may also reduce the dissolved oxygen concentration and increase algae growth, carbon dioxide, iron, manganese, alkalinity, and total dissolved solids. The causes of the detrimental effects can usually be attributed to the differences in the densities of the inflowing water and the stored water, evaporation, wind movements, dissolution and precipitation of mineral species, and biological activity.¹⁸

The processes occurring in new impoundments and the chemical and biological properties observed differ from those of stabilized impoundments.^{19,20} In general, the water quality improves with time. Usually, a minimum dissolved oxygen occurs the first years after the reservoir is filled. It then increases for several years as the effect of the newly submerged organic matter is offset and then stabilizes after about 10 years. Dissolved carbon dioxide and color

vary in an inverse manner. The rate of solution of inorganic minerals from the reservoir basin is generally initially high and decreases with time. For example, in Lake Mead from 1935 to 1950, the salinity of the outflowing water increased compared to the inflowing water. This was initially due to the dissolution of gypsum and halite in the lake basin. The effect decreased with time. Also, the solubility of many compounds found in natural water systems depends on the oxidation states of the elements. For example, compounds of iron (II) and manganese (II) are much more soluble in most natural water environments than compounds of iron (III) and manganese (IV). Due to this solubility, the dissolved iron and manganese concentrations are often abnormally high in anoxic waters or in waters with low oxygen concentrations. These abnormally high concentrations are quite frequently observed during the first few years in the life of new impoundments where corresponding low oxygen concentrations occur.

Thermal stratification of impoundments has been exhaustively treated in the literature;^{17,21a} however, chemical stratification, or layering of waters based on dissolved salts-induced density differences, has received little attention and is usually considered rare in water systems not connected to sea water systems. However, the possibility that chemical stratification can occur has been recognized for many years,²² and the phenomenon is usually the result of influent flows of much different salt content than that of the stored water.

Closely associated with stratified systems are density flows, which are streams of water that flow under, over, or through water of slightly different densities. Density currents which result from

the density differences caused by temperatures and sediment loads have been recognized for some time and have received considerable study.¹⁷ Salt induced density flows are common in sea water systems and estuaries; however, little is available concerning salt induced density currents in non-marine systems. Probably the best documented density flows are those in Lake Mead. These are reported to be temperature, salinity, and suspended matter induced density flows which are overflowing, interflowing, and underflowing and which change seasonally.²³

Eutrophication

Definition of Eutrophication

Limnologists have long recognized two classes of lakes based on the production of organic matter by the biological processes.²⁴ These are oligotrophic lakes, which have a low production of organic matter, and eutrophic lakes, which have a high production. The total production is the sum of all types, but the photosynthetic or primary production is considered the most important since zooplankton and other fauna are largely dependent on it. Although many factors such as temperature, solar radiation, and morphology of the lake basin are involved, this primary production is largely determined by the quality and quantity of nutrients available. Generally, sufficient quantities of carbon dioxide, vitamins, and all other nutrients except nitrogen and phosphorus are present to support luxuriant algae growths. Thus, as suggested by Liebig's Law of the Minimum,²⁵ nitrogen and phosphorus compounds are assumed to limit the fertility of a lake. This association between nutrients and production of

organic matter has prompted many aquatic scientists to use the amounts of nitrogen and phosphorus nutrients in the water system as the basis of oligotrophic and eutrophic classification.

All lakes are destined to be filled with soil and organic deposits even though the process may require eons of time. Young lakes are generally barren with respect to biological life and are oligotrophic. These young lakes, however, act as gathering basins for the waters of the drainage area, reaction pots for the various chemical and biological phenomena, and sedimentation basins for the suspended organic and inorganic matter. Therefore, only a fraction of the nutrients entering these lakes is removed directly in the effluent. Most of them are incorporated in the algae and other forms of life which eventually die and settle to the bottom. Here they are digested by bacteria, protozoa, and worms; and part of the nutrients are solubilized and are recycled to reinforce the production, while some of them remain in the sediments. The net result is that over the years there will be an accumulation of nutrients. With this enrichment, the overall production of organic carbon increases; and the lakes progress from oligotrophic to mesotrophic and finally to eutrophic conditions. This process will continue until the lake is filled to the extent that rooted plants take over and it becomes a marsh land. Then the lake is dead or extinct.

This aging process is an example of eutrophication, which can be defined as a long-term increase in the amount of organic matter in a lake. This means the production of organic matter exceeds that which can be oxidized by the respiration processes or removed by other means and that a net accumulation of living or dead organic matter

results. Due to its dependence on the plant nutrients, however, it is most frequently defined in terms of the rate at which nutrients enter the system.

The primary concern of most workers in this field is not the natural process but cultural or artificial eutrophication. This is the acceleration of the natural process and generally is caused by the increased influx of plant nutrients resulting from the activities of man. These fertilizers can cause an oligotrophic lake to become eutrophic in a few years and frequently cause very serious deteriorations of the water quality. In such lakes, nuisance blooms of algae have occurred which are unsightly and have taste and odors associated with them. Slime has developed on the beaches, several inches of floating scum have accumulated on the surface, and the turbidity has become quite high. Fish kills have occurred due to oxygen supersaturation resulting from high photosynthetic activity²⁶ or due to oxygen depletion resulting from the decay of the large mass of organic matter.²⁷ Hydrogen sulfide can form in the hypolimnion, which excludes fish and other forms of life from the cold bottom water and limits the overall population to warm water species. As a result, bathing, boating, water skiing, and other water sports are often postponed, industrial and municipal water use is hampered, and property values are frequently lowered.

Oligotrophic, eutrophic, and eutrophication are sometimes applied to rivers and streams. "Enrichment in streams" is not the same as eutrophication of lakes, however.²⁸ Due to their turbulence, streams can generally carry a high plankton load and the nuisance conditions do not develop readily. Also, the load of suspended

solids may be so high that algae cannot grow abundantly even though the water is polluted with growth-promoting materials. Nevertheless, many of the same problems often occur. These primarily result from the release of eutrophic lake water or localized pollution sources. For example, algae can accumulate in coves, flow in shallow streams can be restricted by the growth of rooted aquatics, and fish kills can occur due to abnormal oxygen concentrations.

The symptoms of eutrophication can be brought about by many factors which cause an imbalance in the natural biological cycle and thereby cause an accumulation of organic matter in the system. Some workers do not consider all of these processes as eutrophication, while others call them pseudoeutrophication or artificial eutrophication. In either case, these processes are so widely accepted as eutrophication that they must be included even if the original definition must be adjusted. Nevertheless, the undesirable deteriorations in the water quality have caused the concept of eutrophication to definitely be misinterpreted by many people. Rohlich²⁹ points out that it does not mean "cesspool" or is not synonymous with "pollution." Those who have studied it for several years define it as an aging or maturing process and relate it to the biological production of organic matter. Since the atmosphere, runoff, groundwater, and rain are adding nutrients, lakes will undergo eutrophication even if man is not around. Eutrophication may be a slow process which can be detected only after years of careful monitoring; or it may be an accelerated process, such as the transformation of an oligotrophic lake into an eutrophic lake within a few years due to artificial fertilizers or some factor which influences the biological

balance and causes organic matter to accumulate.

Parameters of Eutrophication

In the advanced stages of eutrophication, little scientific aid is required to determine what has happened. Visual observations and foul odors explain it fully. However, to detect cultural eutrophication in its early stages or to measure a slow natural process, intensive monitoring often must be carried out for many years.

The general properties of oligotrophic and eutrophic lakes are given in Table II. A large number of studies are reported in the literature where these properties are used to follow the course of eutrophication. Many of these were reviewed recently at the First International Symposium on Eutrophication.³⁰ One of the more complete studies is that of Lake Washington, Washington.³¹ Prior to 1946, this was a typical oligotrophic lake. As the population of metropolitan Seattle increased, there was an increase in the influx of purified sewage containing high concentrations of nitrogen and phosphorus plant nutrients. With this influx, the quantity of phytoplankton and zooplankton increased, unsightly algae blooms became frequent, and abundant growths of rooted aquatics developed along the shores. Although the production of organic matter increased, the number of different planktonic species decreased and the established species were replaced by new ones. The oxygen was depleted in the hypolimnion during the summer; and organic matter, plant nutrients, and carbon dioxide accumulated there. The overall water quality deteriorated to the extent that a costly project to divert the sewage around the lake to Puget Sound was undertaken.

TABLE II

GENERAL PROPERTIES OF OLIGOTROPHIC AND EUTROPHIC LAKES

<u>PROPERTY</u>	<u>OLIGOTROPHIC LAKES</u>	<u>EUTROPHIC LAKES</u>
Physical Characteristics	Deep, large volume, poor circulation, low temperature	Shallow, circulation effective in recycling nutrients, higher temperature
Turbidity	Low	High
Plant Nutrients	Low	High, accumulate in hypolimnion
Dissolved Oxygen	Abundant at all depths	Depleted in hypolimnion in summer or under ice
Dissolved and Particulate Organic Matter	Low	High
Total Dissolved Solids	Generally low	Variable but generally increases with aging
Primary Productivity	Low	High
Plankton		
Quantity	Poor	Rich
Variety	Many species	Few species
Distribution	To great depth	Trophogenic zone
Diurnal Migration	Extensive	Limited
Blooms	Very rare	Frequent
Indicator Species ^a (characteristic algae groups or genera)	Chlorophyceae Desmids <u>Staarastrum</u> Diatomaceae <u>Tabellaria</u> <u>Cyclotella</u> Chrysophyceae <u>Dinoboyon</u>	Cyanophyceae <u>Anabaena</u> <u>Aphanizomenon</u> <u>Microcystis</u> Diatomaceae <u>Melosira</u> <u>Fragilaria</u> <u>Stephanodiscus</u> <u>Asterionella</u>
Littoral Zone	Limited growth	Generally abundant growths of rooted aquatics

^aD. S. Rawson, Limnol. Oceanog. 1, 18 (1956).

The parameter of eutrophication most used by aquatic scientists is the standing crop of photosynthetic organisms. In general, this involves collecting a large number of samples at various depths and locations at periodic intervals, and concentrating, identifying, and enumerating the algae. As eutrophication progresses, the lakes will have a larger biomass but fewer and different species. This procedure is very expensive, since it is time consuming and requires highly trained personnel. For this reason, it is often estimated by some physical or chemical method. The primary physical methods include approximating the algae volumes or masses by filtering, centrifuging, or allowing the algae to settle out and measuring their weight or volume, and by transparency or turbidity measurements. Transparency, or turbidity, measurements can be obtained by various photoelectric devices. These must then be correlated with the plankton density. Classically, secchi disc transparency or simply visual observations have been used to follow biological production. The chemical methods measure the concentration of a chemical component of the biomass which, to be meaningful, is converted to algae volumes or algae masses. The plant pigments (chlorophylls) and particulate organic phosphorus, nitrogen, and carbon in the epilimnion are the chemical components most frequently measured.³²

The standing crop of zooplankton,³³ fish,³⁴ bottom fauna,³⁵ attached algae, and rooted aquatic plants have also been used to follow the course of eutrophication.

The primary productivity is a major link in the total production of organic matter and is frequently used as a parameter of eutrophication. This is usually determined by light and dark bottle techniques

by measuring the uptake of radioactive carbon or the production of oxygen or determined by following the change of the chemical composition of the natural water.

In an ideal oligotrophic lake, the oxygen is essentially uniform at all depths; while in a typical eutrophic lake during the growing season, it will be above or near saturation in the epilimnion, will decrease through the metalimnion, and will be depleted in the hypolimnion. This distribution is one of the major criteria Sawyer³⁶ uses in classifying lakes. He is sure the lake is eutrophic when it becomes anaerobic.

The rate of oxidative breakdown is dependent on the volume of organic matter available, generally the amount produced in the trophogenic zone. Hutchinson^{21b} defines the lake as oligotrophic if the rate of oxygen depletion in the hypolimnion is between .004 and .003 mg/day/cm² and as eutrophic if between .05 and .14 mg/day/cm². Rates between these limits were considered representative of mesotrophic lakes.

The production or consumption of carbon dioxide by the biological processes should vary inversely to that of oxygen. However, it is difficult to relate quantitatively to the biological activity since its distribution is dominated by the buffering effect of the carbonate system. Alkalinity and pH are widely used, however, to calculate or indicate its change.

In general, photosynthetic productivity is directly related to the concentrations of the phosphate and the inorganic nitrogen nutrients in the trophogenic zone, as long as other factors remain favorable.³⁷ At the time of the spring turnover, these nutrients should

be distributed almost equally at all depths; and only very small amounts of them will be tied up in living organic matter. Statistically, a unit of nitrogen or phosphorus should produce some given number of units of plankton. Thus, the plant nutrient content at this time should be a measure of the potential productivity. In eutrophic lakes, the spring bloom incorporates most of the surface nutrients into organic matter as the solar radiation and temperature increase and the water column becomes more stable. Much of this organic matter then sinks and accumulates in the hypolimnion and in the sediments, and some of the inorganic nutrients will be regenerated. A part of these regenerated nutrients are recycled into the epilimnion; and in some cases, the recycle processes alone can maintain abundant summer populations of phytoplankton. A fall bloom also can occur as the nutrients which have accumulated in the hypolimnion during the summer are mixed with the surface waters.

The use of the amount of nutrients present and their distribution in the natural water system to follow the production of organic matter can be complicated. Their uptake by the phytoplankton depends on the species, the nitrogen to phosphorus ratio, the recycle of nutrients, the nature of the nutrient sources, algae viruses,³⁸ toxins,³⁹ nutrients other than phosphorus and nitrogen,^{40,41} and a multitude of physical properties of the system. Nevertheless, these nutrients, primarily phosphate, are presently and will probably continue to be the parameter of cultural eutrophication.

Beeton⁴² used the conductivity and the concentrations of the major inorganic ions (Ca^{++} , Na^+ , K^+ , SO_4^- , and Cl^-) as a measure of eutrophication of the Great Lakes. Sawyer⁴³ has been quite critical

of using these properties since they are generally not significantly influenced by the biological activity, nor do they limit or promote biological activity in most natural water systems. However, high influxes of major inorganic ions are usually associated with high inputs of nutrients.

The number and variety of remains of biological species in lake sediments are dependent on the processes which have occurred in the overlying water column, and studies of these remains from sediment cores can provide a continuous history of the changes which have occurred for thousands of years.^{44,45} These types of studies indicate that the development of eutrophic conditions can be compared to a sigmoid growth curve for individual organisms and populations; however, man's activities can shorten the linear part of the typical curve to a relatively few years.

Chemical Testing Programs for Eutrophication

Scientists have not always agreed on a best way or a standard technique for measuring the capacity of a lake to grow algae or the tendency of chemicals to stimulate growth. Recently, a task force group was organized to develop a standardized procedure to determine algae growth potential which would be applicable to eutrophication studies.⁴⁶

Any testing program will be defined by the natural water system in question. There are several questions common to all studies, however. Some of these are considered below.

- What should be measured? There are many different measurements used to follow the course of eutrophication, since no single measurement

provides all the information needed to properly evaluate the inter-dependent effects of nutrients or other less defined ecological factors. According to the above discussion, the chemical and physical properties most obviously related to the biological production of organic matter and those most commonly measured are: dissolved oxygen, pH, alkalinity, O_2 -phosphate, total phosphate, ammonia, nitrate, nitrite, organic nitrogen, organic carbon, light penetration, temperature, and total dissolved solids.

Nutrients are important, but just as important as the absolute concentrations of nutrients are the physical characteristics of the water system which will promote the use and recycle of the nutrients by the biota. These include the geographic location of the lake, that is the climate, the vertical stability of the water column, the currents, the geological character of the lake bottom, the lake shore, and the drainage area, and the morphology of the lake basin such as the volume and the length, width, and depth ratios.

- When, how often, and where should the system be sampled?

Eutrophication is defined as a long-term effect and not the seasonal variation in productivity. This means careful measurement of several properties over a period of years is required. Most measurements are made periodically during the growing season. Nitrogen and phosphorus nutrients measured at the time of the spring turnover may be used in some systems.

In most cases, the occurrence of particular types of algae blooms and the sources of nutrients are of more interest than the actual rate of eutrophication. For example, the blue-green algae are considered as the nuisance algae. These appear rather late in the growing

season after other blooms have subsided and after the nitrogen is essentially used up. For these reasons, and because these are dynamic systems, a very large number of sampling locations with samples taken at frequent intervals are desirable.

• What analytical methods should be used? Standardized procedures are generally accepted for most chemical analyses.⁴⁷ These methods do have a number of possible errors associated with them and should be evaluated for the system before they are used. Lee⁴⁸ has recently pointed out some of the improper uses of these methods as well as some of the deficiencies of the tests.

Chemical Thermodynamics Applied to Natural Waters

The influence of chemical reactions in controlling the composition of natural waters has long been recognized. For example, over 100 years ago, Forchhammer⁴⁹ stated that the quantity of elements in sea water is not proportional to the quantity of elements which river water pours into the sea but is inversely proportional to the facility with which the elements of sea water are made insoluble by general chemical or organic-chemical actions in the sea. These actions are difficult to define and to express quantitatively, however, due to the complexity of nature. Only now are enough data beginning to accumulate to make rough predictions about the behavior of some of the simpler systems, and detailed interpretations of real water systems in terms of a modern treatment of the chemistry of aqueous solutions is a relatively new advent.

The formulation of equilibrium models based on the principles of classical chemical thermodynamics has become one of the more valuable

tools for providing some insight into the natural processes. Although thermodynamic principles have been applied to some extent for many years, it was not until Sillen⁵⁰ developed a comprehensive chemical equilibrium model of sea water in 1958 that their utility was fully recognized and the concept of the chemical equilibrium models popularized. Morgan⁵¹ has reviewed the applications and limitations of chemical thermodynamics to the complex natural water systems and describes the formulation of equilibrium models. Models of closed systems at constant temperature and pressure have been the most successful application of thermodynamic principles. These models are prepared by specifying the components and phases which are to model the real system, assuming these are in a state of chemical equilibrium and calculating the unknown composition variables using available thermodynamic data, such as free energies and stability constants.

Sillen's⁵⁰ sea water model was on a geological time scale and attempted to define the thermodynamically stable dissolved chemical constituents. His study was quickly followed by more rigorous quantitative models for generalized natural water systems. For example, Garrels and Thompson⁵² quantitatively evaluated the extent of ion pairing between the major inorganic ions in sea water, Kramer⁵³ and Holland⁵⁴ formulated equilibrium models in their discussions of the history of sea water, and Sillen^{55,56} later formulated more advanced models for sea water.

Generalized fresh water models have been developed by Stumm⁵⁷ and Stumm and Leckie^{58,59} which compare well with the average terrestrial waters. Kramer^{60,61} has developed a series of equilibrium

models for the Great Lakes in a study of the chemical changes that have occurred during the past few decades and their relation to the increased population of the Lakes' shores. His primary purpose was to calculate the upper concentration limits of the fresh water components resulting from natural processes, to calculate the degree of pollution by comparing the actual system with the natural process suggested by the model, and to determine the upper limits due to both the natural and pollution processes. The later models were dynamic models where the temperature and partial pressure of carbon dioxide were varied.

The variables most often considered in these general models were the concentrations of dissolved silica, calcium, magnesium, sodium, potassium, sulfate, chloride, and bicarbonate ions, temperature, and pressure; although other variables, such as strontium, fluoride, phosphate, aluminum, and the transition metals concentrations were qualitatively or quantitatively considered in some studies.

Buffer Capacity of Natural Water Systems

Several important features of natural water systems were suggested by these generalized models. Among other things, Sillen⁵⁰ noted that the buffer capacity of the dissolved carbonates ($\text{CO}_2\text{-H}_2\text{CO}_3\text{-HCO}_3^- \text{-CO}_3^{=}$) was not very large while that of the fine grain silicate minerals, especially clays, was much higher. He doubted the commonly held view that the dissolved carbonate equilibrium controlled the pH of sea water. Equilibrium with these clays could also buffer the concentrations of dissolved silica and many of the major cations.

Dissolved carbonates, which seldom exceed a few millimoles per liter, are inadequate to maintain the relatively narrow range of pH values observed in naturally occurring bodies of water of significant size. That additional buffering action must be contributed by numerous other chemical, physical, and biological activities was confirmed by numerous other experimental and theoretical evaluations.^{51,54,61-64} These evaluations suggest that the dissolved carbonate system may be a mediator and a quite good and reliable indicator of the total buffer systems; but it is not the sole, or even the principal, buffering agent.

Many of the individual capacity contributors, whose sum is the total buffer capacity, were evaluated.⁶² The dissolved acid-base pairs present, such as those represented by ammonia, phosphate, silicate, organic acids, and borates, were evaluated as not being very important compared to even the dissolved carbonates. The heterogeneous physical, chemical, and biochemical processes, such as photosynthesis, biological respiration, aeration, and erosion and interactions of the mineral phases, were found to be potentially the most important. Many individual heterogeneous processes may exert a dominating influence in some isolated systems, even in the presence of other substances that are known buffers. For example, the redox processes can result in high pH values in systems where higher metal oxides act as oxidizers; or they can result in acid conditions when free oxygen is the oxidizer as in biological active environments where the decomposition of organic matter releases large amounts of carbon dioxide.^{65,66} However, the carbonate and silicate mineral interactions appear to offer the highest potential buffer capacity.

This type of treatment has been extended to the buffering of the concentrations of other constituents. However, the relative importance of the heterogeneous carbonate and silicate systems is not presently firmly established.

The equations describing the calcium carbonate equilibria were derived by van't Hoff as early as 1890, and the carbonate system has been the subject of many investigations since that time. Weber and Stumm^{62,63} have recently summarized the more pertinent data in a systematic treatment. Many of these studies, however, attach insufficient significance to the solid phases in the carbonate system.

The effect of the carbonate minerals in natural water systems was recently reviewed by Bricker and Garrels.⁶⁷ They illustrate that the carbonate systems are not as simple as was originally suggested. For example, the polymorphic forms of carbonate minerals found in nature, the reactions kinetics, the occurrence of soluble inorganic carbonate complexes, and the effect of the biota on the biologically active element carbon tend to complicate the system. Nevertheless, the high rate of reaction of water with carbonate minerals generally is accepted, and reasonable equilibrium calculations have been applied to natural waters. However, the carbonates can be important controls only of a few elements, such as calcium and magnesium, in typical systems.

The importance of the silicate system has been illustrated by several workers who concluded that the pH as well as several other important constituents in many natural water systems are actually controlled by reactions between stable or metastable silicate minerals and the waters in contact with them and that these reactions

are rapid enough to be in equilibrium or near-equilibrium with one or more solid phases at all times. They showed definitely that the silicates could no longer be neglected.

Chemical Weathering of Silicate Minerals

The largest portion of the studies of aluminum silicate minerals in natural waters is related to the weathering of the primary minerals. These studies have demonstrated in detail the reactions necessary to produce a given water. Field studies were made by Feth, Roberson, and Polzer⁶⁸ and Bricker, Godfrey, and Cleaves^{69,70} of the behavior of some common silicate minerals in the weathering environment and the effect of the water-silicate reactions on both the minerals and the resulting aqueous solution composition. They obtained geochemical balances of the dissolved and suspended constituents derived from rain, snow, and the rocks and mineralogical data in relation to the rock composition and their weathering products. A number of treatments are also available where equilibrium considerations (models) have been applied in conjunction with available chemical, geological, and physical observations.⁶⁷⁻⁷²

These studies suggest that the dissolved constituents in the waters result from the attack of soil waters containing high concentrations of carbon dioxide, thus with a low pH, on typical rock-forming aluminum silicate minerals, such as the feldspars, hornblende, and biotite. These primary minerals are unstable in the weathering environment and are altered to clay minerals plus a solution which is in steady state equilibrium with these minerals. Kaolinite ($H_4Al_2Si_2O_9$) is the stable weathering product in most primary weathering

environments. At areas of severe weathering, such as the drainage divides, equilibrium appears to exist in typical systems between gibbsite, kaolinite, and the solution which sets a lower limit of the dissolved silica of about two mg/l. When waters containing relatively high concentrations of cations and dissolved silica contact the primary minerals, such as the deeper circulating ground waters, montmorillonite may be the stable weathering product. These reactions appear to be relatively rapid and have been suggested to approach equilibrium with one or more solid phases at all times.

Quartz is the thermodynamic stable form of silica at the temperatures of terrestrial waters and is one of the more abundant minerals of rocks. Although the concentrations of dissolved silica in most fresh water systems are near that expected from equilibrium with quartz, laboratory experiments suggest quartz approaches solubility equilibrium only slowly. For example, quartz samples placed in water solutions show non-measurable dissolution after three years of exposure.⁷⁹ Likewise, the laboratory studies show that it does not precipitate readily.

The lower limit for most natural water conditions of dissolved silica is apparently determined by the conversion of kaolinite to gibbsite. The upper limit of dissolved silica appears to be determined by the equilibrium of kaolinite and montmorillonite. For example, as the waters acquire more cations and silica from various sources, they react with kaolinite to form other clays, which appear to be predominantly montmorillonite in most areas. The equilibrium between kaolinite, montmorillonite and the aqueous phase limits the

dissolved silica concentration of typical systems at about 60 mg/l. This also buffers the concentrations of the major cations.

Equilibria of Silicate Minerals in Sea Water

As the streams and rivers dump their dissolved and suspended load into the ocean, there arises the problem of disposal of the constituents in order to maintain the relative constant composition of the ocean. A series of studies^{64,74-77} has led to the suggestion that equilibrium with the aluminum silicate minerals may be the dominant process. A type of inverse weathering reaction in the ocean, or at least during early diagenesis before deposition and burial, has been suggested between dissolved silica, bicarbonate, cations, and degraded aluminum silicate minerals supplied to the ocean by terrestrial waters which fixes the dissolved silica, the alkali metal ions, and the pH of sea water.^{64,76,77} The cations, degraded aluminum silicates, and dissolved silica are incorporated into a cation-aluminum-silicate, and carbon dioxide and water are formed. These reactions can account for the disposal of the constituents brought into the ocean by streams, the occurrence of minerals in recent sediments, and the composition of sea water, while other suggested processes do not. The major objection to the proposal is the slowness of the reactions. Mackenzie and Garrels⁷⁴ and Mackenzie, et al.⁷⁵ however, have shown that the ocean water responds rapidly to the silicate minerals. They placed some common silicate minerals, kaolinite, chlorite, illite, muscovite, and montmorillonite, in sea water and observed that the silica concentration dissolved in sea water responded rapidly to the detrital silicates and that the

pH values tended to cluster around 7.8 for all minerals except for montmorillonite. They suggested the attainment of equilibrium and that montmorillonite was the stable aluminosilicate residue. It was also observed that the concentrations of the ions in sea water lie near that expected from equilibrium between kaolinite, montmorillonite, and the solution.

Oxidation-Reduction Equilibria

That real systems are dynamic systems and are not in true equilibrium is obvious. The equilibrium calculations can only provide boundary conditions toward which the systems must be proceeding. However, partial equilibria, those involving some but not all couples, are frequently approached even though total equilibria are not; and this is responsible for the success in the models noted above.

The most obvious states of non-equilibria are among the elements whose occurrence is affected by the biological activity, such as carbon, nitrogen, oxygen, sulfur, and phosphorus; and this activity is closely associated with oxidation and reduction reactions.^{78,79} In contrast to the solubility of acid-base equilibrium models, equilibrium oxidation-reduction models cannot be rigorously related to the real system. This is primarily because oxidation-reduction reactions are often slow, the reaction products are often controlled by kinetics, and because there is a continual cyclic input of solar energy. The solar energy can be converted into chemical energy by photosynthesis. This produces non-equilibrium concentrations of carbon, nitrogen, and sulfur compounds in a reduced oxidation state. All non-photosynthetic reactions, however, must release energy and will tend to

restore equilibrium. These chemical reactions are slow and are generally only noticeable when catalyzed by the biological activity. The overall effect is to produce significant gradients within the water column. Generally, the surface is far from equilibrium, while the biologically active soil water contact is much closer to equilibrium.

Morris and Stumm⁸⁰ have established such an equilibrium model and attempted to interpret, in a general way, the redox patterns observed in natural waters. In their treatment, water in equilibrium with atmospheric oxygen had a well-defined redox potential. At this potential, carbon, nitrogen and sulfur should exist in their highest oxidation state. Carbon should exist as CO_2 , HCO_3^- , or $\text{CO}_3^{=}$, nitrogen should be present as NO_3^- , and sulfur as $\text{SO}_4^{=}$. Even the dissolved nitrogen gas (N_2) should be present largely as NO_3^- . Due to the conversion of solar energy into chemical energy by the photosynthetic processes, however, much of these elements exist in nature in their reduced state, mainly in organic compounds.

When the energy source is removed, for example, by the sinking of the organic matter, the non-photosynthetic processes tend to restore equilibrium by catalyzing reactions releasing energy. In a closed system containing organic material, for example carbohydrates, oxidation will occur first by reduction of dissolved oxygen. As the oxygen concentration decreases, the redox potential changes accordingly. The reduction of dissolved oxygen will be followed by a reduction of nitrate to nitrite. If MnO_2 is present, it will be reduced at about the same potential. Reduction of FeOOH to Fe(II) should occur next. As the oxidation potential is further increased,

CO_2 would be reduced to methane and SO_4^{--} to HS^- . Then ammonification should occur. This sequence is that which is observed in a vertical section of a well-eutrophied lake. In general, they found that all reactions considered, except those involving N_2 , were sufficiently biologically mediated so that they tended to occur in the order of their thermodynamic potential.

Equilibria in the Solution Phase

In considering equilibria in natural water systems, the data used in the thermodynamic equations and the results obtained are activities. Presently, comparison of the models with the real systems requires translation to and from analytical concentrations and activities. This requires a means to evaluate the activity coefficients and to evaluate the degree of ion-pairing within the aqueous phase.

Garrels and Thompson⁵² have also pointed out that the manner of presentation of the results of chemical analyses of natural waters implicitly reflects the theories concerning the nature of salt solutions. For example, older analyses were presented in terms of the individual salts such as NaCl , CaCl_2 , and Na_2SO_4 . Because of the development of the concept of complete dissociation of strong electrolyte and of partially dissociated or undissociated chemical species, most analyses are presently reported in terms of simple ions such as Na^+ , Ca^{++} , Cl^- , and SO_4^{--} and such species as HCO_3^- , CO_3^{--} , and H_3BO_3 . The analytical report lists dissolved species currently accepted as being present in the natural water systems and approximates, in a rough manner, a chemical model of the solution phase of the system.

Studies of natural waters using chemical thermodynamics illustrate many more dissolved chemical species must be present than are listed in the classical chemical analysis. This is summarized in a recent treatment of the coordination chemistry of sea water by Martin.⁸¹ The most obvious species are the ion pairs formed from the major components. There is also considerable thermodynamic data available concerning these complexes, such as the compilation by Sillen and Martell.⁸²

Garrels and co-workers^{52,83a} have considered these associations as well as activities in their model of the distribution of major dissolved species in sea water. These were calculated from the analytical concentrations using stability constants and estimates of the activity coefficients. The essential validity of their calculations has been shown by a number of independent methods.^{52,84-89}

In fresh water systems, it is generally assumed that the activity is equivalent to the concentration. Hem,⁹⁰ however, sets a practical limit for this assumption as 500 to 800 ppm total dissolved solids. This will vary, however, with the degree of accuracy required and the water type. He emphasized the importance of using activities in studies of natural waters and prepared a nomogram to simplify the computation of activity from measured concentrations. He did not consider ion pairing.

Sillen⁹¹ has pointed out the advantages of using the ionic medium activity scale in sea water. In natural systems where the ionic strengths are such that the common approximations formulas can be used with some confidence, the infinite dilution activity

scale is advantageous. For ionic strengths found in most fresh water systems, the Debye-Hückel equation⁹² is sufficiently accurate.

CHAPTER IV

EXPERIMENTAL PROCEDURES AND DESCRIPTION OF DATA

General Description

Chemical and physical properties of the reservoir were observed periodically from May, 1966, to May, 1967, and monthly from May, 1967, to June, 1968. The location of the sample stations are shown in Figure 2. The analyses of water samples include the total analytical concentrations of the major inorganic constituents, the concentrations of the free ions and the complex bound components, their activities, and related physical properties. These properties are listed in Table III.

Samples of sediments were obtained in the fall of 1966 at a cross section below the convergence of the two rivers. The results of x-ray diffraction studies and analyses for trace metals on these sediments and suspended solids samples are reported.

Analysis of Water Samples

Most of the methods used were similar in substance to those in APHA Standard Methods,⁴⁷ ASTM Manual on Industrial Waters,⁹³ and USGS Water-Supply Paper 1454.⁹⁴

Until September, 1967, all samples were taken by means of a G.M. Manufacturing Company two-liter, clear plastic water sampler.

TABLE III

CHEMICAL AND PHYSICAL PROPERTIES INCLUDED IN THE WATER ANALYSIS

Ca^{++}	CaSO_4°	Cl^-	O_2	Temperature
Mg^{++}	MgSO_4°	SO_4^{--}	H_2S	Suspended Solids
Na^+	CaCO_3°	HCO_3^-	CO_2	Dissolved Solids
K^+	MgCO_3°	CO_3^{--}		Total Calcium
Sr^{++}	NaHCO_3°	NaSO_4^-		Total Magnesium
CaHCO_3^+	$\text{H}_4\text{SiO}_4^{\circ}$	KSO_4^-		Total Sodium
MgHCO_3^+	$\text{H}_2\text{CO}_3^{\circ}$	NaCO_3^-		Total Potassium
H^+ (pH)		F^-		Total Bicarbonate
MgF^+		H_3SiO_4^-		Total Carbonate
		HS^-		Total Sulfate
		S^{--}		Total Fluoride
				Total Silicon
				Total Sulfide

The remaining samples were taken using a modified Kemmerer water bottle. The samples were stored in polypropylene or polyethylene bottles until analyzed.

Temperature was measured in situ using either a Yellow Springs telethermometer or an Industrial Instruments RB Solu-bridge except in May and July, 1967. Due to mechanical failures, May and July temperatures were estimated with a mercury thermometer as soon as the samples were brought to the surface.

Specific conductance was measured in situ as micromhos at 25° C. with an Industrial Instruments RB Solu-Bridge in August, October, and November, 1966, and August, September, and October, 1967. The remaining values were obtained in the laboratory at 25° C. with an Industrial Instruments RC-1B conductivity meter equipped with a dip-type conductivity cell.

Suspended matter was determined using the gravimetric method developed by Bansé, Falls, and Hobson.⁹⁵

The pH was determined at the time of sampling. A Beckman Model G pH meter was used for samples taken until September, 1967. The remaining values were measured using a Hellige comparator.

Dissolved oxygen was determined using the Alsterberg (Azide) modification of the Winkler method on samples taken until September, 1967; and the remaining values were obtained in situ using a Precision Scientific galvanic cell oxygen analyser.

Sulfide was determined by a colorimetric methylene blue method. The samples were preserved in the field using a zinc acetate-sodium carbonate solution and were analyzed in the laboratory as soon as was practical.

Chloride determinations were by silver nitrate titration using a Sargent-Malmstadt Automatic Potentiometric Titrator and a potentiometric end point.

Sulfate was determined by a turbidity method.

Bicarbonate concentration was assumed to be equivalent to the bicarbonate alkalinity and was determined by titration with a strong acid. For samples taken in August, 1966, May, July, and August, 1967, and February and April, 1968, the end points were determined by the inflection points of the titration curves developed using a Sargent Model C Constant Rate Burette and a Sargent pH Recording Adapter connected to a Sargent SR Recorder. The end points for the remaining titrations were determined using color indicators (Phenolphthalein and methyl purple).

Sodium, potassium, strontium, and manganese were determined by atomic absorption spectrophotometric procedures using a Perkin-Elmer Model 303 spectrophotometer.^{96,97}

Silicon was determined by the molybdenum blue procedure.

Calcium and Magnesium were determined by the modified Standard Methods EDTA (ethylene diamine tetraacetic acid) titrations of Katz and Navone.⁹⁸ This modification permits the measurement of both calcium and magnesium with the same sample. A Sargent-Malmstadt Automatic Spectro/Electro Titrator was used for the titrations.

Fluoride was determined using a fluoride ion sensitive electrode.⁹⁹ The cell consisted of the fluoride sensitive electrode, the sample solution, and a saturated calomel electrode. The sample was compared with a standard solution of potassium fluoride

where the fluoride activity was calculated from the Debye-Hückel equation.⁹² No other correction was made for the liquid junction potential.

Iron analyses were based on the bathophenanthroline ferrous iron colored complex.^{100,101} All samples were filtered through a 0.45 μ membrane filter before analysis.

Calculation of the Concentrations and Activities of Individual Dissolved Chemical Components

Chemical Components Included in the Treatment

The concentrations of all chemical species which make up a percent or so of the total analytical concentration of the major components were determined from the total analytical concentrations, stability constants, and estimates of the activity coefficients. These species and the major components are listed in Table III. The evaluation of the available data from this system and from similar systems suggests that these components make up more than 99% of the dissolved solids.

Free ions and complexes involving these major components were included in the analyses if they exceeded one percent of the total concentration of that component. Some complexes may not have been included because of insufficient data to indicate their importance. There is no evidence of strong interactions of the cations with chloride. For example, NaCl° , CaCl^+ , MgCl^+ , SrCl^+ , and KCl° were evaluated as not occurring or occurring in insignificant amounts.¹⁰² No complexes between potassium and bicarbonate and carbonate are

indicated.¹⁰³ Also, associations of a higher degree than ion pairs, such as $\text{Ca}(\text{SO}_4)_2^{--}$ and $\text{Ca}(\text{OH})_2(\text{CO}_3)^{-4}$, were evaluated as non-contributing.⁵² The dissociation constants for the hydroxides, such as NaOH° , CaOH^+ , and MgOH^+ , are large; but at pH values below 8.5 their occurrence can be neglected.¹⁰²

If we accept that only those species listed in Table III occur in significant amounts in the solution, the total concentration of each component, which can be assumed to be equivalent to the analyzed value, can be expressed by the sum of the dissolved species. This is shown in Equations 1 through 10.

$$[\text{Total Ca}] = [\text{Ca}^{++}] + [\text{CaSO}_4^\circ] + [\text{CaCO}_3^\circ] + [\text{CaHCO}_3^-] \quad (1)$$

$$[\text{Total Mg}] = [\text{Mg}^{++}] + [\text{MgSO}_4^\circ] + [\text{MgCO}_3^\circ] + [\text{MgHCO}_3^-] + [\text{MgF}^+] \quad (2)$$

$$[\text{Total Na}] = [\text{Na}^+] + [\text{NaSO}_4^-] + [\text{NaCO}_3^-] + [\text{NaHCO}_3^\circ] \quad (3)$$

$$[\text{Total K}] = [\text{K}^+] + [\text{KSO}_4^-] \quad (4)$$

$$[\text{Total HCO}_3] = [\text{HCO}_3^-] + [\text{CaHCO}_3^+] + [\text{MgHCO}_3^+] + [\text{NaHCO}_3^\circ] \quad (5)$$

$$[\text{Total CO}_3] = [\text{CO}_3^{--}] + [\text{CaCO}_3^\circ] + [\text{MgCO}_3^\circ] + [\text{NaCO}_3^-] \quad (6)$$

$$[\text{Total SO}_4] = [\text{SO}_4^{--}] + [\text{CaSO}_4^\circ] + [\text{MgSO}_4^\circ] + [\text{NaSO}_4^-] + [\text{KSO}_4^-] \quad (7)$$

$$[\text{Total Si}] = [\text{H}_4\text{SiO}_4] + [\text{H}_3\text{SiO}_4^-] \quad (8)$$

$$[\text{Total F}] = [\text{F}^-] + [\text{MgF}^+] \quad (9)$$

$$[\text{Total Sulfide}] = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{--}] \quad (10)$$

Stability Constants and Estimates of Activity Coefficients

Stability constants vary with both temperature and pressure, or depth. Over the relatively narrow temperature range considered

in this study, van't Hoff's rule^{83b} provides a satisfactory measure of the variations with temperature; and the stability constants were expressed in this form where data were available. Some of the constants could not be evaluated with the available data as a function of temperature, and others appear not to be known accurately enough to merit correction. The effect of pressure appears to be insignificant over the depth range of the reservoir water. The constants used in the treatment of this data are listed in Table IV.

The activity coefficients of the uncharged species were taken as 1.0. They can be estimated by the expression:

$$\log f = k_m I \quad (28)$$

where k_m is the salting coefficient, f is the activity coefficient, and I is the ionic strength and is defined as:

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \quad (29)$$

where m is the molality and Z is the charge of the i -th ion in solution.^{104a} If the salting coefficient is compared to that of H_2CO_3 for ionic strengths found in Keystone Reservoir, the deviation from the value of 1.0 assumed is much less than one per cent.^{104b} Thus, there is little or no accuracy lost by approximating the activity coefficients for the uncharged species as 1.0.

The activity coefficients for the charged species were calculated using the Debye-Hückel equation:

$$-\log f = \frac{AZ^2 \sqrt{I}}{1 - \dot{a}B\sqrt{I}} \quad (30)$$

where A and B are constants characteristic of the solvent and \dot{a} is a

TABLE IV

EQUILIBRIUM REACTIONS AND STABILITY CONSTANTS INVOLVING THE DISSOLVED COMPONENTS

Equation Number	Reaction	Stability Constant, K =	Log K
11	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^{\#c}$	$\{\text{H}_2\text{CO}_3^{\#}\}/\{\text{CO}_2\}$	$- 540.0/T - 0.777^a$
12	$\text{HCO}_3^- + \text{H}^+ = \text{H}_2\text{CO}_3^{\circ}$	$\{\text{H}_2\text{CO}_3^{\circ}\}/\{\text{H}^+\}\{\text{HCO}_3^-\}$	$+ 630.0/T + 4.238^a$
13	$\text{CO}_3^{--} + \text{H}^+ = \text{HCO}_3^-$	$\{\text{HCO}_3^-\}/\{\text{H}^+\}\{\text{CO}_3^{--}\}$	$+ 860.0/T + 7.447^a$
14	$\text{Ca}^{++} + \text{HCO}_3^- = \text{CaHCO}_3^+$	$\{\text{CaHCO}_3^+\}/\{\text{Ca}^{++}\}\{\text{HCO}_3^-\}$	$+ 1.26^a$
15	$\text{Ca}^{++} + \text{CO}_3^{--} = \text{CaCO}_3^{\circ}$	$\{\text{CaCO}_3^{\circ}\}/\{\text{Ca}^{++}\}\{\text{CO}_3^{--}\}$	$+ 3.20^a$
16	$\text{Mg}^{++} + \text{HCO}_3^- = \text{MgHCO}_3^+$	$\{\text{MgHCO}_3^+\}/\{\text{Mg}^{++}\}\{\text{HCO}_3^-\}$	$+ 1.16^a$
17	$\text{Mg}^{++} + \text{CO}_3^{--} = \text{MgCO}_3^{\circ}$	$\{\text{MgCO}_3^{\circ}\}/\{\text{Mg}^{++}\}\{\text{CO}_3^{--}\}$	$+ 3.40^a$
18	$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3^{\circ}$	$\{\text{NaHCO}_3^{\circ}\}/\{\text{Na}^+\}\{\text{HCO}_3^-\}$	$- 0.25^a$
19	$\text{Na}^+ + \text{CO}_3^{--} = \text{NaCO}_3^-$	$\{\text{NaCO}_3^-\}/\{\text{Na}^+\}\{\text{CO}_3^{--}\}$	$+ 1.27^a$
20	$\text{Ca}^{++} + \text{SO}_4^{--} = \text{CaSO}_4^{\circ}$	$\{\text{CaSO}_4^{\circ}\}/\{\text{Ca}^{++}\}\{\text{SO}_4^{--}\}$	$- 292.7/T + 3.288^a$
21	$\text{Mg}^{++} + \text{SO}_4^{--} = \text{MgSO}_4^{\circ}$	$\{\text{MgSO}_4^{\circ}\}/\{\text{Mg}^{++}\}\{\text{SO}_4^{--}\}$	$- 1190.5/T + 6.350^a$
22	$\text{Na}^+ + \text{SO}_4^{--} = \text{NaSO}_4^-$	$\{\text{NaSO}_4^-\}/\{\text{Na}^+\}\{\text{SO}_4^{--}\}$	$+ 0.72^a$
23	$\text{K}^+ + \text{SO}_4^{--} = \text{KSO}_4^-$	$\{\text{KSO}_4^-\}/\{\text{K}^+\}\{\text{SO}_4^{--}\}$	$- 673.6/T + 3.106^b$
24	$\text{H}^+ + \text{HS}^- = \text{H}_2\text{S}$	$\{\text{H}_2\text{S}\}/\{\text{H}^+\}\{\text{HS}^-\}$	$+ 1500./T + 1.932^a$
25	$\text{H}^+ + \text{S}^{--} = \text{HS}^-$	$\{\text{HS}^-\}/\{\text{H}^+\}\{\text{S}^{--}\}$	$+ 1470./T + 7.911^a$
26	$\text{H}^+ + \text{H}_3\text{SiO}_4^- = \text{H}_4\text{SiO}_4^{\circ}$	$\{\text{H}_4\text{SiO}_4^{\circ}\}/\{\text{H}^+\}\{\text{H}_3\text{SiO}_4^-\}$	$+ 9.7^a$
27	$\text{Mg}^{++} + \text{F}^- = \text{MgF}^+$	$\{\text{MgF}^+\}/\{\text{Mg}^{++}\}\{\text{F}^-\}$	$+ 1.82^a$

^a Reference 82.^b P. B. Hostetler, A. H. Truesdell, and C. L. Christ, *Science* **155**, 1537 (1967).^c $\text{H}_2\text{CO}_3^{\#} = \text{true H}_2\text{CO}_3$; $[\text{H}_2\text{CO}_3] = [\text{CO}_2] + [\text{H}_2\text{CO}_3^{\#}]$

value dependent upon the effective diameter of the ion.⁹² The values of A and B were calculated from the expressions:

$$A = \frac{1.825 \times 10^6}{(\epsilon T)^{3/2}} \quad (31)$$

$$B = \frac{50.3 \times 10^8}{(\epsilon T)^{1/2}} \quad (32)$$

where T is the temperature in degree Kelvin and ϵ is the dielectric constant of the solvent and is given by

$$\epsilon = 87.740 - 0.40008t + 9.3980 \times 10^{-4}t^2 - 1.410 \times 10^{-6}t^3 \quad (33)$$

where t is the temperature in degree Centigrade.^{92,104} The values of \bar{a} are given in Table V and appear to not be influenced significantly by temperature.

The values of the ionic strength, I, will depend on the charged species only. In calculating the ionic strength from the analytical concentrations, the ionic strength was first estimated assuming that the total concentration is equal to the concentration of the free ion. These values were used to estimate the activity coefficients, which in turn were used to estimate the concentrations of the ionic components. These were then used to recalculate a new value for the ionic strength, and the process was repeated until a convergence tolerance was satisfied.

For the calculations, the molarity was taken as equivalent to the molality. In these solutions, the error is much less than one per cent.

The relationship between concentration and activity is defined by Equation 34.

TABLE V

VALUES OF THE EFFECTIVE RADIUS OF IONS

$\overset{\circ}{a}_1 \times 10^8$	ion
3.0	K^+ , Cl^- ^a
3.5	F^- , HS^- ^a
4.0	Na^+ , HCO_3^- , SO_4^{--} ^a All charged ion pairs ^b
4.5	CO_3^{--}
5.0	Sr^{++} , S^{--} ^a
6.0	Ca^{++} ^a
8.0	Mg^{++} ^a

^aI. M. Klotz, "Chemical Thermodynamics", Englewood Cliffs, New Jersey, Prentice-Hall, 1950, p. 331.

^bReference 52.

$$a = f c$$

(34)

Computation Technique

A computer program was written and used for the calculations. A flow sheet, listing of the program, and example output are given in Appendix A. A complete description of the sample and the measured physical and chemical properties are read into the program, the distribution of the major dissolved species is calculated, and the complete analytical description is listed in tabular form as the output.

With reference to Appendix A, the first phase of the program is the initialization step. The ion size parameters used in the Debye-Hückel equation, the activity coefficients of the uncharged chemical species, which are set equal to 1.0, the stability constants which are not expressed as a function of temperature, and the tolerance levels to be used in the iterative procedures are defined by constants. The parameters to be calculated are initialized. The data is then read. The order that they are read into the program is (1) the number of stations that were sampled on a given date, (2) the date they were sampled, (3) the station number of the first data set, (4) the number of depths sampled at that station, and (5) the data from the first sample at the corresponding station and depth. The sample data include the depth, temperature, conductivity, suspended solids, pH, oxygen, and the analytical concentrations of strontium, chloride, sulfide, sulfate, calcium, magnesium, sodium, potassium, and silica, and the activity of fluoride. The input data are read in units consistent with those of common usage. The stability constants,

the dielectric constant of water, and the Debye-Hückel constants A and B, all of which are expressed as a function of temperature, are calculated next. In the final initialization step, the concentrations and activity of the chemical components are converted to units of moles per liter (m/l).

In the first phase of the calculation part of the program, the ionic strength is approximated. As the first approximation, the free, non-paired ions are assumed to be the only components present in the solution and these are equal to the analytical concentrations. The ionic strength is then calculated using these ionic concentrations by Equation 29. These values are used to calculate the first estimate of the activity coefficients of the charged species (Equation 30). To simplify later calculations, these values of the activity coefficients are then used to calculate an apparent stability constant; that is, a stability constant that can be expressed in terms of concentrations rather than activities.

Using the above approximations, the concentrations of the ionic chemical species are calculated which are later used to correct the estimate of the ionic strength. In this calculation phase, a system of non-linear algebraic equations must be solved. These equations express the total concentrations in terms of the free ions and result from the substitution of the equations for the stability constants (Equations 11 through 27) into the equations for the mass balances (Equations 1 through 10). For example, these equations are of the form:

$$\begin{aligned}
 [\text{Total Ca}] = & [\text{Ca}^{+2}] \left(1 + (K'_{\text{CaHCO}_3^+} + \frac{K'_{\text{CaCO}_3^0}}{K'_{\text{HCO}_3^-} \{H^+\}}) [\text{HCO}_3^-] \right. \\
 & \left. + K'_{\text{CaSO}_4^0} [\text{SO}_4^{--}] \right)
 \end{aligned} \tag{35}$$

where the K' refers to the apparent stability constant and [component] refers to the concentration of the component.

Methods are not presently available for solving general systems of non-linear algebraic equations. However, for specified systems, solutions may exist. These solutions may be unique or not depending on the peculiarities of the given system. For the specific system of non-linear equations encountered in this study, solutions were readily obtained using Liebmann's approximation technique.¹⁰⁵ For this set of equations, the concentrations of the anions were assumed to be entirely uncomplexed, i.e. the concentrations of the anions were assumed to be equal to the analytical concentrations of the anions, the distributions of the chemical species were then calculated, and the original estimate was corrected in terms of the results obtained. The procedure was repeated until all equations were satisfied within a predetermined tolerance level.

These results are used to calculate the concentrations of the remaining charged species, which are then used to correct the original estimate of the ionic strength. The entire process is repeated until the ionic strength does not change between successive approximations.

Once these equations are solved, the remaining species concentration and activity can be calculated from Equations 1 through 34 in a straightforward, but tedious, manner. The concentration of the dissolved solids was calculated as being equal to the sum of the dissolved components. The total fluoride and total carbonate were calculated in the program from the mass balance equations (Equations 6 and 9).

The essential parts of the output are given in Appendix B.

Analyses of Sediment and Suspended Solids

Descriptions of the sediment samples, trace metal analyses, and total, organic, and inorganic carbon content are given in Appendix C. X-ray diffraction studies of selected sediment samples were also made. The minerals calcite, quartz, kaolinite, montmorillonite, and illite were found in all samples examined.

Similar x-ray diffraction analyses were made on samples of suspended solids separated by filtering the water samples through a 0.45 μ membrane filter. The solids were removed from the filters mechanically. Except for calcite, the same minerals were detected. Calcite was detected in none of the suspended solids samples.

Samples of sediments were obtained using a Pflager core sampler. A Norelco x-ray diffraction unit was used for the analyses and standard procedures were applied.^{106,107} Analyses of the clay minerals were on the two micron and smaller size fraction. Oriented samples prepared on glass slides and samples treated with ethylene glycol, in order to distinguish montmorillonite and illite, were used.

Analyses for the trace metals were obtained using a Baird-Atomic two meter, grating, emission spectrograph. A d-c arc excitation method and a photographic detection system were used. Standard clay samples obtained from the U.S. National Bureau of Standards and a Jarrel Ash Densitometer-comparator were used for quantitation.

Analyses for carbon were obtained using a Leco Carbon Analyzer equipped with a thermoconductivity-type detector. Distinction between

organic and inorganic carbon, or carbonates, was obtained by analyses of non-treated samples and samples treated with hydrochloric acid to remove the carbonates.

CHAPTER V

GENERAL PHYSICAL-CHEMICAL PROPERTIES OF KEYSTONE RESERVOIR

June, 1965, to June, 1966

During the period from June, 1965, to June, 1966, discharges from the reservoir were primarily from the epilimnion. Eley, Carter, and Dorris¹⁵ suggested that during this time, salt-heavy water from the Cimarron River underlaid the lighter water from the Arkansas River and accumulated in the bottom of the reservoir. The dense water was shut off from the atmosphere and it became anoxic. Hydrogen sulfide, carbon dioxide, and probably the nutrient elements, such as ammonia and phosphate, were produced by the anoxic oxidation of the organic matter and were trapped in the hypolimnion.

Complete analysis of only one sample was obtained during this period. This was the analysis of a sample taken at Station 4 at 20 meters just above the water-sediment interface on May 5, 1966. The results are illustrative of the extreme conditions of the anoxic hypolimnion. The dissolved solids were 5,240 mg/l, the sample was anoxic, had a strong odor of hydrogen sulfide, and had a pH of 7.8. For comparison, temperature, dissolved solids,* oxygen, and pH data from

*The dissolved solids were calculated from the expression:

$$\text{Dissolved solids} = .674 \times \text{Conductivity} + 24.0$$

which was derived from the data reported in this work. The relation between conductivity and dissolved solids is considered in the ASTM Manual, p. 115 (See Reference 93).

Eley¹⁰⁸ from the same station at approximately the same date are plotted in Figures 3, 4, 5, and 6.

One of the principle problems associated with the impoundment of natural water is eutrophication, and one of its more obvious symptoms is illustrated here by the anoxic conditions in the hypolimnion. The differences in the density of the inflowing waters from the two rivers and the reservoir management practices during this period dominate the general picture; but almost all new reservoirs require several years to stabilize. In the first few years, there is an abnormal consumption of oxygen due to the oxidation of the newly submerged vegetation. This could contribute significantly to the rapidity of the development of the eutrophication symptoms.

August, 1966

Because of the severe build-up of stagnant water in the reservoir, a program to drain the hypolimnion was initiated in July, 1966. Increasing amounts of bottom water were discharged from the reservoir until the total discharge was bottom water by August 2, 1966.

It was previously suggested that this release of bottom water reduced the stratification and allowed mixing to greater depths.¹⁵ Nevertheless, analyses of samples from Station 5 on August 20, 1966, show that although chemical stratification may have been reduced, the lake was still strongly stratified (Figures 3-6, Appendix B). A strong chemocline and thermocline occurred at about 12-14 meters. The water in the hypolimnion was anoxic, contained up to 7.5 mg/l hydrogen sulfide, had a low pH, and contained relatively larger amounts of dissolved carbon dioxide and total bicarbonate.

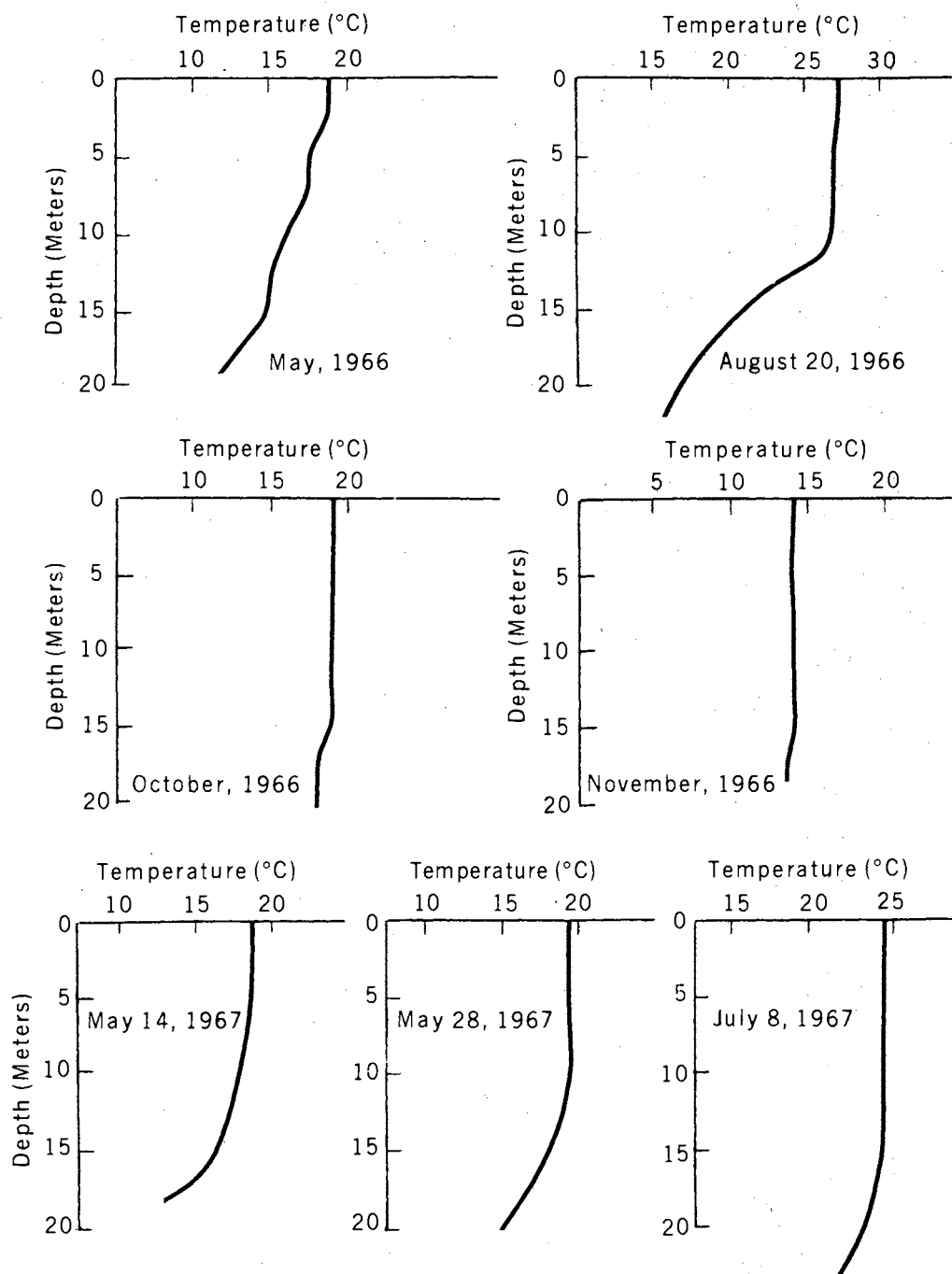


Figure 3. Temperature Profiles. Data for May, 1966 were derived from Eley, Reference 108.

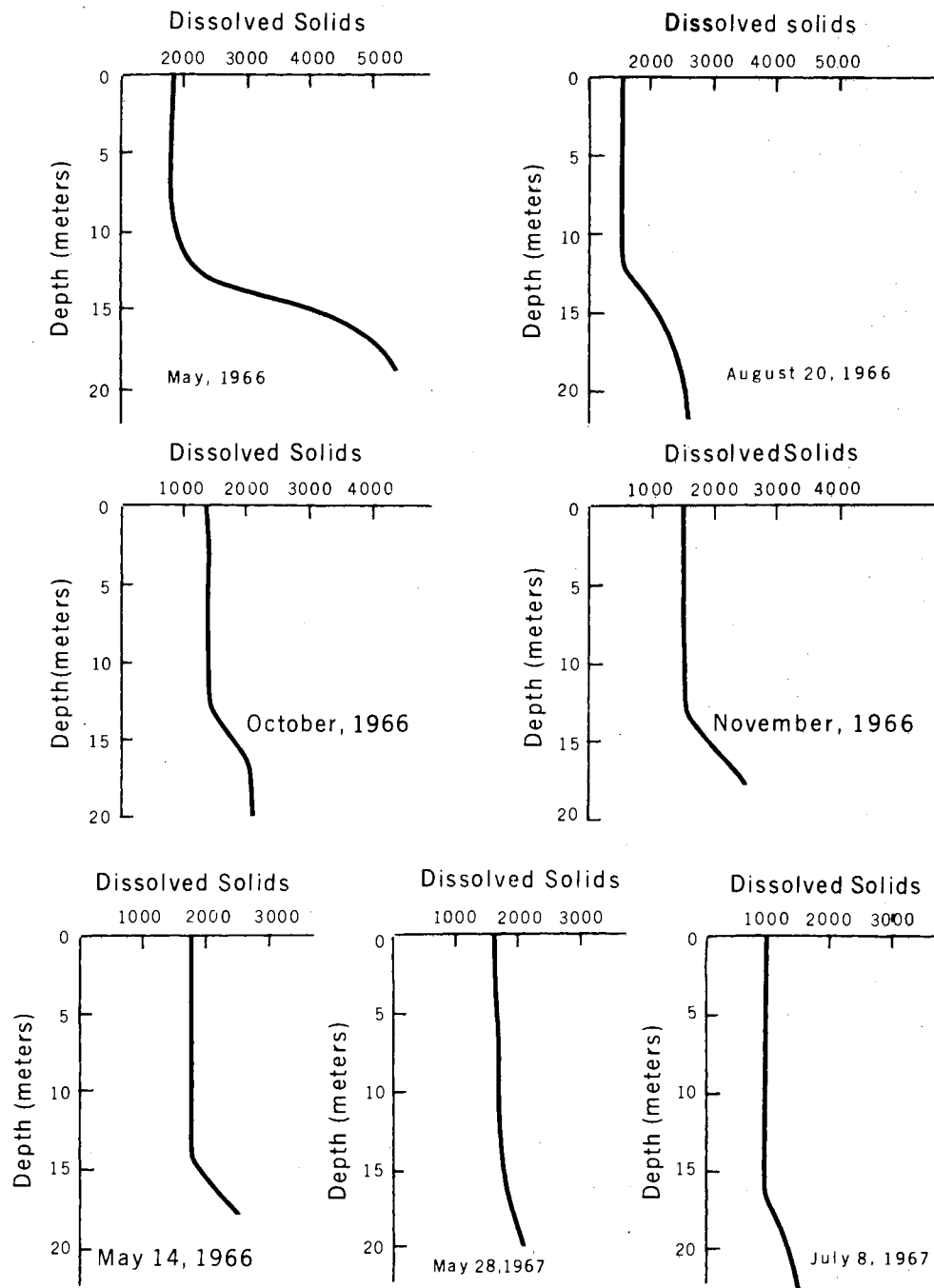


Figure 4. Dissolved Solids Profiles. Data for May, 1966 were from Eley, Reference 108. All values are mg/l.

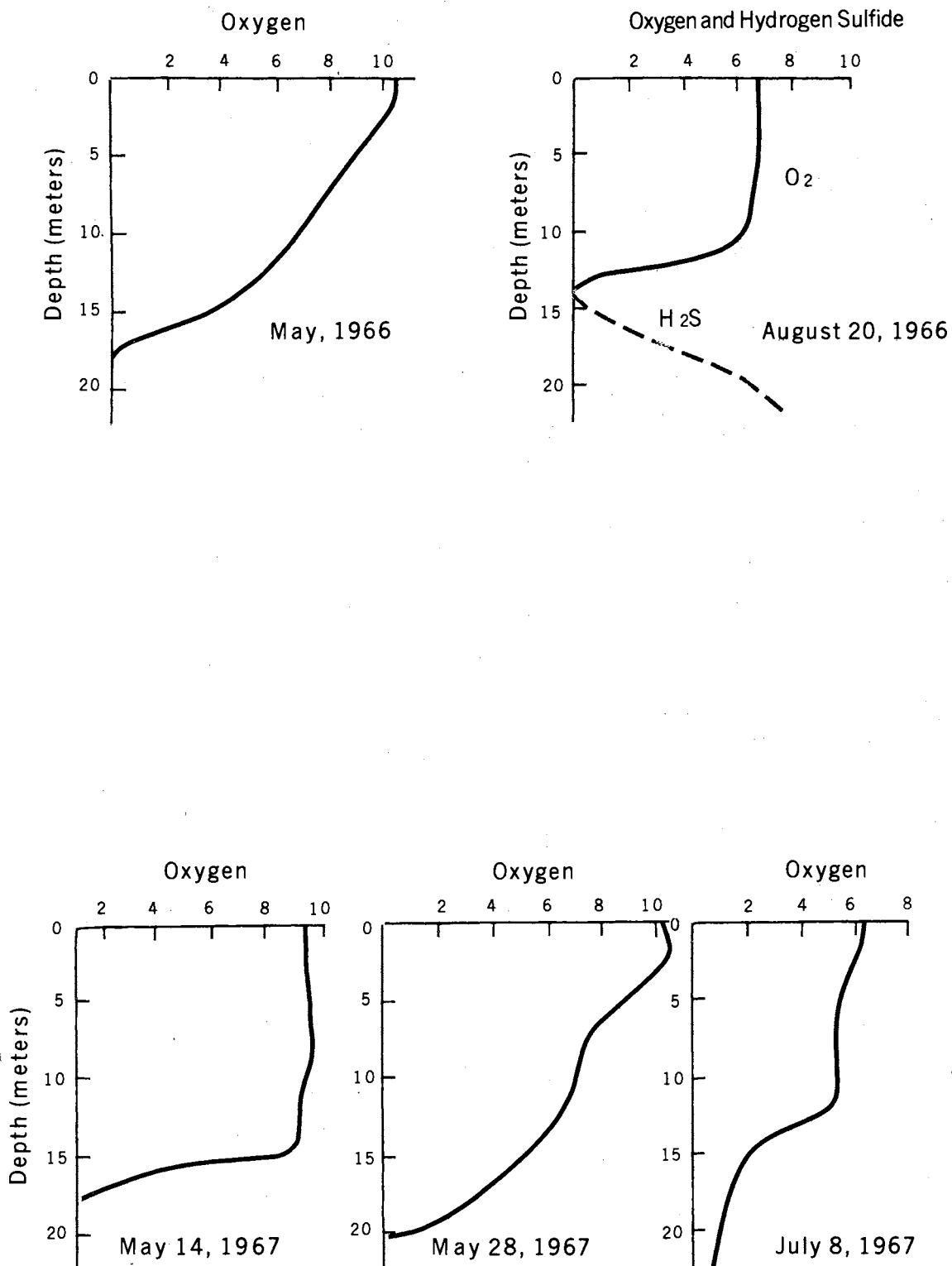


Figure 5. Oxygen and Hydrogen Sulfide Profiles. Data for May, 1966 from Eley, Reference 108. All values are mg/l.

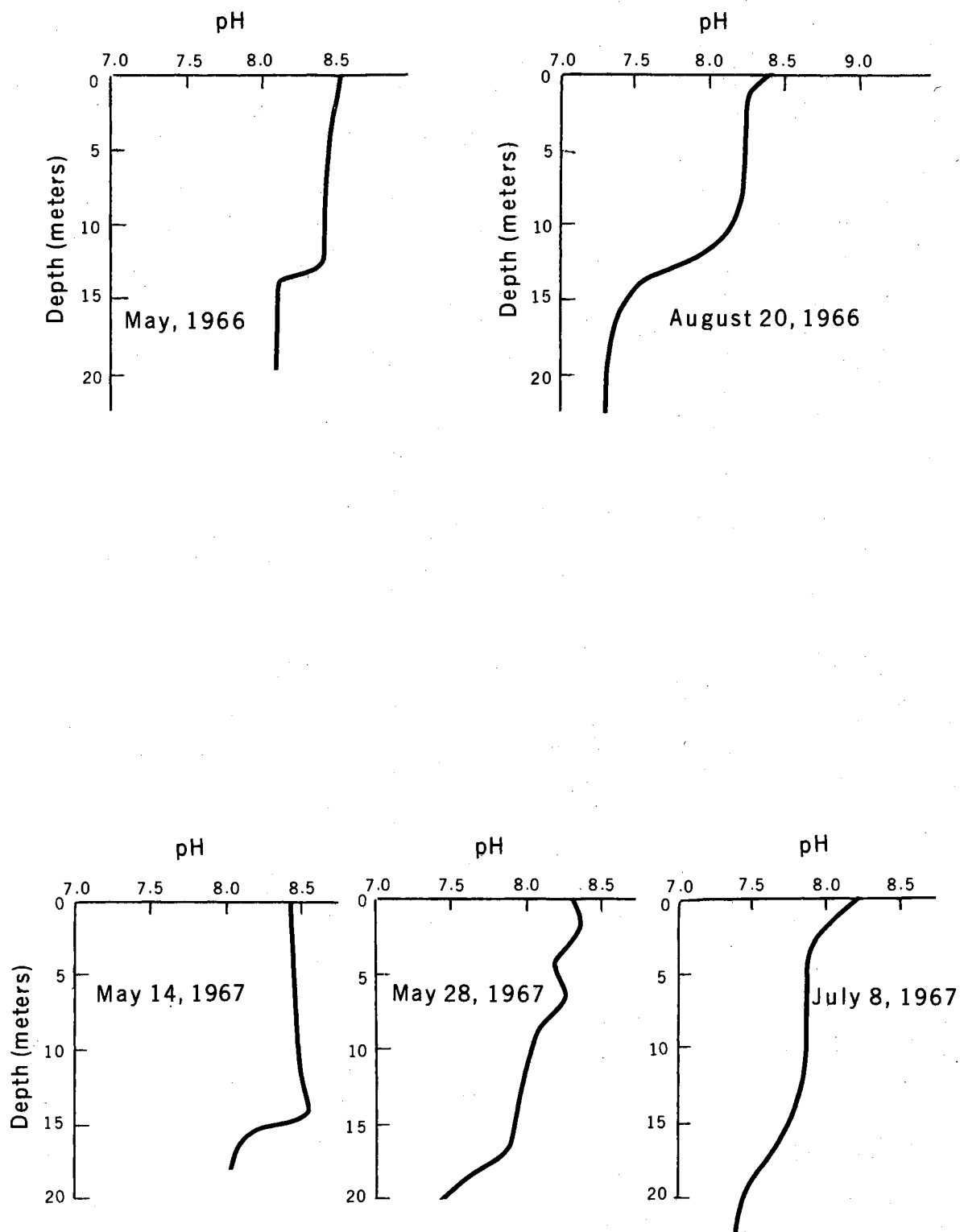


Figure 6. pH Profiles. Data for May, 1966 are from Eley, Reference 108.

Overall, the distribution of the major components resembled that of the dissolved solids. Components which are directly influenced by the oxidative breakdown in the hypolimnion, such as sulfate and carbonate, had different distributions in some cases. Iron and manganese were considerably higher in the hypolimnion, which was expected due to the greater solubility of these elements at increased oxidation potentials (Appendix B).

August, 1966, to June, 1968

From August, 1966, until the end of this study in June, 1968, release of water from the reservoir was almost entirely from the lower layers through the sluice gates or power penstocks.

That the Cimarron River water is consistently more dense than that from the Arkansas River and that this density difference is due to the dissolved solids has previously been shown.¹⁵ The average seasonal distribution of dissolved solids derived from monthly observations from June, 1967, to June, 1968, illustrated in Figure 7, clearly shows high concentrations of dissolved solids at the head and along the bottom of the Cimarron River arm. In general, the saline waters occur as a continuous layer. This suggests that the salt-heavy water from the Cimarron River underflowed the less dense stored water which originated primarily from the Arkansas River, flowed along the bottom with a minimum amount of mixing, and was released preferentially through the dam. Since the normal release from the reservoir far exceeds the average flow of the Cimarron River, the severe accumulation and stagnation of dense water previously observed was not expected or observed.

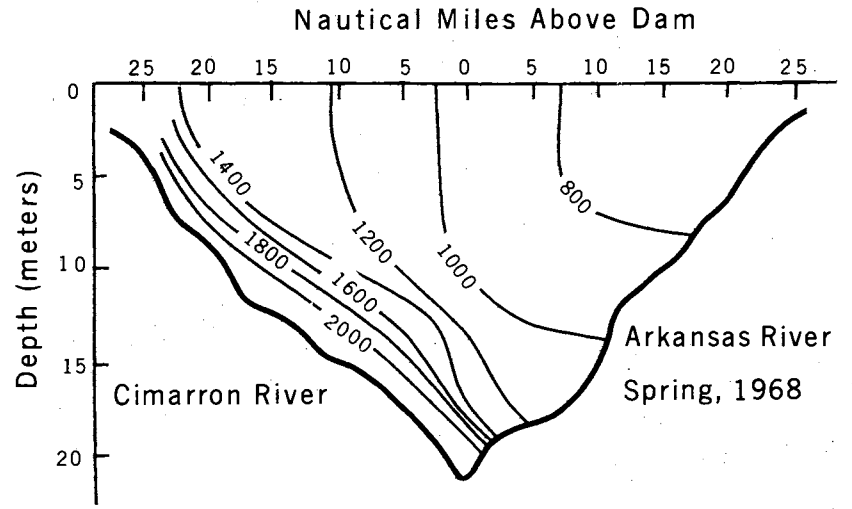
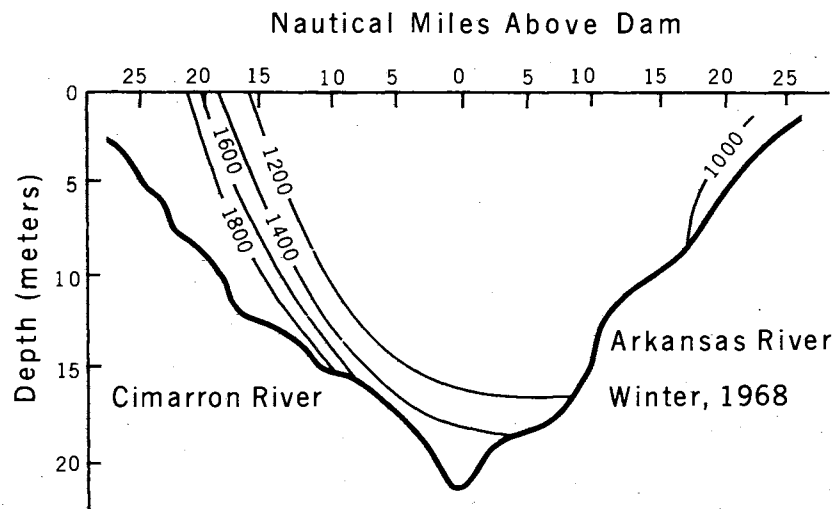
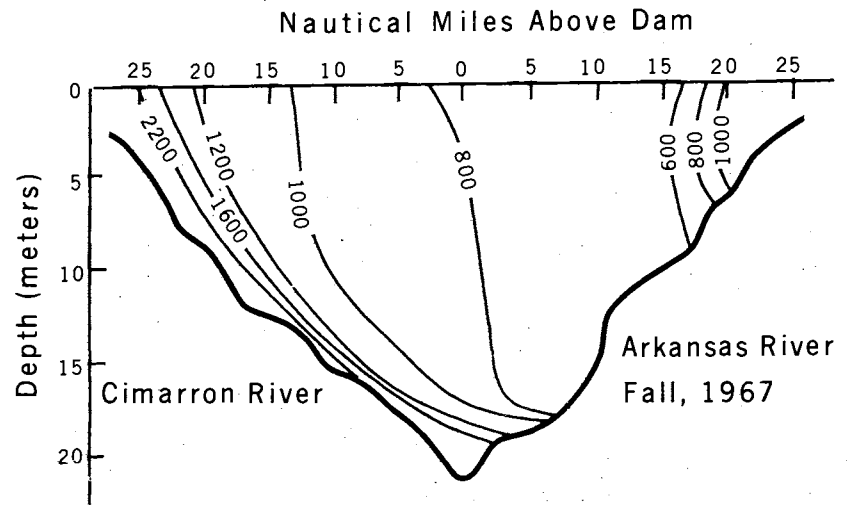
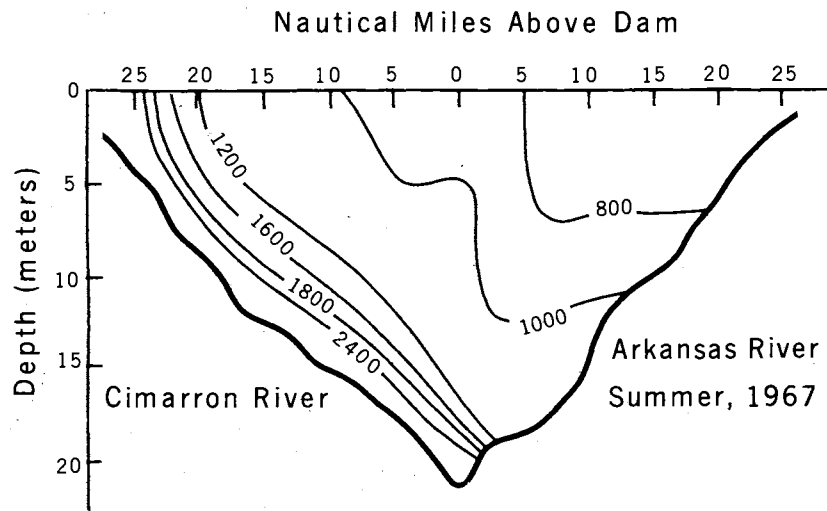


Figure 7. Seasonal Distributions of Dissolved Solids. All values are mg/l.

In the summer of 1967 and spring of 1968, water from the Arkansas River was more dilute than the stored water; while in the fall of 1967 and the winter of 1968, it was slightly more saline. The rainfall in the summer and fall, 1967, and winter and spring, 1968, was 51, 11, 5, and 33% of the total during this period.¹⁰⁹ This is illustrated in Figure 8 by a plot of the average biweekly flow into the reservoir against time. Waters with lower inflow rates are expected to be more saline. The lowering inflow rates from summer to winter and the suggested parallel increase in dissolved solids probably account for more saline waters at the head of the Arkansas arm. However, the increased salt content was apparently insignificant in creating persistent density currents similar to those in the Cimarron arm. Other forces acting on the waters, such as wind forces, would be expected to dominate the physical mixing and circulation.

Although complete sample data for both arms of the reservoir were not available from August, 1966, to May, 1967, samples at a single station, 5, for October, November, 1966, and May 14, May 28, and July 8, 1967, showed that the bottom water was consistently more saline (Figure 4). This could also be explained by the suggested bottom flowing density currents.

In most cases, the distribution of the major components was closely related to that of the total dissolved solids. As a whole, the reservoir was more dilute from June, 1967, to June, 1968, than for the preceding year. However, the concentrations of dissolved silica and fluoride were definitely higher.

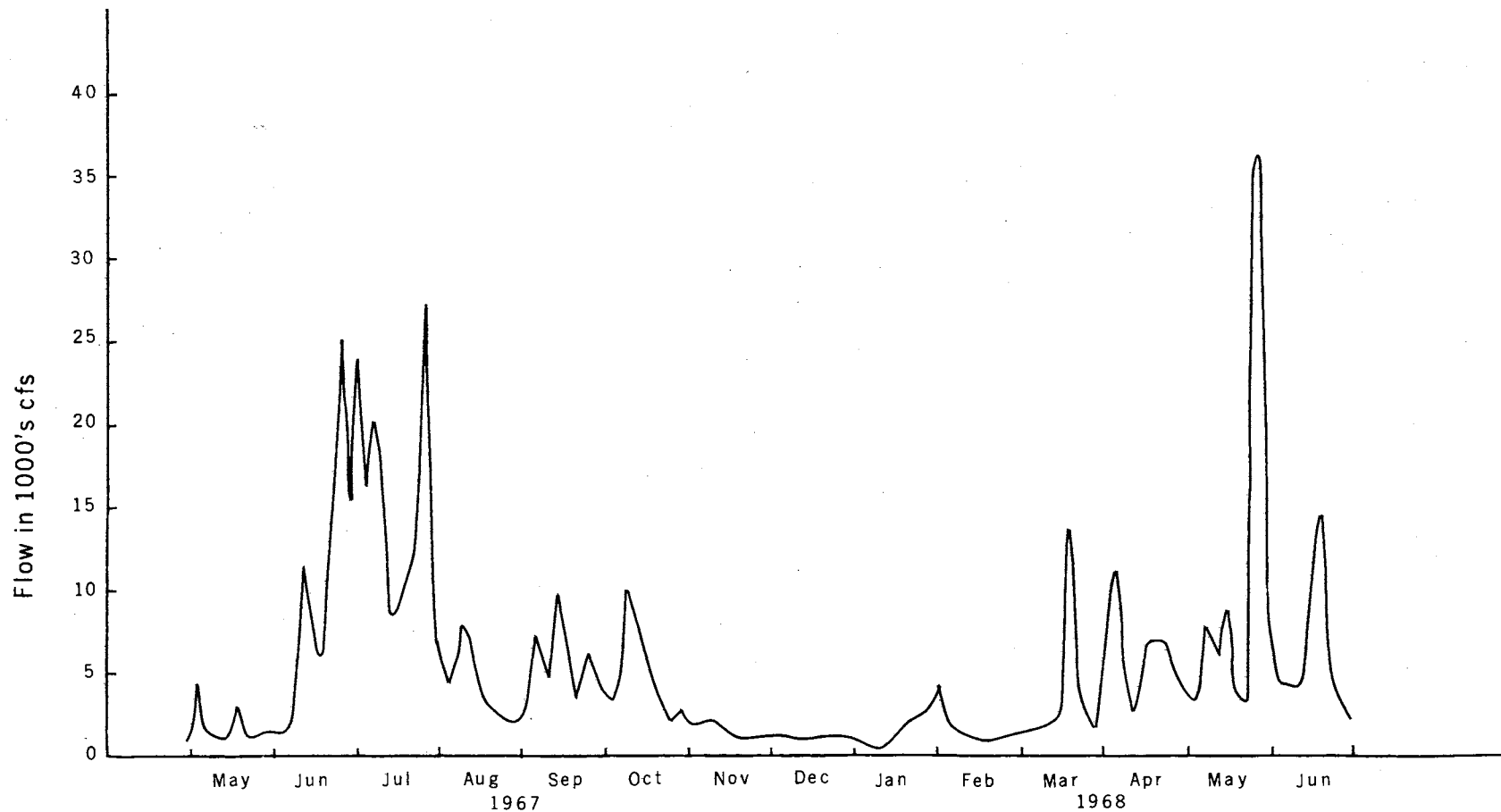


Figure 8. Rate of Flow of Water into Keystone Reservoir. Flows are biweekly averages. Flow rates were calculated from Reference 109.

The management program to drain the lower layers of the reservoir also prevented the development of a stable thermocline. This is illustrated in Figure 9. Similar temperature distributions are suggested from the data from the single section, 5, for October, 1966, to July 8, 1967, shown in Figure 3. Except for spring, 1968, the temperature throughout the reservoir varied only about three degrees. In spring, 1968, large volumes of warmer water were entering the reservoir; this is, the reservoir was being warmed by the relatively rapid influx of warm water, which could result in the observed temperature distribution.

Suspended solids, shown in Figure 10, can also contribute to density currents. Although there is some indication that the suspended solids were greater along the bottom of the Cimarron arm and could contribute to the water density, they were not likely to be the most dominant factor in establishing the density current. Their spatial distribution could be accounted for by their being carried by the current along the bottom, being concentrated there by sinking, or originating by the disruption of the sediments. Their distribution was probably determined by a combination of these effects.

One of the advantages of impoundments is the reduction of suspended solids. As the waters moved toward the dam, the average suspended solids were notably reduced. In general, the minimum was displaced toward the Cimarron arm. The highest suspended solids were observed during the periods of greatest inflow, while the lowest was during the periods of lowest inflow.

The oxygen dissolved in natural waters is largely determined by the exchange with the atmosphere. However, oxygen is fundamental

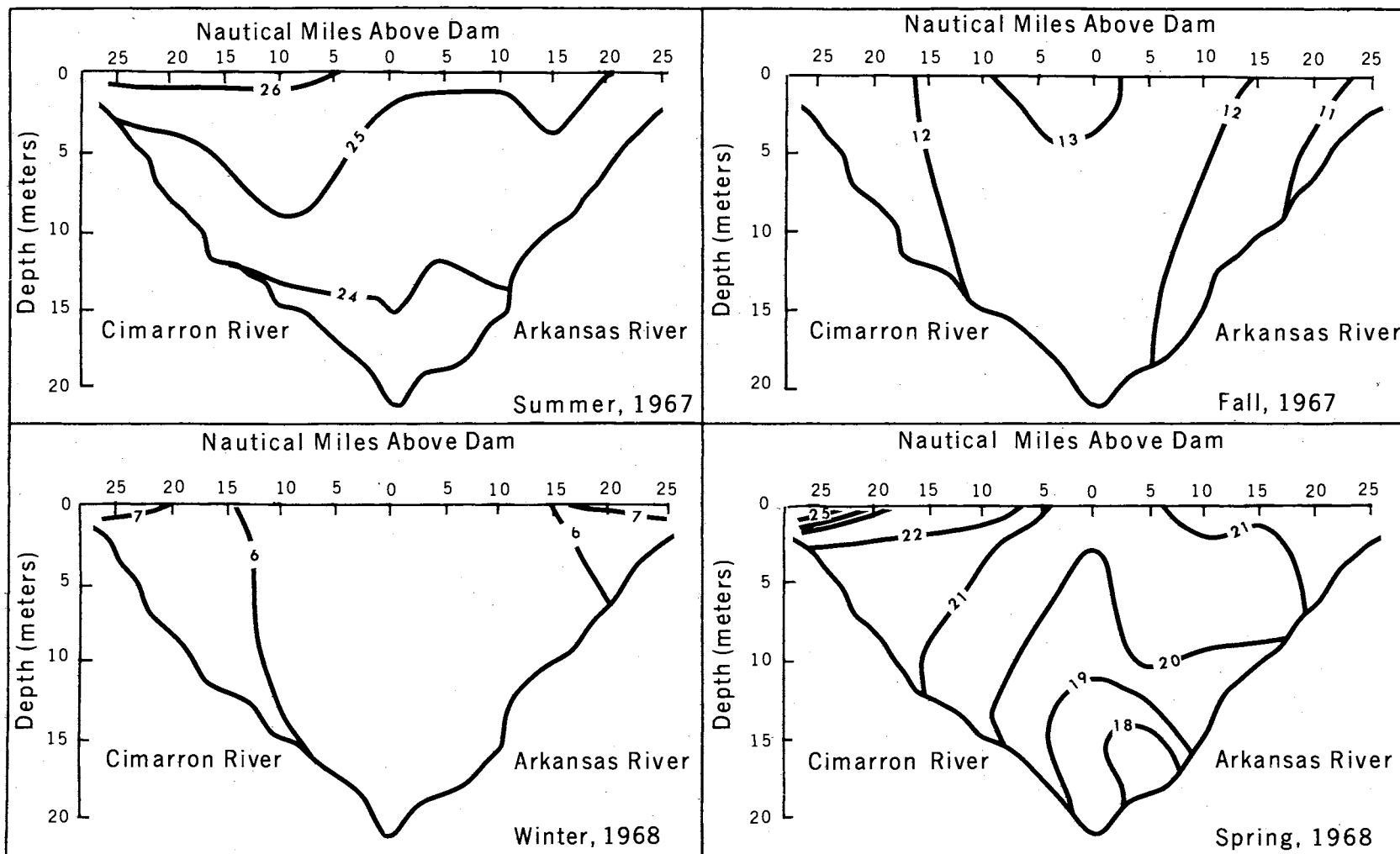


Figure 9. Seasonal Distributions of Temperature. Values are degrees centigrade.

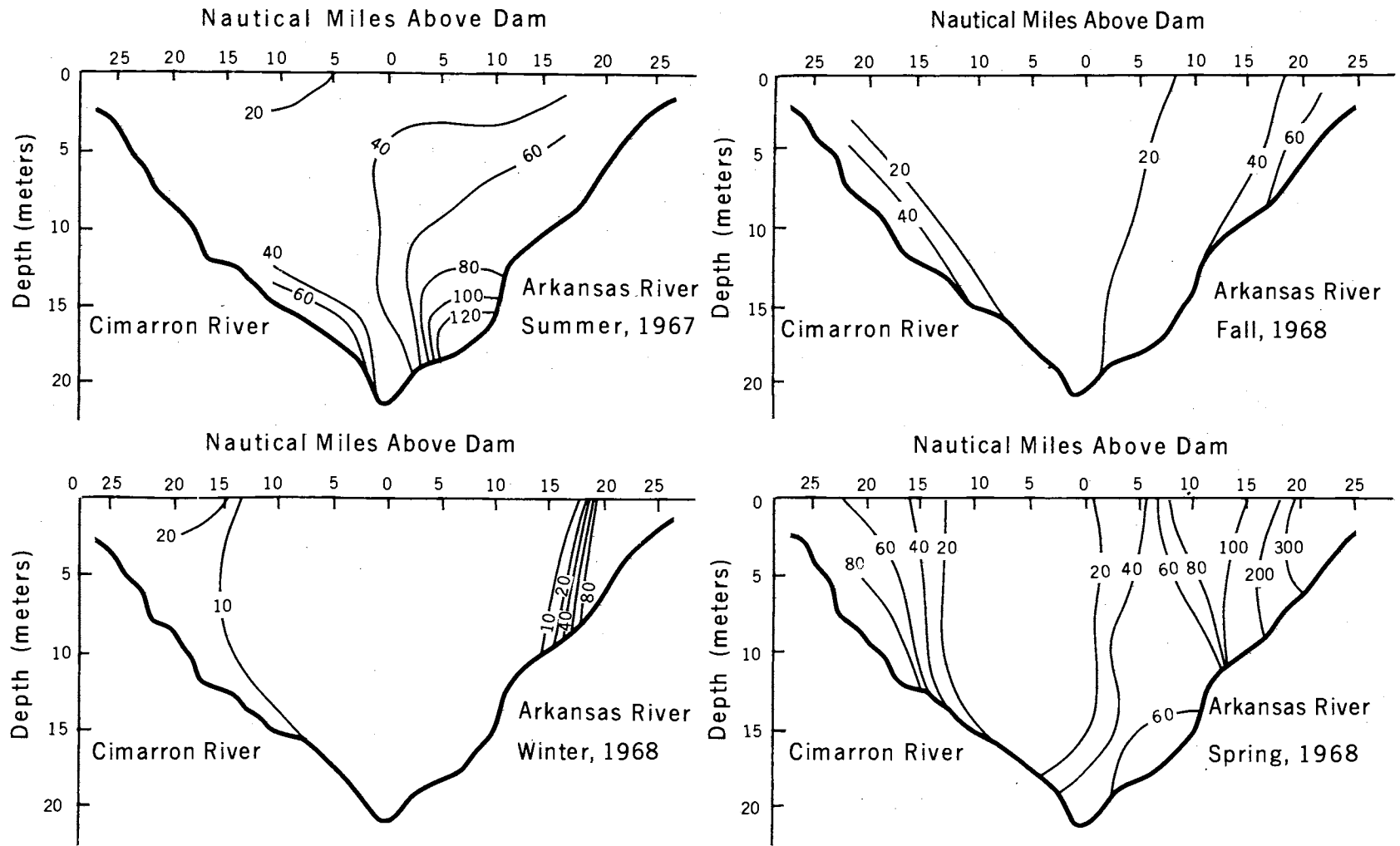


Figure 10. Seasonal Distributions of Suspended Solids. All values are mg/l.

in the biological cycle and its concentration can deviate notably from that expected from equilibrium with the atmosphere.

Figure 11 shows the average concentrations of oxygen at each station as a function of the average temperature. In the colder months, the values were near the saturation values; while during the warmer months, the values were well below saturation. The seasonal distribution of dissolved oxygen is shown in Figure 12. In the fall and winter, the oxygen was more or less uniformly distributed vertically; while in the spring and summer, it was reduced in the bottom of the reservoir. These deficiencies are commonly observed in reservoirs as the biological activity increases. This increased activity usually occurs when the solar radiation and temperature increase, and when the water column becomes more stable. The water along the bottom of the Cimarron River arm of the reservoir generally contained lower concentrations of dissolved oxygen than the overlying waters compared to that of the Arkansas arm. The greater vertical stability of the Cimarron waters, which prevents contact of the dense waters with the atmosphere, is a possible explanation of this observation.

Eutrophication

On the bases of phosphate data from August, 1966, to August, 1967, Eley¹⁰⁸ has suggested that the rate of eutrophication of Keystone Reservoir could be one of the largest ever observed. It was previously pointed out that no single parameter provides all the information needed to properly evaluate the interdependent effects of the ecological factors and that careful measurements of several

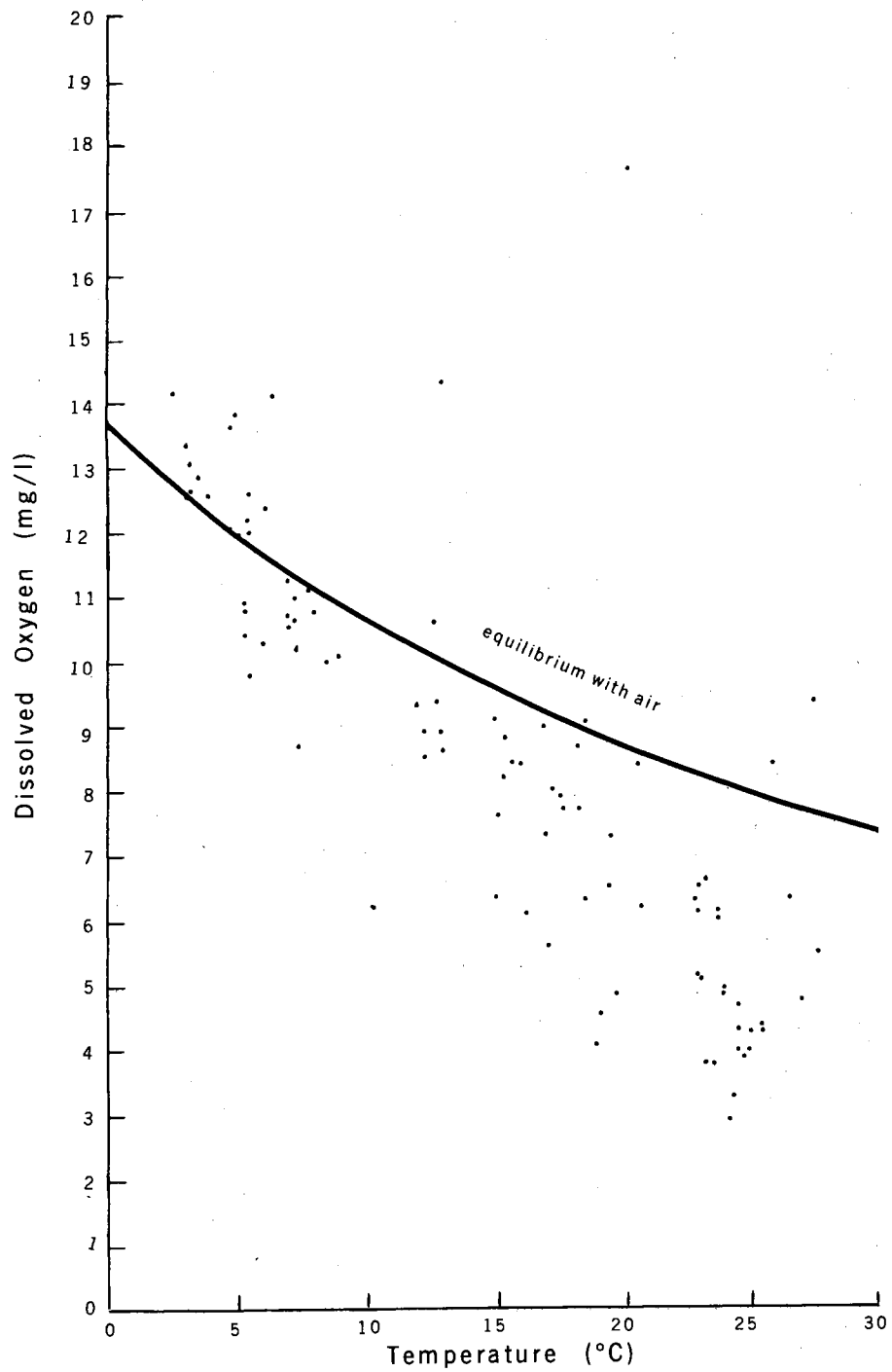


Figure 11. Saturation of Keystone Reservoir Waters with Respect to Oxygen. Data are averages from each station sampled. Saturation data are from G. A. Truesdele, A. L. Downing, and G. F. Lowden, *J. Appl. Chem.* 5, 53 (1955).

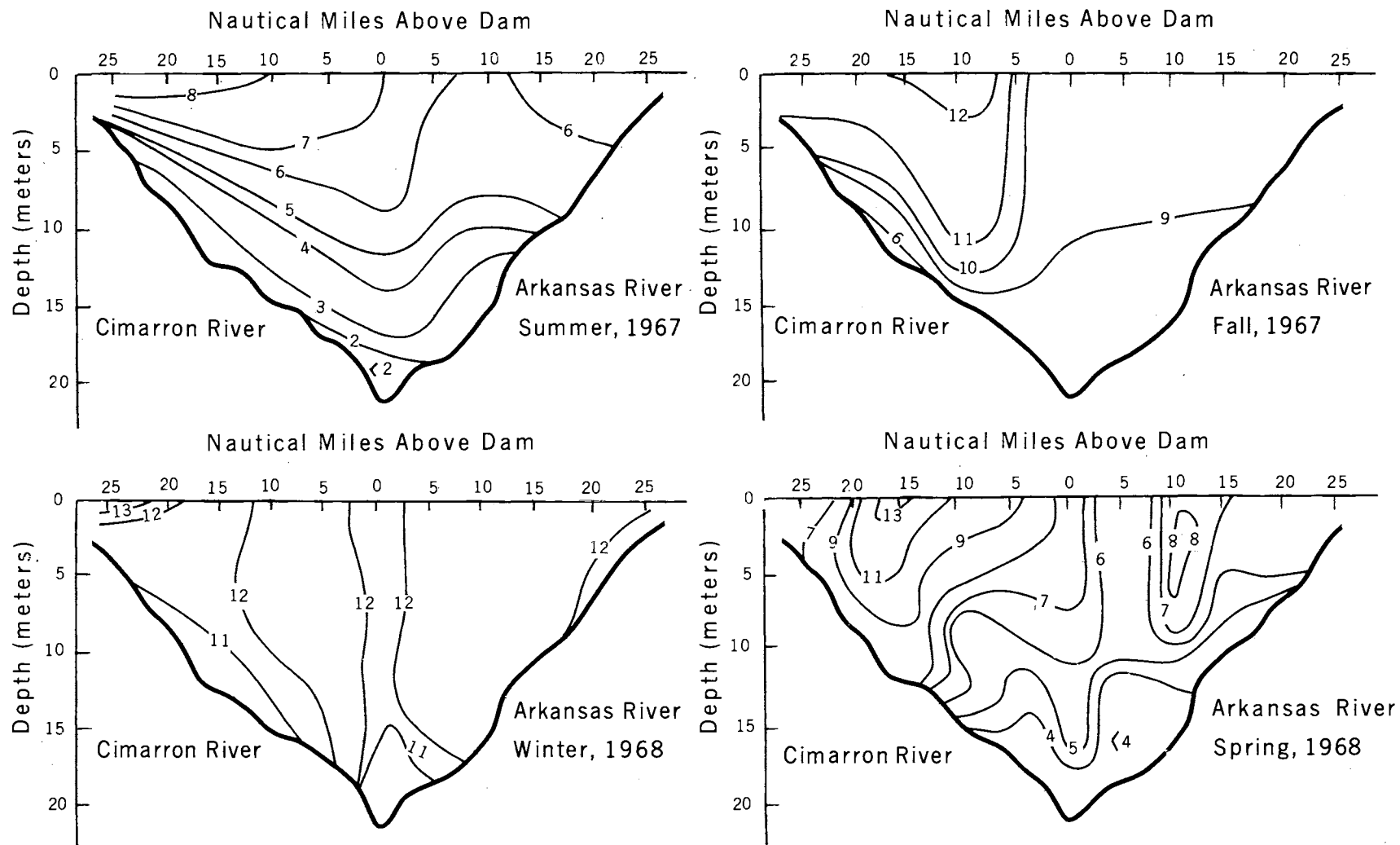


Figure 12. Seasonal Distributions of Dissolved Oxygen. All values are mg/l.

properties over a period of years is required. This seems to be especially applicable to Keystone Reservoir, since it is subject to highly variable influxes of waters and it responds rapidly to reservoir management practices.

Prior to August, 1966, the reservoir definitely exhibited the symptoms of the advanced stages of eutrophication. However, the reservoir management practice of releasing the dense bottom water lessened the symptoms of eutrophication enormously.

The properties available in this report most often correlated with eutrophication are dissolved oxygen, pH, alkalinity, turbidity or suspended solids, temperature, and dissolved solids. There appears to be no correlation between these properties and a very high rate of eutrophication. The quality of the water actually appears to be improving. However, these were measured over too short a time period to be meaningful, and only oxygen and perhaps pH offer a very reliable index of the production of organic matter. The suspended solids, or turbidity, are primarily determined by the non-biological suspended load. These tend to mask any effects caused by biological organisms. High influxes of dissolved solids are frequently related to high inputs of the nutrients. However, the high concentrations of dissolved solids which originate primarily from natural sources will tend to hide increased influxes associated with nutrients from artificial sources. These could be a major, or even dominant, source of nutrients. The temperature, alkalinity, and pH of the water are also dominated by the natural processes, although their vertical distribution may be quite good indicators.

One of the justifications for building Keystone Dam was to remove the suspended solids in order to minimize silting of the proposed navigation channel downstream. The reservoir basin is expected to fill with sediments at a relatively rapid rate. This effect alone should cause the rate of eutrophication, or aging of the reservoir, to be greater compared to similar systems.

The possibility of inorganic chemical reactions controlling the concentrations of dissolved inorganic phosphate in natural waters is frequently ignored. This is considered later in this paper in the discussion of the equilibria of the system.

Sediments

Sediments can frequently document processes that may be occurring in the water column. In an attempt to identify any process that may be occurring in the sulfide environment, a series of samples were analyzed for trace metals, total, inorganic, and organic carbon and mineral make-up. The chief processes of interest were the concentration of certain elements by the biota and their accumulation in the sediments and direct inorganic precipitation of metal sulfides or similar compounds. The results of the study are summarized in Appendix C.

Only two samples were uniquely different: Samples 5-5-66 and 5N-1. Sample 5N-1 was obtained from a shallow core in 13 meters of water and was composed of hard, black materials mixed with what appeared to be submerged grass roots and stems. It did not appear to be representative of sediments formed in the reservoir; rather it

appeared to be part of the original reservoir bed. Sample 5-5-66 was a sample of black sediments obtained from a water sampling bottle at the water-sediment interface in the deeper part of the reservoir at a time when the hypolimnion was anoxic. Compared to other samples taken at later dates, the sample is concentrated with respect to manganese, boron, and gallium and contains lower amounts of titanium, vanadium, and nickel.

The concentrations of boron in all samples is higher than that usually found in fresh water systems but is within the range observed in sea water systems. Sample 5-5-66 contains about three times more boron than the other samples. High concentrations of boron have been associated with clay minerals.¹¹⁰ It apparently is associated with illites where it replaces aluminum with respect to silicon in the tetrahedral position. Also, it is well noted that certain elements can be concentrated by the biota and that boron is required for the growth and metabolism of higher plants¹¹¹ and algae.¹¹² There is inadequate data to explain the high concentration of boron in this environment. However, in this environment where very slow oxidation of organic matter is occurring and where the accumulation of organic matter at the sediment-water interface would be expected, its association with the biota is strongly suggested. The oxidation of the organic matter by anaerobic bacteria after deposition and the release of the products to the water may account for the absence of similar values in the other samples studied from the sulfide environment.

The high concentration of manganese might also be associated with the organic matter. The solubility of inorganic manganese

compounds is usually much larger in reducing environments, and oxidized sediment surface layers have been reported to contain more manganese than reduced muds.¹¹³

The fine grain crystalline minerals that may be formed with the metals are very difficult to evaluate by x-ray diffraction methods, and none were observed in these studies. These minerals are quite unstable in an air environment, and their diffraction patterns are weak and easily masked by other minerals.

Currents in Keystone Reservoir

The spacial distributions of the physical and chemical properties discussed above suggest that two distinct current patterns exist within the reservoir depending on whether the water is released from the upper or lower layers of the lake. A possible representation of these two currents is illustrated in Figure 13. When water is released from the upper layers, the heavy Cimarron water flows along the bottom until it reaches the deepest part of the reservoir and then accumulates there. The lighter Arkansas River water flow will distribute itself in the epilimnion and will flow considerable distances up the Cimarron arm. A back flow, as illustrated in the figure, must occur to conserve mass. Frictional forces along the pycnocline would be expected to produce an inverse current in the hypolimnion.

When water is released from the bottom layers of the reservoir, the dense Cimarron water will flow along the bottom and out the dam. The lighter Arkansas water, which is about five times the volume of the Cimarron water, will exhibit its strongest flow in the lower

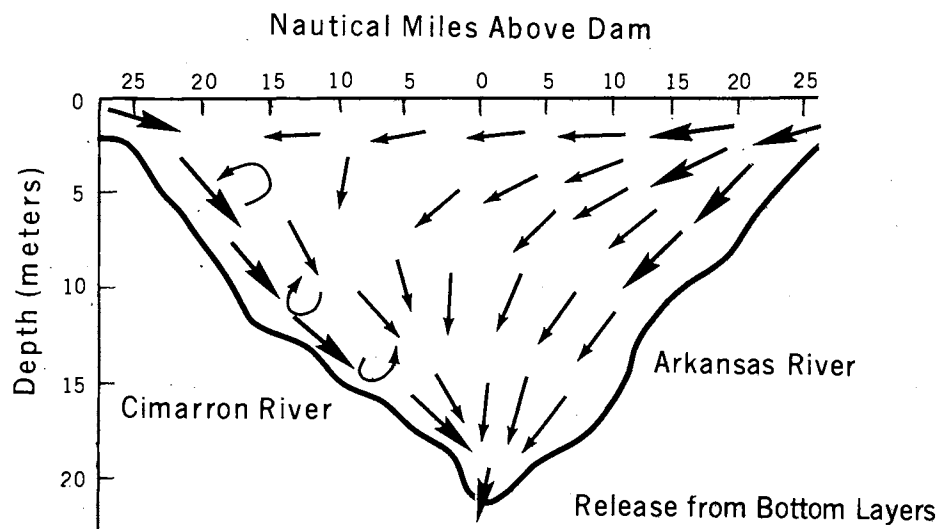
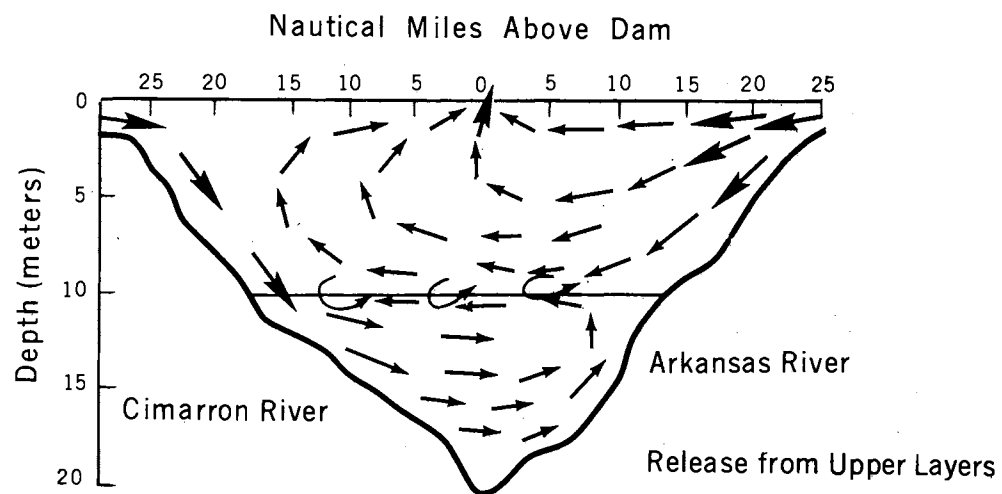


Figure 13. Hypothetical Flow Patterns in Keystone Reservoir.

half of the Arkansas arm, flowing toward the outlet gate. Lighter flows are expected in the upper layers. Some of the lighter water will flow up the Cimarron arm considerable distances before sinking to the outlet.

These suggested flows are highly schematic and simplified, however, since there are many other forces which may come into play in addition to the suggested density difference and forced convection. For example, the effect of winds will surely dominate the surface currents. The surface currents will probably be in the direction of the wind, while various types of counter currents would be expected at intermediate depths.

CHAPTER VI

EQUILIBRIA OF THE NATURAL WATERS OF KEYSTONE RESERVOIR

Philosophy of Equilibrium Models

The formulation of equilibrium models of real natural water systems is based on the assumption that the composition of the waters is governed by chemical reactions between the gas, liquid, and solid phases that make up the systems at various stages in the hydrological cycle and that these reactions are rapid enough to approach a state of equilibrium within the average lifetime of the system. This implies that the components of the gas, liquid, and solid phases which make up any given system are in a state of chemical equilibrium.

The value of the inorganic models is that, if they are workable, they are simple. The objective is to illustrate some of the regulatory factors that determine the composition of the water. The results are generalized conclusions, but these may be the basis for considering dynamic processes. That is, an equilibrium time independent model must be a prerequisite for consideration of a time dependent dynamic model of the individual processes in the real system.

The models developed in this study are inorganic, time independent, equilibrium models for closed systems. Although they are inorganic models, they do not exclude the biological activity or

consider them non-contributing. For example, the paths taken to obtain the final equilibrium states are not relevant; they must merely be reversible. Whether a solid phase, such as calcite, dissolves or precipitates by a complicated or unknown biochemical process or by a complicated and partly known inorganic process is not pertinent. In the formulations of models of closed systems, no inputs of mass or energy are considered.

The formulation of the models can be visualized as a hypothetical experiment in which the phases, which are to model the system, are mixed together and are allowed to react until they obtain a state of chemical equilibrium. These phases are usually a gas phase, a solution phase, and a number of solid phases of defined composition. It is assumed that all of these phases exist together throughout the hypothetical experiment. Equilibrium is assumed and the composition variables, or the activities of the dissolved components, are calculated using available thermochemical data. The models are then compared to the real systems.

The models are limited in several ways and, at best, can only represent a simplified situation. True equilibrium is not necessarily attained in all respects in the real system. How closely equilibrium is approached will depend mainly on the reaction time available and the rate of mixing. Ionic reactions in aqueous solutions are usually very rapid. They frequently reach equilibrium as fast as the reactants can be mixed. Heterogeneous reactions approach equilibria at a much slower rate; thus, the length of time available and the degree of mixing in nature are very important. In ground water,

turbulent river, and shallow lake systems, the phases are usually thoroughly mixed. In deep lakes, however, the rate of mixing is normally much smaller, but the time available for mixing is larger. In both cases, the time available for mixing and for the reactions to reach a state of completion is usually much larger than the hours allowed for the equivalent reactions to reach equilibria under laboratory conditions.

Due to our lack of knowledge about real systems, many species may be overlooked or wrong ones may be used in their place. The exact composition of the mineral phases in the sediments is not always known. Knowingly, highly idealized formulas must be used to represent what must be a very complex mineral. The available free energy data or equilibrium constants are frequently not known with sufficient precision and some data are lacking. There is frequently considerable discrepancy among the data, especially for the aluminum silicate minerals. Also the method used to describe the real system, which is compared with the models, may be inadequate.

Despite the many inadequacies, equilibrium models are becoming the most valuable tools available for formulating adequate experimental and theoretical descriptions of natural water systems. In this study, they are applied to the relatively saline and dynamic system of Keystone Reservoir. This appears to be a unique application of the models.

History of the Natural Waters of Keystone Reservoir

Before the heterogeneous equilibria of a natural water system, such as Keystone Reservoir, can be considered, the various phases

that the waters are in contact with and have contacted during their history must be defined in some manner. One approach to attempt to define these phases is to reconstruct the history of the waters.

The minerals and mineraloids which make up lake sediments, bedrocks, soils, and suspended solids which natural waters contact are frequently ill-defined, and their chemical composition is not always known with much certainty. Even though the solid phases may be very complex, well-known minerals with well-established chemical formulas are used to represent the solid phases in this study. Their definition is based on the geologic setting and the suggested bedrock and soil mineralogy of the drainage basin described by Jordon,¹² x-ray diffraction studies which are reported in Chapter IV of this report, and established principles of the chemistry of minerals.

Based on the description of the drainage area in Chapter II, it appears that the waters entering the reservoir are of at least two distinctly different origins. One type originates in the area where the Permian rocks are exposed at the earth's surface in western Oklahoma and south-central Kansas. The ground waters and surface waters are known to come into contact with very large quantities of the minerals associated with chemical sedimentary rocks, such as halite (NaCl), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), and silica (SiO_2). In some areas in this region, the waters are saturated with the relatively less abundant and very soluble halite. The silicate minerals are also abundant and are present in shales and in the soils of the area. The clay minerals, such as kaolinite, montmorillonite, illites, and fragments of quartz, are the minerals most commonly associated with the shales and the soils.

As the waters from this region drain into the main streams, they mix with waters which originate from areas where the highly soluble organic and chemical sedimentary rocks are not abundant. In the Rocky Mountains, the waters acquire their chemical properties primarily by the weathering of igneous rocks which are composed chiefly of minerals such as the feldspars, quartz, and the ferromagnesium minerals. The rocks and soils between the Rocky Mountains and the area of the Permian rocks are mainly sandstone, siltstone, and caliche which consists mainly of quartz, clay minerals with a high silica content, such as kaolinite and montmorillonite, and calcium carbonate. This area also receives the least amount of rainfall.

Even before they reach the main streams, waters issuing from the evaporites mix with the more dilute waters; but the greatest dilution is expected from the waters originating outside the areas of the Permian rocks. For example, the average dissolved solids in the Salt Fork of the Arkansas River at Tonkawa, Oklahoma, is about 2,102 mg/l. These waters are diluted by the waters in the Arkansas River coming from Kansas to an average of 867 mg/l by the time they reach Ralston, Oklahoma. The waters from the two areas continue to mix until they reach the head of the reservoir. In the area of the reservoir itself, rocks of the Pennsylvanian geological age occur at the surface. These are primarily shales composed of clay minerals, but the limestone minerals are widely abundant. In this area, which is composed of about the eastern half of Oklahoma, the waters are diluted further.

The waters entering the reservoir carry relatively large loads of suspended solids. One of the justifications for construction of

Keystone Dam was to form a settling basin for the suspended solids of the Arkansas and Cimarron Rivers to minimize silting of the proposed navigation channel downstream. These suspended solids are primarily degraded clay minerals such as kaolinite and montmorillonite. The x-ray diffraction analyses of suspended solids in the reservoir water, reported in Chapter IV, show that kaolinite, montmorillonite, and illite compose the major fraction of the suspended solids. Calcite, however, was also found in the sediments. Quartz is abundant in all areas of the drainage basin.

If the above discussion is representative of the actual situation, an approximation of the physical and chemical actions which determine the composition of the waters of Keystone Reservoir can be made. This approximation is that the waters originating in the area where the Permian rocks occur acquire their chemical composition by the dissolution of the common chemical evaporites such as gypsum, calcite, dolomite, and halite and by dissolution or incongruent reactions of the clay minerals such as kaolinite, montmorillonite, and illite. Waters from this region are removed from the evaporite minerals and are added to the streams and rivers where they are diluted by fresher waters, mainly those originating from the western part of the drainage basin. The waters now contact a new group of solid phases which are present as suspended solids and the stream bed. These are composed mainly of the degraded clay minerals and calcite. As these waters flow down the rivers into the reservoir, they are mixed with the suspended solids and the river and lake sediments, and congruent as well as incongruent reactions continue to occur.

The sediments are composed of approximately the same minerals as the suspended solids.

These represent the major actions occurring in the system.

The composition of the water can also be influenced by many other processes such as components added by rain water, evaporation and precipitation, man-made pollution, and others too numerous to mention. However, the interactions considered above appear to be the dominating ones which determine the composition of the Keystone Reservoir natural water system and are the ones which will form the guidelines for the formulations of the equilibrium models below.

Equilibrium Reactions

Carbonate System

The water analyses presented in this study illustrate that many more dissolved chemical species exist than are reported in the usual water analyses. For the dissolved carbonates, these are illustrated in Figure 14 using data taken on August 20, 1966, when the hypolimnion was anoxic. At that time, the complete spectrum of the observed distributions of the carbonates occurred. The free bicarbonate ion accounted for about 90 mole per cent of the total dissolved carbonates. In the hypolimnion, the pH was lower and the concentrations of free carbon dioxide increased significantly, while that of the carbonate ion and the cation-carbonate ion pairs decreased. The free carbonate ion accounted for 30 to 40 per cent of the carbonate. The MgCO_3° and CaCO_3° ion pairs constituted the bulk of the remaining carbonate.

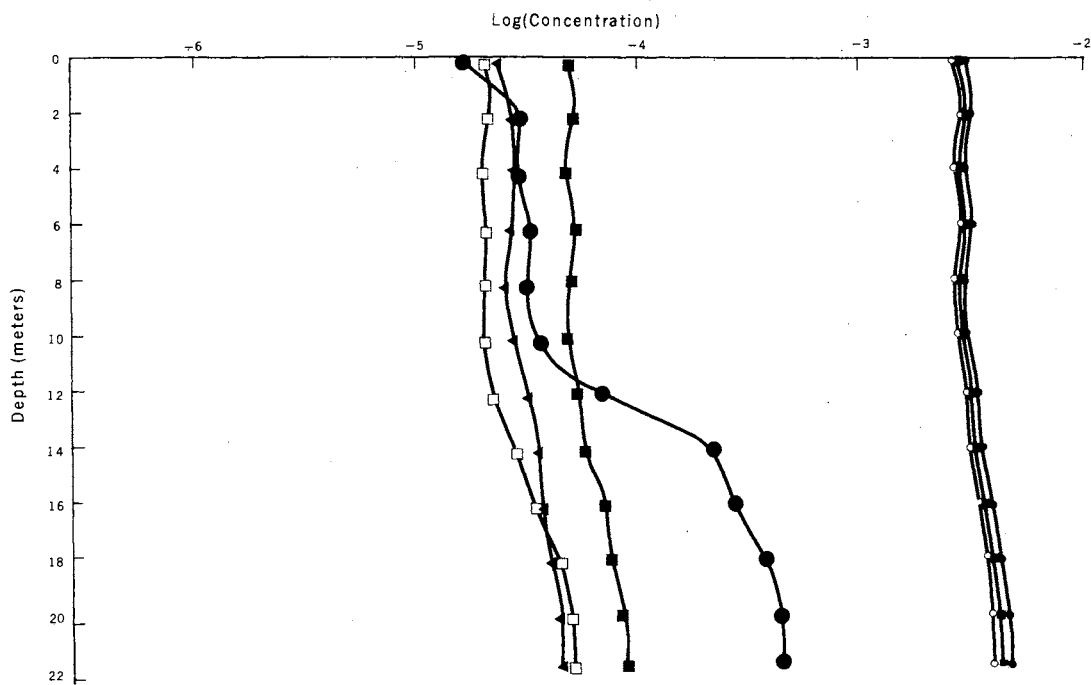
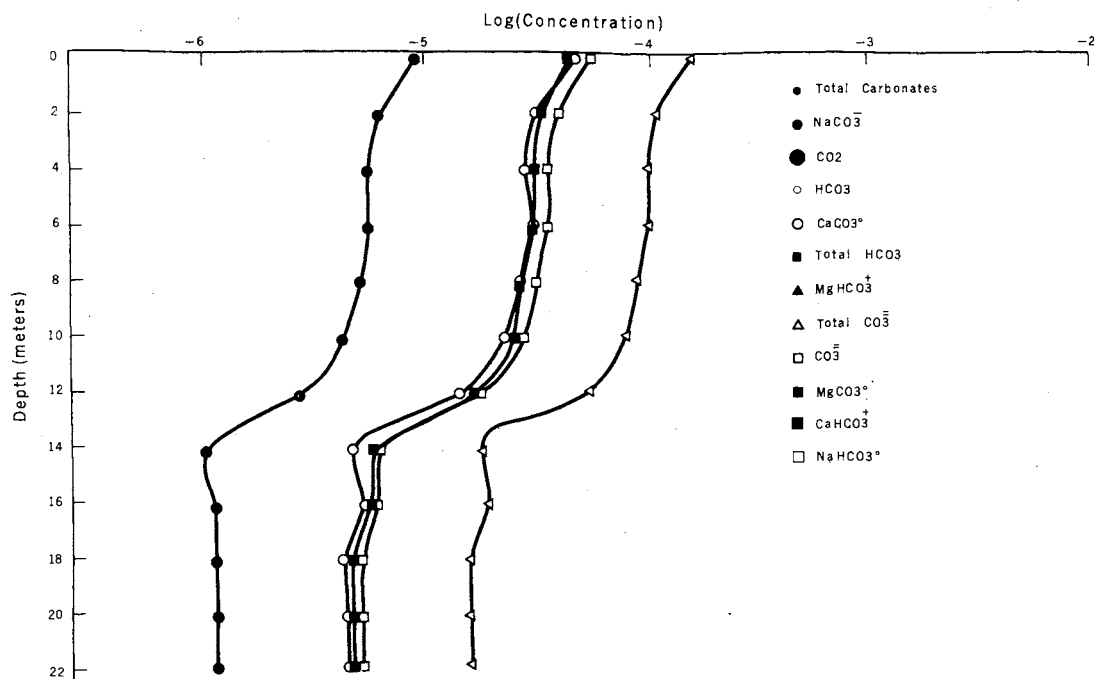


Figure 14. Distribution of Dissolved Carbonates. Data are from Station 5 and were obtained on August 20, 1966.

The carbonates are derived mainly from the carbonate minerals and the atmosphere. Ideally, the dissolved carbon dioxide should be determined by the partial pressure of carbon dioxide of the atmosphere. The data shown in Figure 15 illustrate that the waters were supersaturated with carbon dioxide, however. This is a common occurrence in natural waters and is usually attributed to the aerobic or anaerobic decay of organic matter in the water, soil, and sediments. The rate of exchange of carbon dioxide with the atmosphere is difficult to determine and remains largely unknown; however, it appears to be the limiting kinetic step.

There are three polymorphic forms of calcium carbonate and two hydrates which occur in nature. These all have different solubilities. Calcite is the thermodynamic stable form and appears to be the most important in fresh water systems. Aragonite, however, composes a large amount of recent sediments and is being deposited under conditions in which calcite is the stable phase.

The solution and precipitation of calcite appear to be rapid, and it has been observed to precipitate in lakes.²³ It was also observed in the sediment samples from Keystone Reservoir. Values of the activity product, $\{Ca^{++}\}\{CO_3^{--}\}$, for all samples are plotted in Figure 16 as a function of temperature. Although there is considerable scatter, the points fall around the theoretical values for saturation with calcite. Most of the samples were undersaturated.

Magnesium is generally associated with carbonates; and like calcium carbonate, there are several different forms found in nature. Magnesite ($MgCO_3$), the magnesium calcites, and the double carbonate

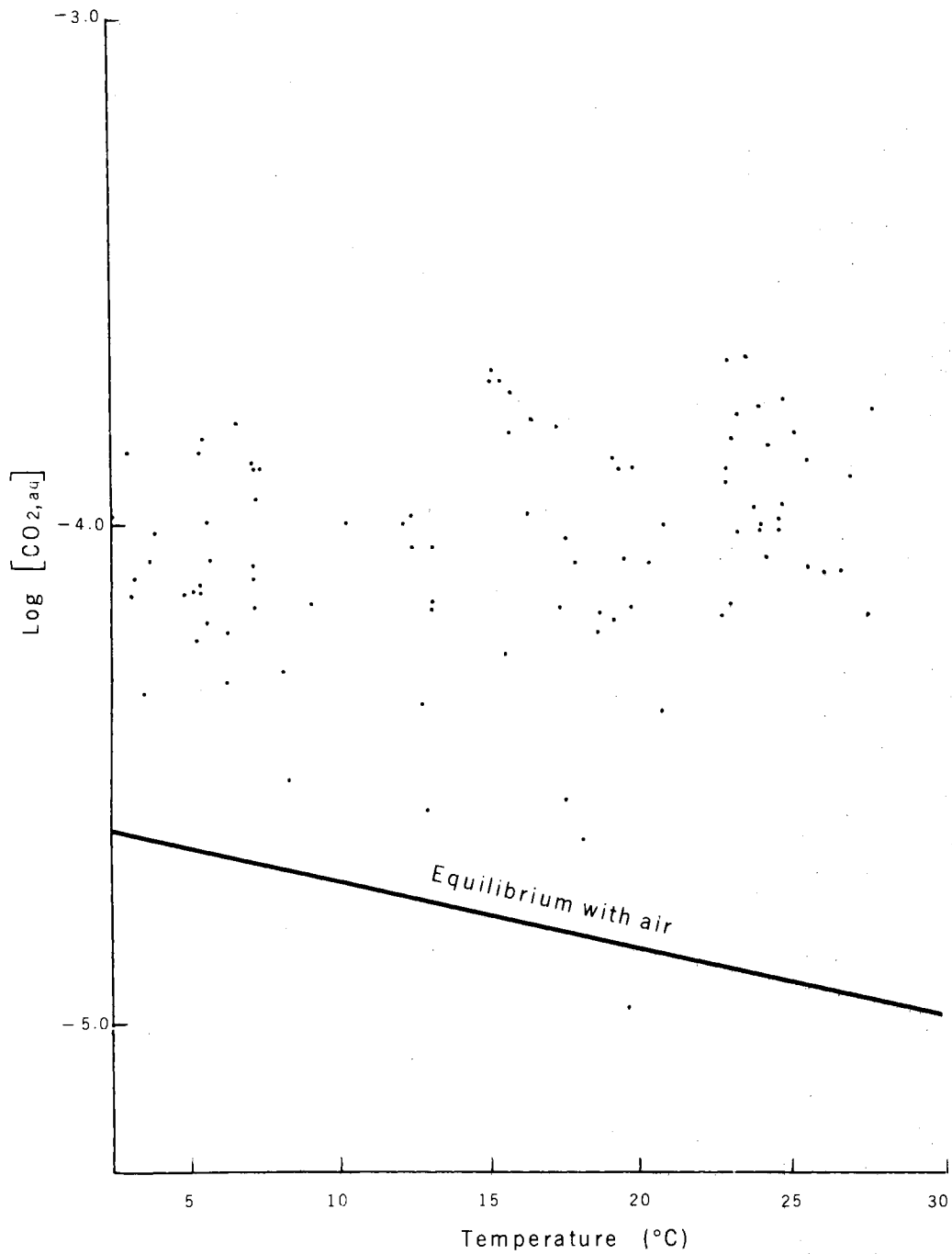


Figure 15. Saturation of Keystone Reservoir Water with Respect to Carbon Dioxide. Data are averages from each station sampled. Saturation data are from A. A. Markam and K. A. Kobe, *J. Am. Chem. Soc.* **63**, 449 (1941).

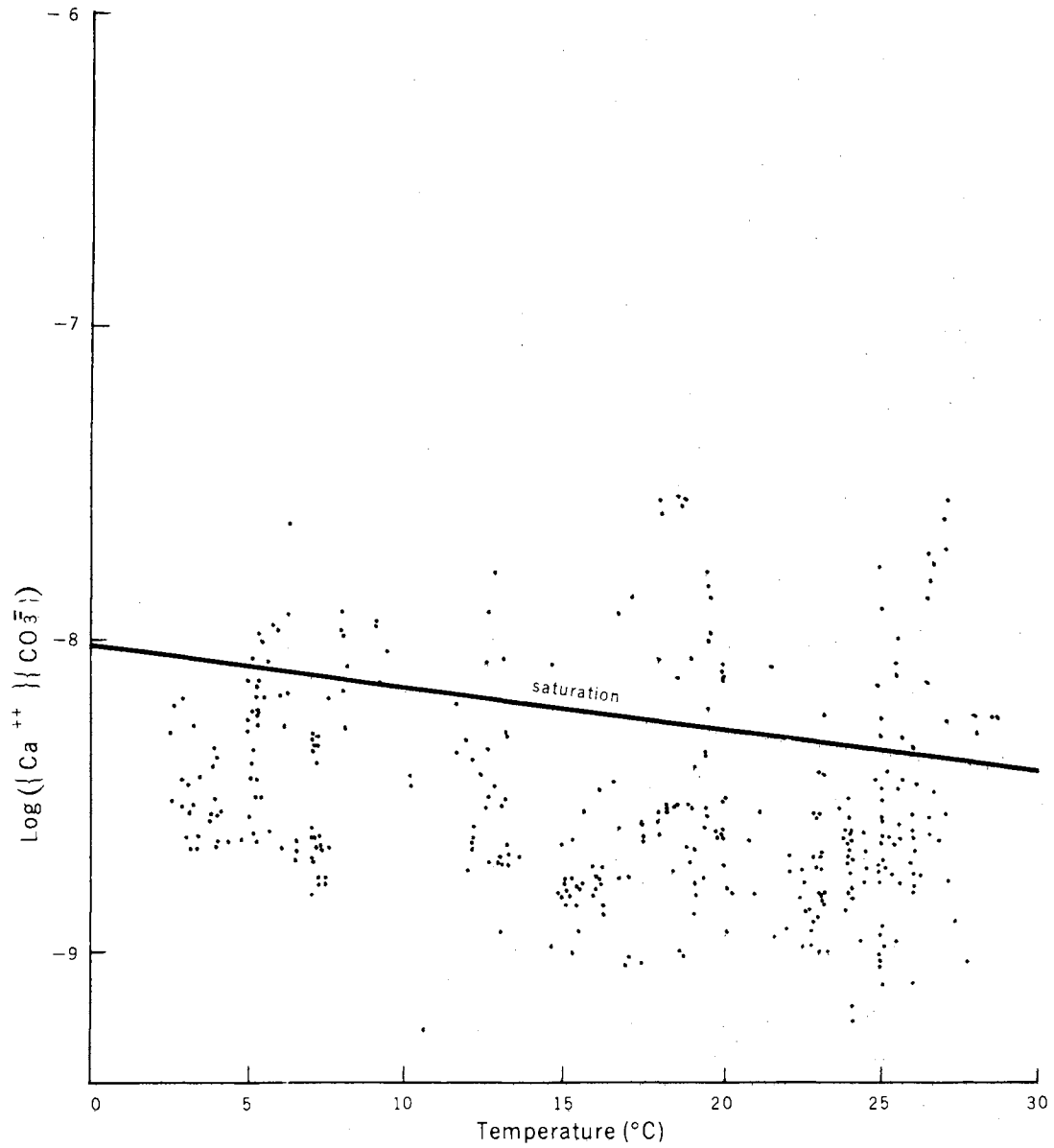


Figure 16. Saturation of Keystone Reservoir Water with Respect to Calcite. Saturation data are from T. E. Larson and A. M. Buswell, J. Am. Water Works Assoc. 34, 1667 (1942).

with calcium, dolomite ($\text{CaMg}(\text{CO}_3)_2$), are the more abundant forms. The activity products $\{\text{Mg}^{++}\}\{\text{CO}_3^{--}\}$ illustrated in Figure 17 for all samples suggest that the waters were undersaturated in respect to magnesite.

Dolomite constitutes a large per cent of carbonate rocks and is associated with the Permian evaporites. The data illustrated in Figure 18 for the activity product, $\{\text{Ca}^{++}\}\{\text{Mg}^{++}\}\{\text{CO}_3^{--}\}^2$, show that most of the values fall around the theoretical value for saturation with dolomite. Most samples appear to be undersaturated.

In their review of the carbonate system, Bricker and Garrels⁶⁷ suggest that the precipitation of the magnesium carbonates, especially dolomite, is very rare in fresh water systems and is unimportant in controlling the composition of the waters. Both laboratory studies and evaluations of field data suggest that the precipitation reactions do not occur readily, and supersaturated conditions can be maintained almost indefinitely. However, in areas underlain by dolomite bed rocks, the waters are frequently saturated with respect to dolomite.

Strontianite (SrCO_3) is also commonly associated with carbonate sediments. In sea water, strontium partly replaces calcium in the aragonite structure and plays a major role in the carbonate chemistry. The activity products, $\{\text{Sr}^{++}\}\{\text{CO}_3^{--}\}$, for all samples shown in Figure 19 suggest that the waters were undersaturated with strontianite but approach saturation as an upper limit. Overall, much less is known about strontium in natural waters.

Chloride System

The chlorides form no significant amounts of complexes with the

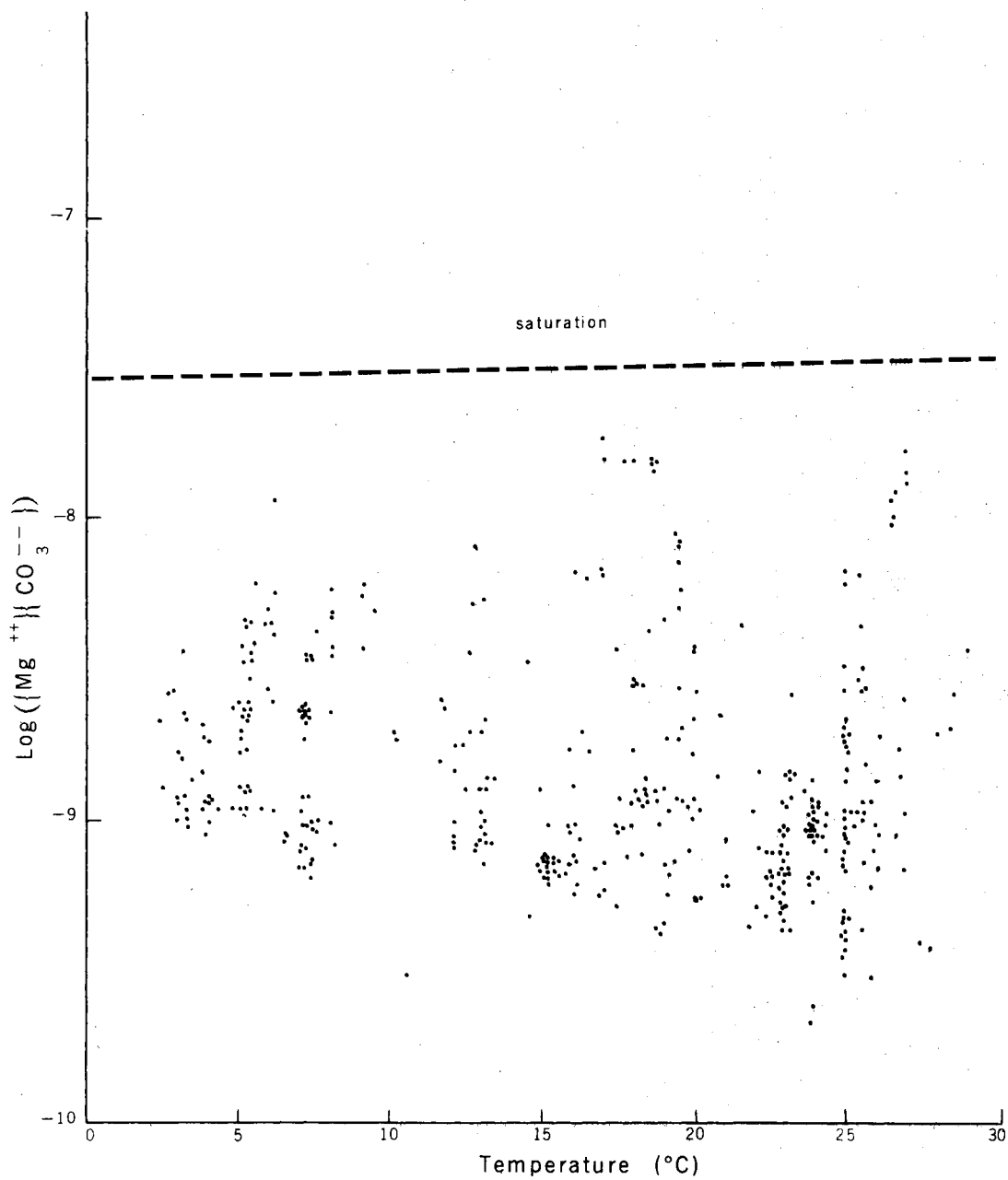


Figure 17. Saturation of Keystone Reservoir Water with Respect to Magnesite (MgCO_3). Saturation data are from Reference 82.

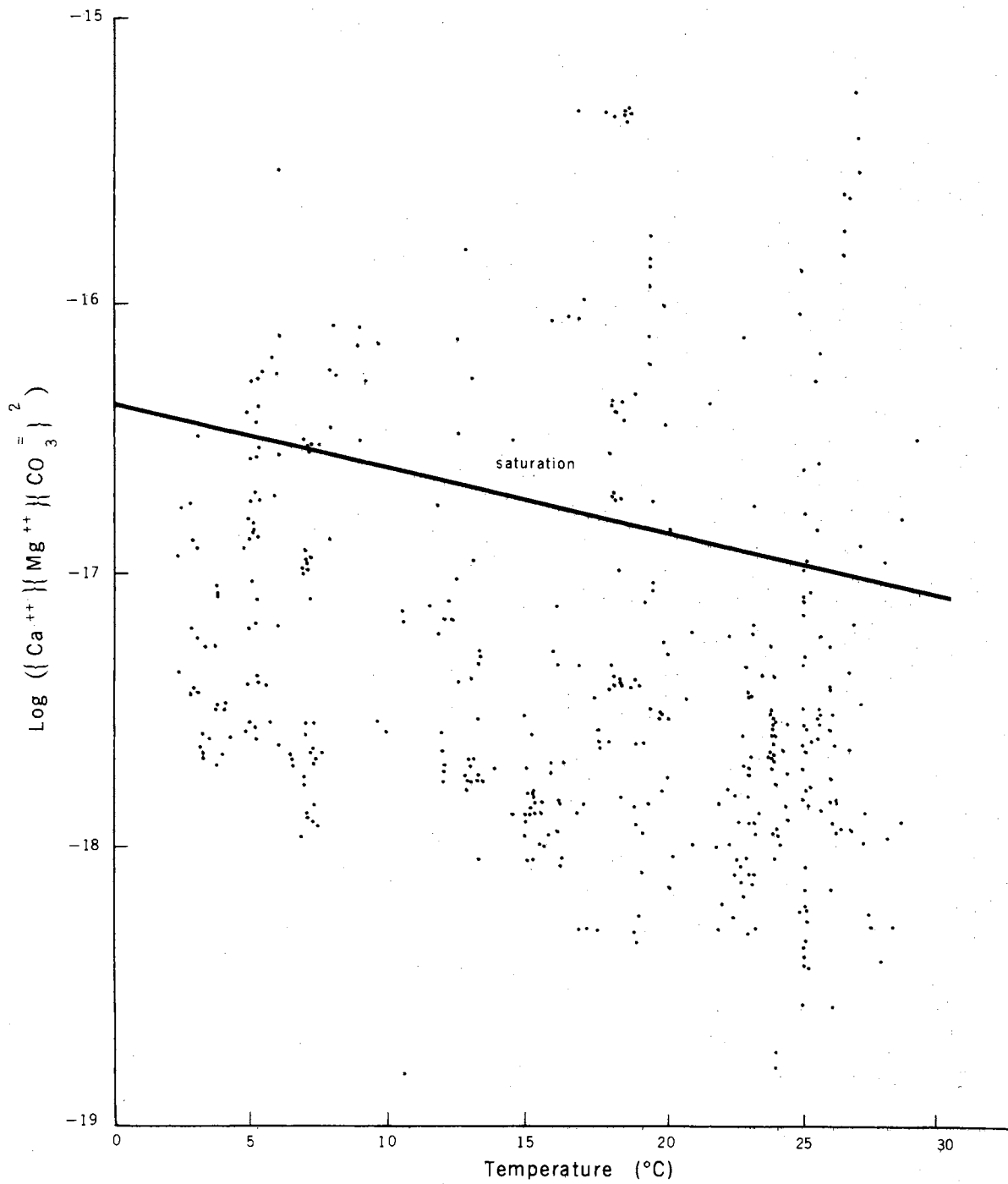


Figure 18. Saturation of Keystone Reservoir Water with Respect to Dolomite, $(\text{CaMg}(\text{CO}_3)_2)$. Saturation data are from Reference 61.

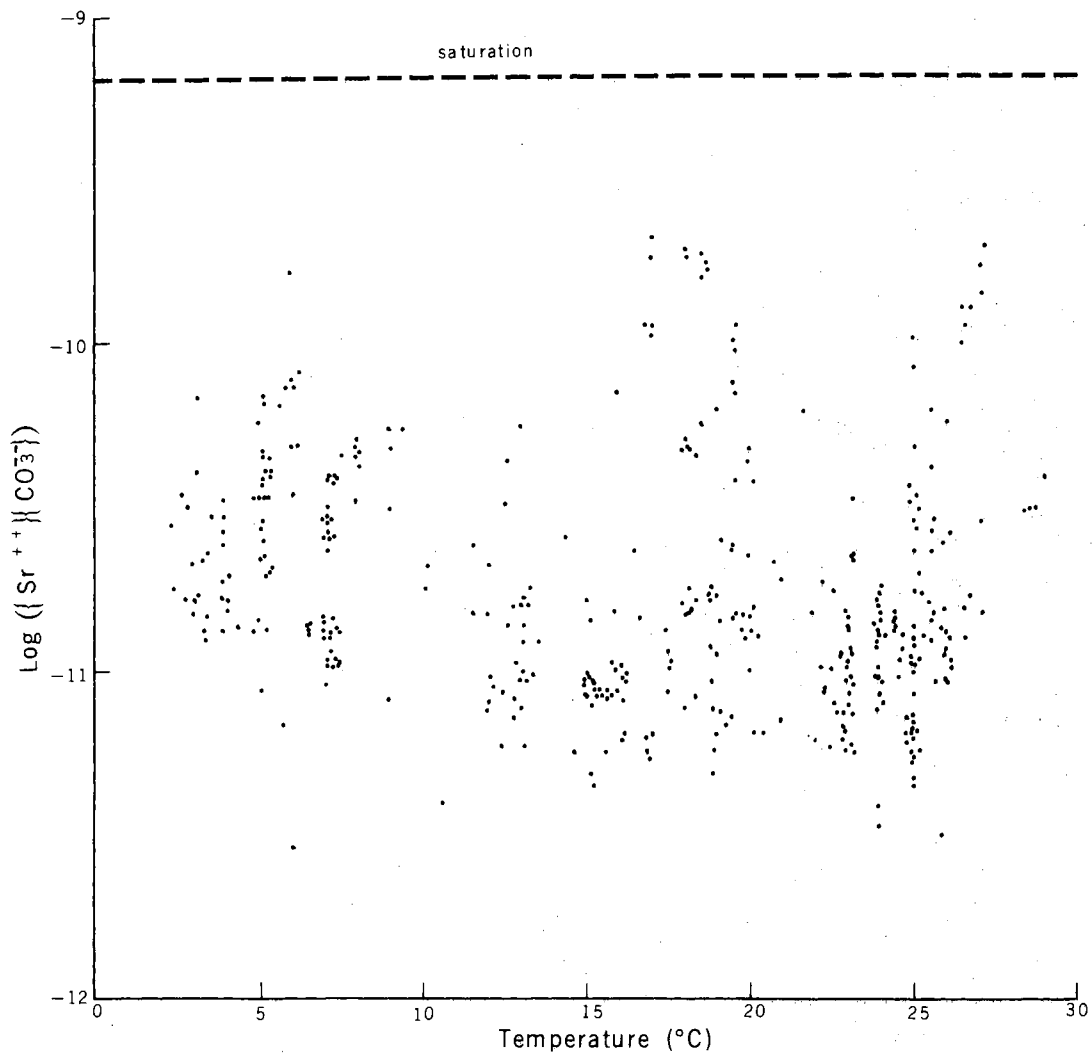


Figure 19. Saturation of Keystone Reservoir Water with Respect to Strontium Carbonate. Saturation data were derived from W. M. Latimer, 'Oxidation Potentials,' 2nd. ed., N. Y., N. Y., Prentice Hall, 1952.

cations considered here. In this system, they originate primarily from the solution of halite. Halite is the only known equilibrium with chloride which would limit its concentration in natural water systems; but saturation with respect to halite is almost impossible to obtain in Keystone Reservoir.

Sulfate System

The distribution of the various sulfate species in the solution phase is illustrated in Figure 20 for data from August 20, 1966. About 80 per cent of the total sulfate occurred as the free sulfate ion. The calcium, magnesium, and sodium ion pairs accounted for varying proportions of most of the remainder while KSO_4^- contributed far less than one per cent.

Most of the sulfate in Keystone Reservoir is derived from the solution of gypsum from the Permian red beds, and these waters are diluted to varying degrees before they enter the reservoir. Gypsum is not expected to precipitate in the reservoir; however, equilibrium with gypsum during the dissolution may occur, and this would set an upper limit of that found in the reservoir. The activity product, $\{\text{Ca}^{++}\}\{\text{SO}_4^{--}\}$, for all samples are shown in Figure 21. As expected, the waters were far from equilibrium most of the time.

Strontium sulfate would be expected to be associated with the gypsum deposits. The waters of the reservoir, like gypsum, were far from saturated with it.

Silicate System

The nature of aluminum silicate minerals in water systems does

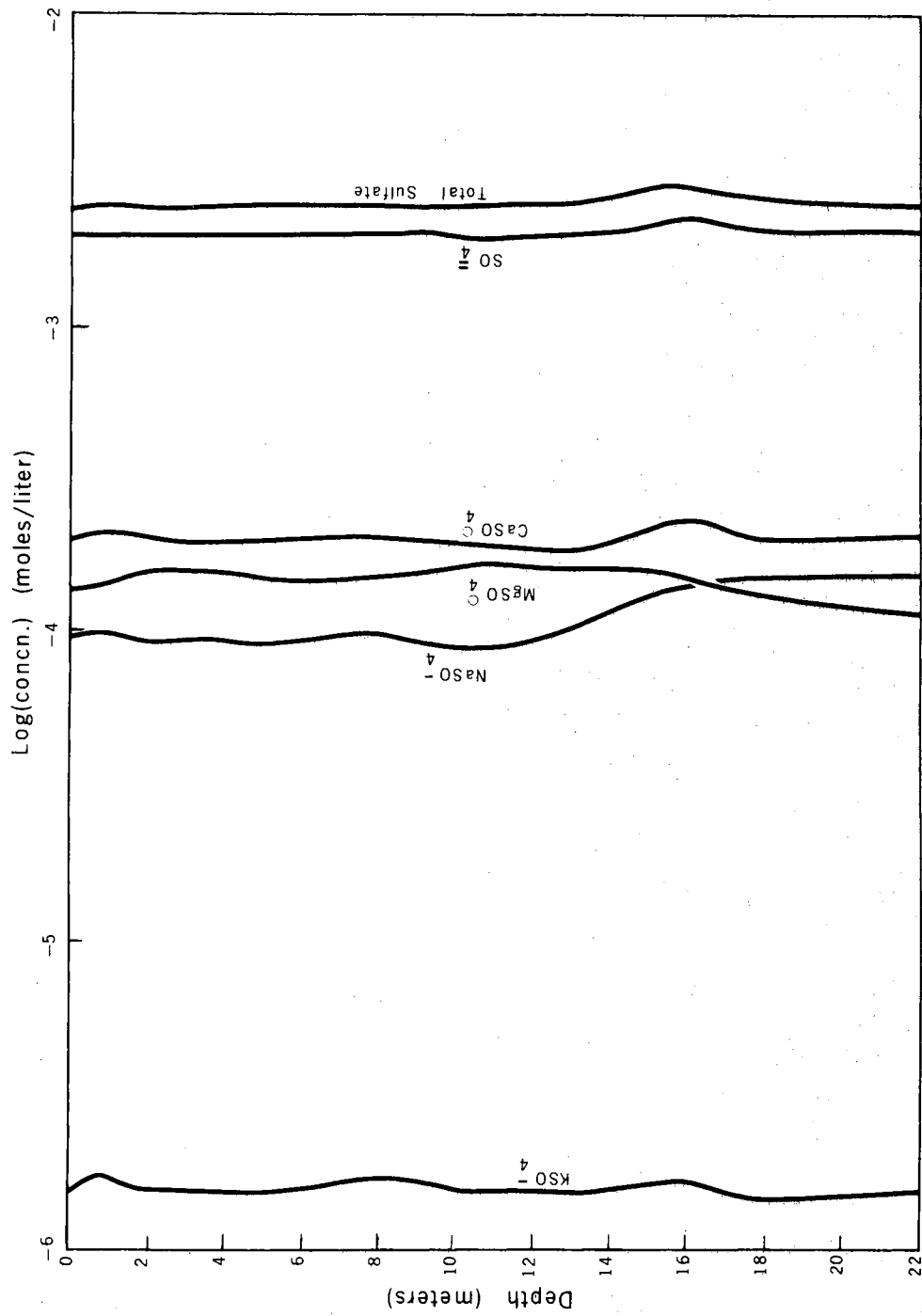


Figure 20. Distribution of Dissolved Sulfates.

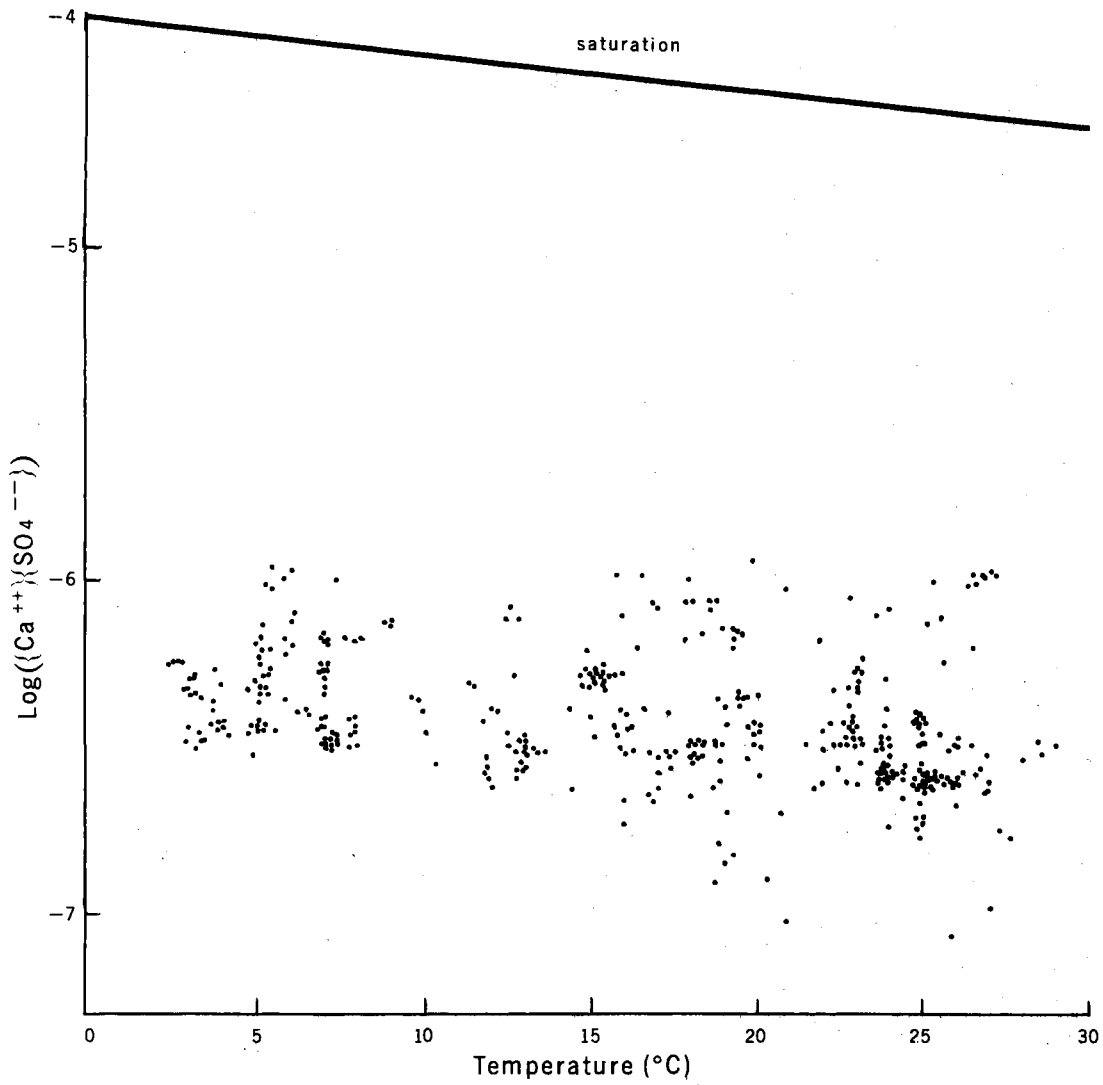


Figure 21. Saturation of Keystone Reservoir Water with Respect to Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Saturation data were derived from W. M. Latimer, 'Oxidation Potentials,' 2nd. ed., N. Y., N. Y., Prentice Hall, 1952.

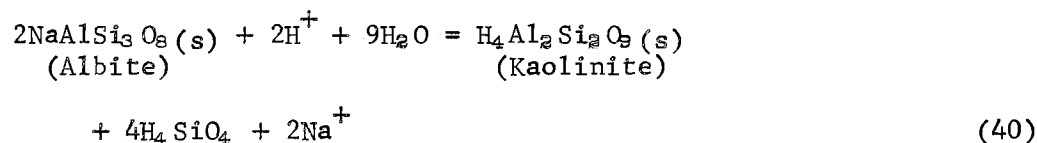
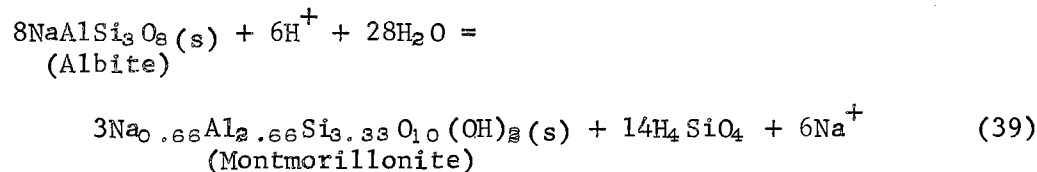
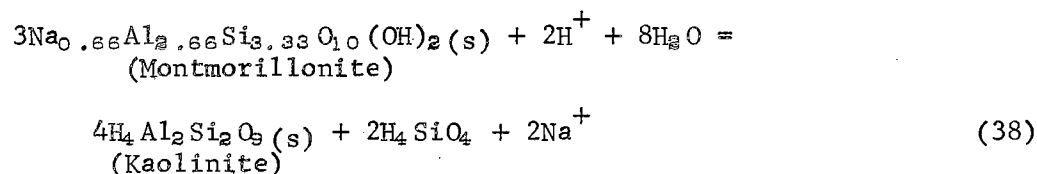
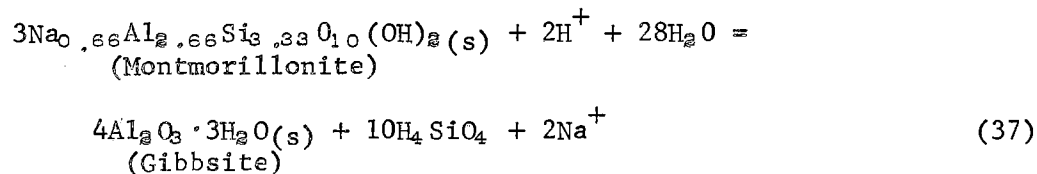
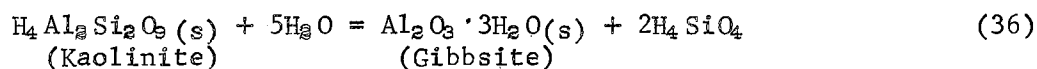
not appear to be adequately known. Also, free energy data for aluminum silicate minerals at low temperatures is limited and many conflicts in the data exist. However, if simplified formulas for the aluminum silicate minerals are assumed to represent what must be highly complex, naturally occurring minerals, enough data are available to derive some useful stability relations.

Predominance diagrams,^{1,14} or stability diagrams,^{8,9c} compiled from chemical thermodynamic data are useful in understanding the silicate reactions. The diagrams are prepared by writing the equations for the more probable transitions between the minerals and balancing them by assuming that aluminum is conserved in the solid phase and adding the cations and $H_4SiO_4^0$ to conserve electric neutrality and the elements. The equilibrium constants are calculated from the free energy of formation of the constituents involved in the reaction. The assumption is made that the activity of any solid is unity.

The diagrams below represent only pure hydrous alkali aluminosilicate systems, and they do not take into consideration variations in the composition of the minerals which occur in nature. Similar diagrams have often been used to attempt to utilize limited data, or even simulate data, in order to gain qualitative, or at best, semi-quantitative impressions of a possible actual situation. Also, remarkably different diagrams can be obtained by choosing different constants and formulas. Nevertheless, they offer the best means available to evaluate the silicate system.

The reactions considered in the $Na_2O-Al_2O_3-SiO_2-H_2O$ system are

shown in Equations 36 to 41.



The diagram shown in Figure 22 was derived from data of Feth, Roberson, and Polzer⁶⁸ and is similar to those used by other workers.

The analyses from Keystone Reservoir suggest that the waters are stable with respect to kaolinite or montmorillonite, and the values scatter around the montmorillonite-kaolinite boundary. This suggests equilibrium reactions between sodium ions, dissolved silica, and kaolinite and sodium montmorillonite and hydrogen ions.

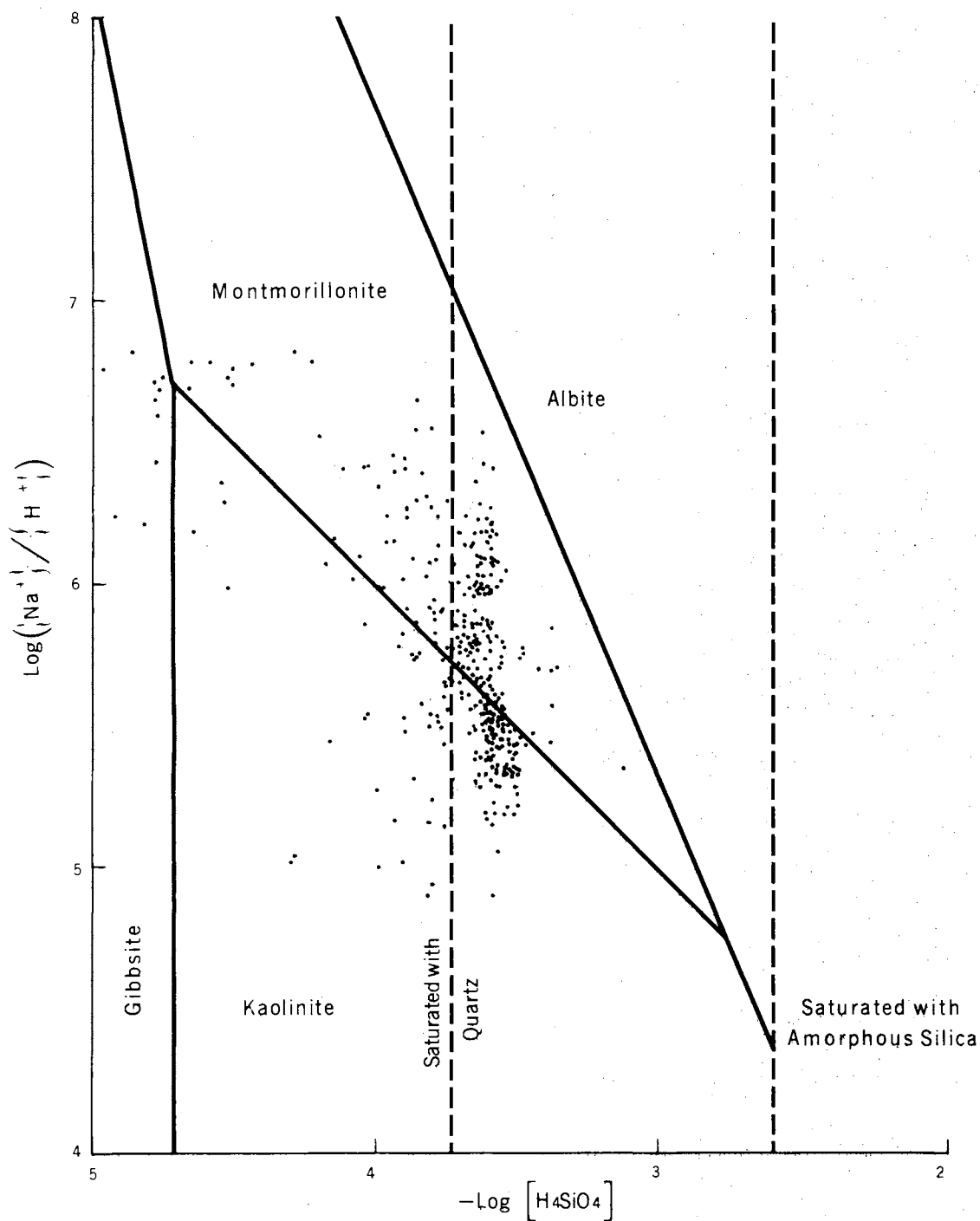
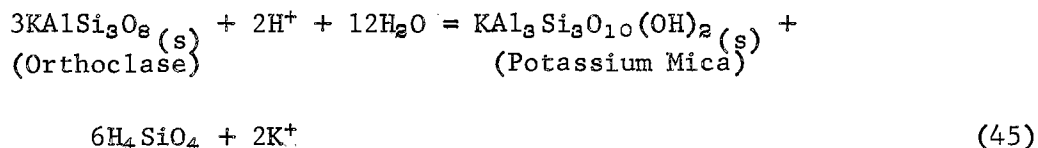
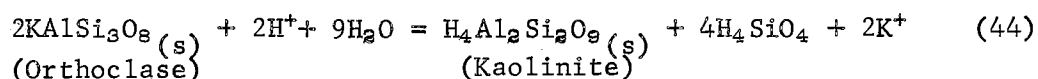
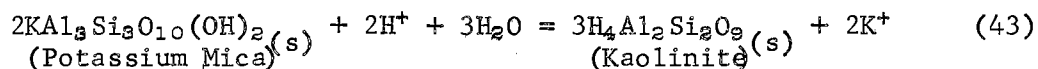
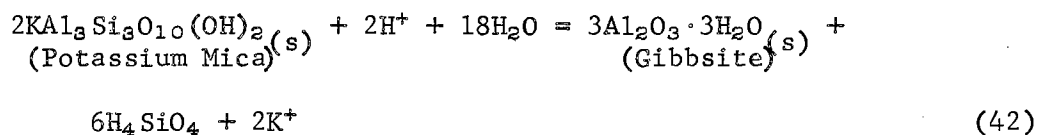


Figure 22. Stability Relations of Phases in the System $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and One Atmosphere Total Pressure. Plotted data are observed values. The diagram was derived from Reference 68.

Such a reaction could buffer, or control, the concentrations of dissolved silica, sodium, and the pH. Both kaolinite and montmorillonite were identified by x-ray diffraction studies in all sediment and suspended solid samples analyzed. Similar controls of Na^+ , pH, and dissolved silica have been suggested in the weathering environment and in the ocean.

The rate of solution or precipitation of quartz is usually accepted to be too slow in nature to be of much consequence in affecting the concentration of dissolved silica. It is of interest to note, however, that the observed values are near that expected from saturation with quartz.

The reactions considered to prepare a similar diagram for the $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system are given by Equations 36 and 41-45.



The diagram shown in Figure 23 was derived from Feth, Roberson, and Polzer⁶⁸ and shows the same general features as those derived by other workers. The analyses plotted on the diagram from Keystone Reservoir suggest that the system is within the kaolinite stability field.

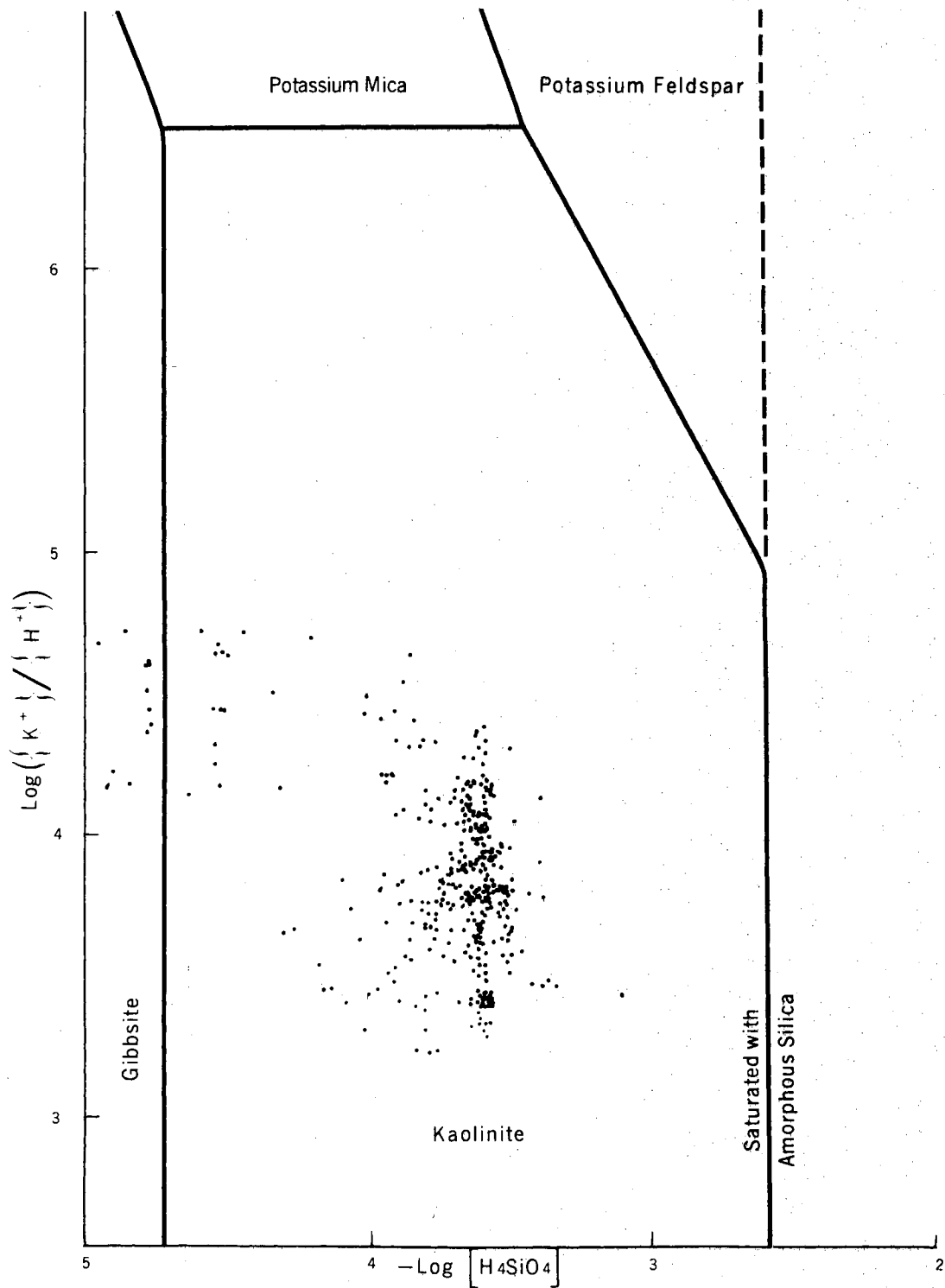
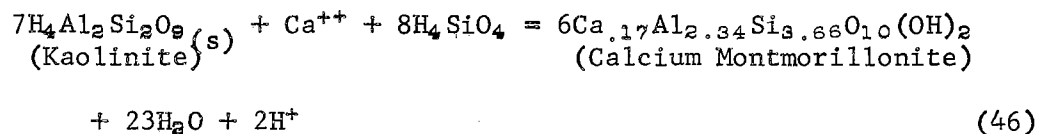


Figure 23. Stability Relations of Phases in the System $K_2O-Al_2O_3-SiO_2-H_2O$ at 25°C and One Atmosphere Total Pressure. Plotted data are observed values. The diagram was derived from Reference 68.

In sea water, equilibrium between a potassium mica, kaolinite, and the solution has been suggested which sets the ratio $\{K^+\}/\{H^+\}$ at about 10^6 . The data from this system are far removed from this boundary; however, x-ray diffraction studies show an abundance of illite and illites are known to undergo exchange reactions with potassium ions. In this system where the reactions times are not very large, it is not unreasonable to suggest a metastable equilibrium system between kaolinite, the solution containing the dissolved components H^+ , K^+ , and $H_4SiO_4^\circ$, and a poorly crystalline, poorly defined, layered silicate, such as an illite, which may limit the potassium concentration in the system.

The $CaO-Al_2O_3-SiO_2-H_2O$ system is illustrated in Figure 24. The reactions used to prepare the diagram are given by equations 36, 41, and 46.



The equilibrium constants used to prepare the diagram were obtained from the work of Stumm and Leckie.⁵⁸

The data from analyses of waters from Keystone Reservoir plotted on the predominance diagram fall primarily within the stability field of kaolinite and appear to lie near the kaolinite-montmorillonite boundary. This could suggest equilibrium reactions involving these phases.

Phosphate System

As previously noted, Eley¹⁰⁸ found that the total phosphate

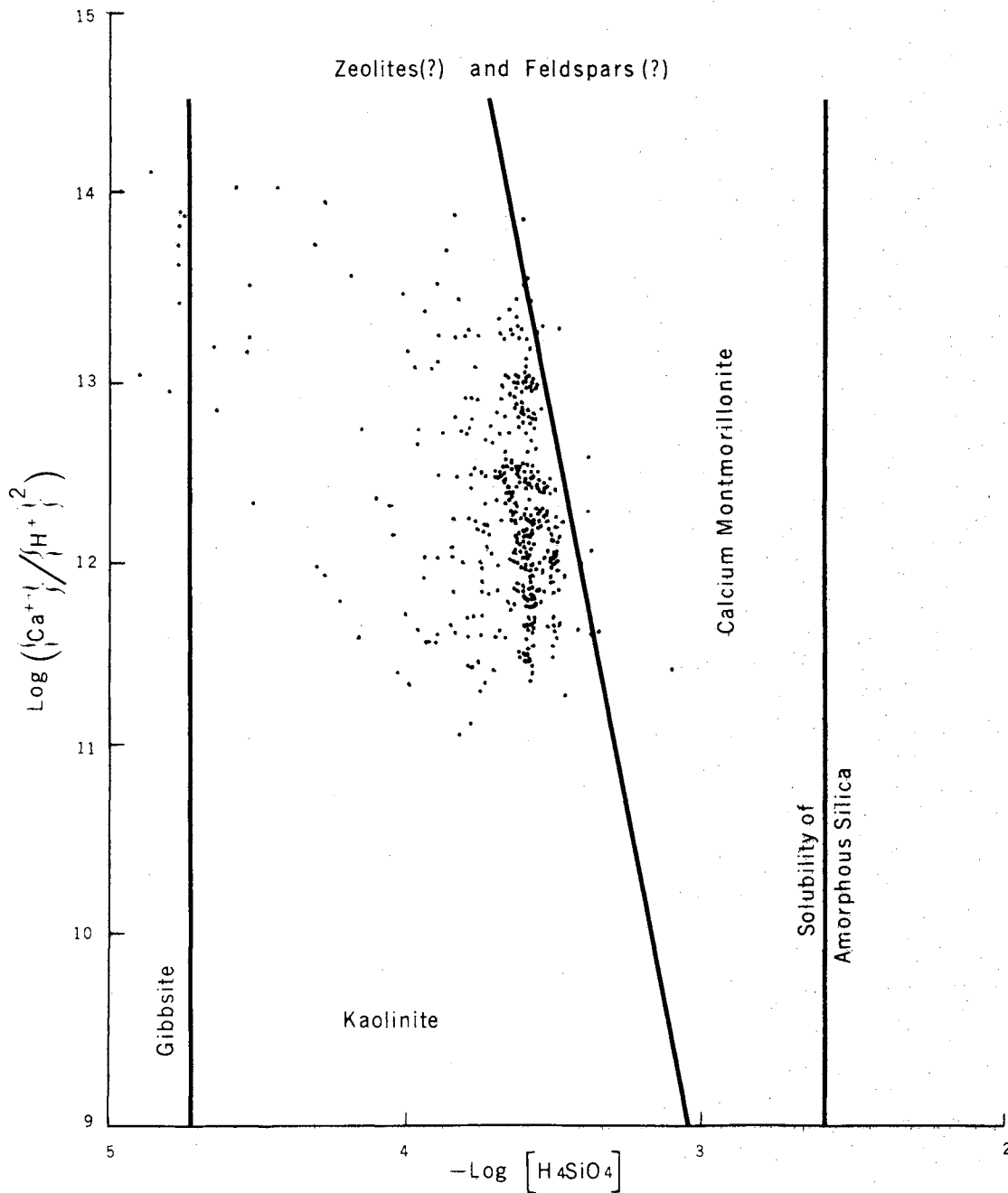


Figure 24. Stability Relations of Phases in the System $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ at 25°C and One Atmosphere Total Pressure.

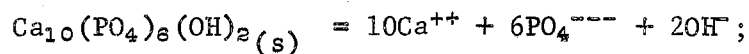
concentration in the reservoir increased approximately 320 per cent from September, 1966, to August, 1967. If this increase is correlated to eutrophication, it would be one of the largest rates ever observed.

Interrelationships between phosphorus and the biota have received and are continuing to receive considerable study; but little attention has been given the effect of heterogeneous inorganic reactions on the gross phosphorus content of natural waters. Kramer⁶⁰ has suggested that equilibrium with hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$ may control the gross phosphate concentrations in the Great Lakes, and deviations of the actual phosphate and the phosphate required to saturate hydroxyapatite would be a good empirical index of the degree of "biological use" of the lake. In this study, adequate phosphate and supplemental data are not available for a detailed evaluation of the saturation of the lake water with apatite. As a rough estimate, however, the phosphate concentration that would be expected if equilibrium did exist is calculated from the observed data for August, 1966, and May 14, May 28, July 8, July 28, August 20, and September 14, 1967, and compared to the data of Eley¹⁰⁸ during the same period.

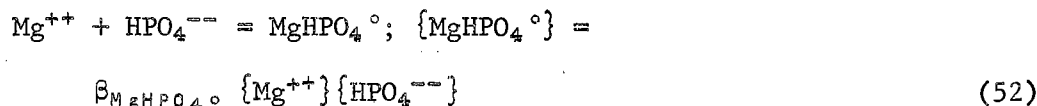
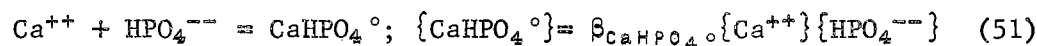
The total inorganic phosphate can be calculated by Equation 47.

$$\begin{aligned}
 [\text{Total } PO_4^{-3}] &= [HPO_4^{-2}] + [H_2PO_4^{-1}] + [CaHPO_4^{\circ}] \\
 &+ [MgHPO_4^{\circ}]
 \end{aligned}
 \tag{47}$$

The reactions and the corresponding stability relationships involving the phosphate species are illustrated in Equations 48 to 51.



$$\{\text{PO}_4^{---}\}^6 = K_{\text{ap}} / \{\text{Ca}^{++}\}^{10} \{\text{OH}^-\}^2 \quad (48)$$



The braces distinguish activity from concentration, which is indicated by brackets. The averages of the observed activities for the hydrogen, calcium, magnesium, and hydroxide ions at Station 4 or 5 (Appendix B) were used in these equations to calculate the activities of the phosphate species. These activities were converted to concentrations using the activity coefficients of 1.0 for the uncharged species and the activity coefficients estimated from the Debye-Hückel equation (Equation 30) for the charged species. The ion size parameter, \bar{a} , was 4 for PO_4^{---} , HPO_4^{--} , and H_2PO_4^- and the ionic strengths were available from the analyses. These results were substituted into Equation 47 to obtain the total inorganic phosphate concentrations. The values of the equilibrium constants are given in Table VI.

The results of the calculations are given in Table VII and are compared with the data of Eley¹⁹⁸ in Figure 25. The values used in the calculations were averages and excluded samples of anoxic waters,

samples with abnormally low oxygen concentrations, and samples with abnormal total dissolved solids.

TABLE VI

CONSTANTS USED TO CALCULATE THE PHOSPHATE
TO SATURATE HYDROXYAPATITE

Temp. °C	$pK_{ap}^{a,c}$	$pK_w^{a,c}$	$-pK_1^{a,c}$	$-pK_{12}^{a,c}$	$-p\beta_{CaHPO_4}^{b,c}$	$p\beta_{MgHPO_4}^{b,c}$
10	112.76	14.53	12.59	7.25	2.7	2.5
15	113.19	14.35	12.51	7.23		
20	113.64	14.17	12.43	7.21		
25	113.99	14.00	12.36	7.20		
30	114.40	13.83	12.29	7.19		

^aReference 60. ^bReference 82.
^cThe "p's" refer to negative logarithms to the base 10.

TABLE VII

PHOSPHATE CONCENTRATIONS NEEDED TO SATURATE
HYDROXYAPATITE IN KEYSTONE RESERVOIR

Date	Stat.	Temp.	$p\{H^+\}^a$	$p\{OH^-\}$	$p\{Ca^{++}\}$	$p\{Mg^{++}\}$	Calculated $PO_4^{-3}, mg/l$
8-20-66	5	26.8	8.27	5.67	3.00	3.19	.0007
5-14-67	5	18.1	8.48	5.76	2.98	3.23	.0008
5-28-67	5	19.2	8.12	6.08	2.95	3.22	.0017
7-8-67	5	25.0	7.89	6.11	3.17	3.52	.0037
7-29-67	4	25.5	7.68	6.30	3.18	3.57	.0087
8-20-67	4	23.9	7.61	6.43	3.14	3.47	.0115

^aReference 60

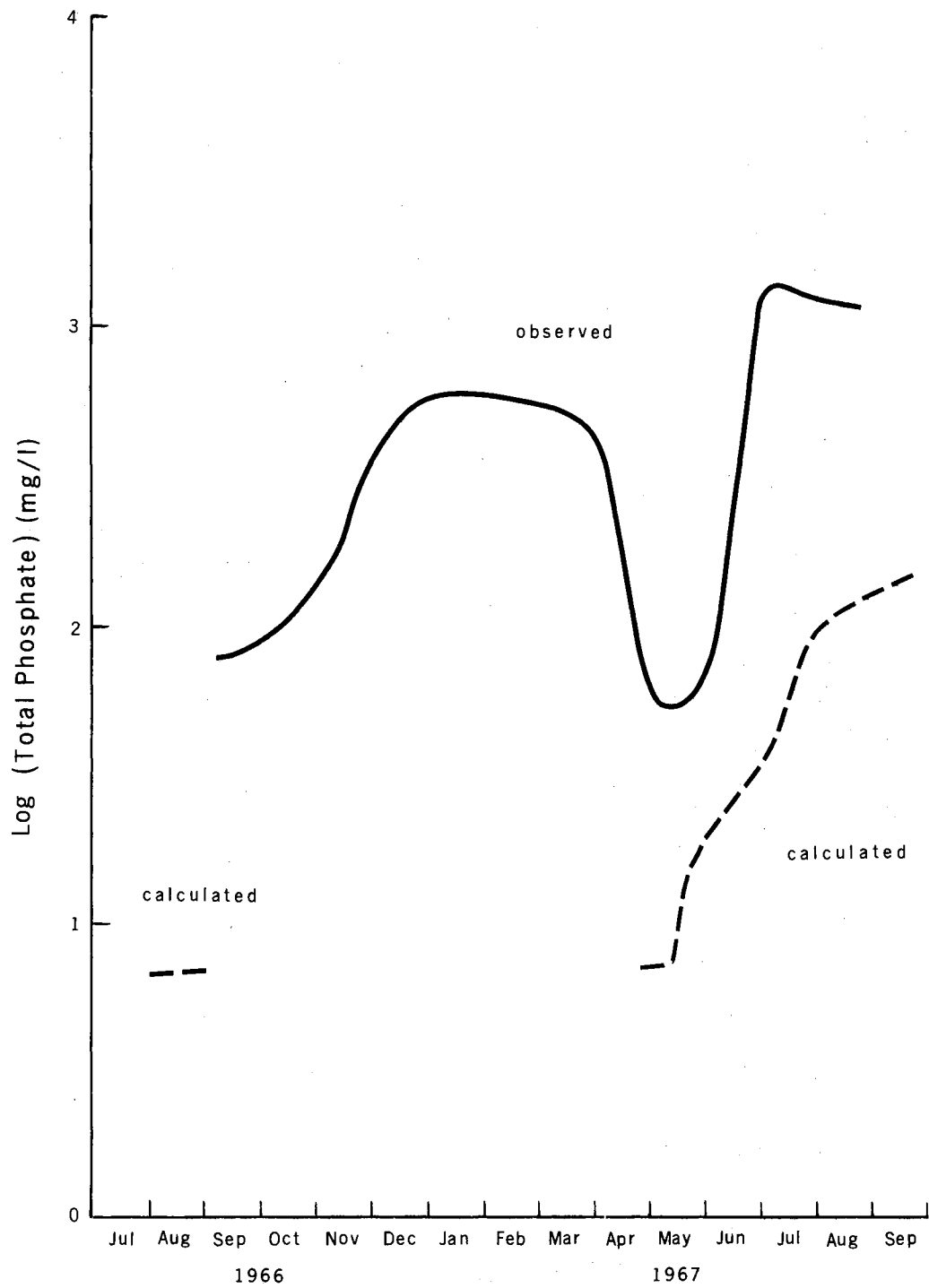


Figure 25. Phosphate Needed to Saturate Hydroxyapatite.

The calculated values show an increase of about 17 fold during this time period. In general, the waters became more dilute with respect to calcium, due to the amount of rainfall and due to the practice of releasing the saline bottom water, and the pH decreased. The overall effect was to increase the amount of phosphate required to saturate apatite.

Comparison with the observed values suggest that the waters would be super-saturated with respect to apatite by a factor of about 10. This could be a result of the slowness of the precipitation reaction or a result of systematic errors in the calculations or in the analyses.

Although this comparison is subject to a number of errors, the waters appear definitely to be saturated, or super-saturated, with respect to hydroxyapatite; and the ease that it can be precipitated under laboratory conditions would suggest that it should be precipitating from the waters. This heterogeneous reaction could control, or at least buffer, the phosphorus content in the waters of the reservoir.

Equilibrium Models

A series of equilibrium models were developed based on the history of the natural waters of Keystone Reservoir suggested above. These were (1) an evaporite model prepared by mixing the solid phases representative of the local exposed Permian rock formations with distilled water and exposing them to air with a specified partial pressure of carbon dioxide, (2) a diluted clay-calcite model prepared by diluting the solution phase from the evaporite model,

mixing the clay minerals and calcite with it, and exposing the mixture to air containing carbon dioxide, (3) a diluted clay model prepared by diluting the solution phase from the evaporite model, adding the clay minerals to it, and exposing it to air containing carbon dioxide, (4) a variable dilution clay-calcite model prepared in the same manner as the diluted clay-calcite model but the degree of dilution was allowed to vary, and (5) a variable dilution clay model which is the equivalent of the diluted clay model in which the degree of dilution was varied.

Evaporite Model

This model is of the area of the Permian rocks. The phases used to reconstruct the system were (1) gypsum, (2) dolomite, (3) calcite, (4) celestite (SrSO_4), (5) kaolinite ($\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$), (6) Sodium montmorillonite ($\text{Na}_{.66}\text{Al}_{2.66}\text{Si}_{3.33}\text{O}_{10}(\text{OH})_2$), (7) Calcium montmorillonite ($\text{Ca}_{.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10}(\text{OH})_2$), (8) the solution, and (9) air containing carbon dioxide. A number of papers report the occurrence of halite in this area, the dissolution of which adds very large amounts of sodium and chloride to the waters. However, soluble halite has been preferentially leached from the solid materials available to the surface and shallow ground waters. As a result, halite is not present in sufficient quantities to allow equilibrium with the total water masses of the area. Waters of this area that are saturated with halite represent very isolated cases and are very unique in nature. Thus halite was not considered as a phase in the model. It was considered only as a contributor to

the ionic strength of the solution phase. Gypsum, dolomite, and calcite were included because of their known occurrence in the area and because of their general association with chemical evaporites. Celestite, or strontium sulfate, was included because of its suggested association with the abundant gypsum beds.

The silicate minerals are more difficult to represent as simple chemical compounds. Both their structure and the reactions they undergo are complex and are ill-defined. Nevertheless, kaolinite, sodium montmorillonite, and calcium montmorillonite were defined by idealized formulas and were included as solid phases in the model to represent the clay minerals. Quartz was not included, since its reactions appear to be too slow in nature to be of much consequence in affecting the concentration of dissolved silica. For example, laboratory experiments show that quartz samples mixed with water solutions exhibit non-measurable dissolution after three years. Likewise, quartz does not precipitate readily. The illites could be modeled by solid phases such as a potassium mica and may undergo important reactions which regulate the concentration of potassium in the solution phase. However, they are not included in the general models and were discussed separately above in this chapter.

Ideally, the partial pressure of carbon dioxide in the solution phase should be equal to that of the gas phase. If air is the gas phase, it should be approximately $10^{-3.5}$ atmospheres. However, this is seldom observed. Natural waters are almost always supersaturated with respect to the atmospheric carbon dioxide. This is

commonly attributed to the production of carbon dioxide by the biological processes and the slow exchange with the gas phase or slow mixing of the gas phase in contact with the solution with the air masses. For the purpose of formulation, a series of models at different partial pressures of carbon dioxide were prepared to illustrate the influence of the apparent super-saturation of carbon dioxide.

The minimum number of components which must be specified to copy this system is ten, and they can be represented by (1) H_2O , (2) CO_2 , (3) CaO , (4) MgO , (5) SrO , (6) Na_2O , (7) SO_3 , (8) SiO_2 , (9) Al_2O_3 , and (10) HCl .

To calculate the equilibrium composition, the maximum number of unknown concentrations, or activities, must equal the number of independent relationships, such as equilibrium constants, concentration or stoichiometric conditions, and electroneutrality. In terms of the Gibbs phase rule, which is valid for complete equilibrium, the number of variables, F , that can be chosen independently is restricted by the minimum number of components, C , necessary to copy the equilibrium system and the number of phases, P . This is expressed by equation 54.

$$F = C + 2 - P \quad (54)$$

The restrictions imposed on the system by the various equilibrium conditions is dealt with here by the Gibbs phase rule. Only F variables can be assigned in order to define the system. This also suggests that if there are the right number of phases specified, the composition of the solution would be fixed.

For this model system, there are 10 components and 9 phases. According to the phase rule, three variables can be chosen independently. These were (1) temperature, (2) pressure, and (3) chloride ion concentration. The average temperature at Tulsa and the average temperature of the water of the reservoir was approximately 15° C., and this value was used as the temperature of the model. The pressure of the model was one atmosphere. The concentration of the chloride ion was chosen as $10^{-1.5}$ molar, which was representative of the values reported by the U.S. Geological Survey for streams in this area.¹⁴

The equilibrium reactions, the equations for the equilibrium constants for these reactions, the equation for the charge balance, and the values for the equilibrium constants are given in Table VIII. The equations for the chemical reactions are based on well-known and well-established equilibrium reactions for which values of the equilibrium constants or free energy data are available. The ion pairs were not included in the treatment to simplify the calculations. Only the charged ion pairs would have any effect on the results and would only appear in the equation for the charge balance. However, they were not present in amounts that would affect the charge balance to a large extent; and the presence of negatively charged ion pairs would tend to offset the presence of the positively charged pairs. Considering the accuracy of the thermochemical data, the non-ideality of the real system to which the results are to be compared, and the negligible effect of the approximation on the end result, the charged ion pairs were not included in the

TABLE VIII

THERMOCHEMICAL DATA AND EQUATIONS USED TO DEVELOP
CHEMICAL EQUILIBRIUM MODELS

EQUATION NUMBER	REACTIONS AND EQUATIONS
55	$H_2O = H^+ + OH^-$ $\{OH^-\}\{H^+\} = 10^{-14.35^a}$
56	$CO_2(g) + H_2O + H_2CO_3$ $\{H_2CO_3\}/P_{CO_2} = 10^{-1.33^b}$
57	$HCO_3^- + H^+ + H_2CO_3$ $\{H_2CO_3\}/\{HCO_3^-\}\{H^+\} = 10^{6.42^c}$
58	$CO_3^{--} + H^+ = HCO_3^-$ $\{HCO_3^-\}/\{H^+\}\{CO_3^{--}\} = 10^{10.43^d}$
59	$CaCO_3(s) = Ca^{++} + CO_3^{--}$ $\{Ca^{++}\}\{CO_3^{--}\} = 10^{-8.22^e}$
60	$CaMg(CO_3)_2(s) = Ca^{++} + Mg^{++} + 2CO_3^{--}$ $\{Ca^{++}\}\{Mg^{++}\}\{CO_3^{--}\} = 10^{-16.67^f}$
61	$CaSO_4 \cdot 2H_2O(s) = Ca^{++} + SO_4^{--} + 2H_2O$ $\{Ca^{++}\}\{SO_4^{--}\} = 10^{-4.44^g}$
62	$SrSO_4(s) = Sr^{++} + SO_4^{--}$ $\{Sr^{++}\}\{SO_4^{--}\} = 10^{-6.5^h}$
63	$3Na\text{-montmorillonite}(s) + 2H^+ + 8H_2O$ $= 4Kaolinite(s) + 2H_4SiO_4 + 2Na^+$ $\frac{\{Na^+\}^3\{H_4SiO_4\}^2}{\{H^+\}} = 10^{4^i}$
64	$6Ca\text{-montmorillonite}(s) + 23H_2O + 2H^+$ $= 7Kaolinite + Ca^{++} + 8H_4SiO_4$ $\frac{\{Ca^{++}\}\{H_4SiO_4\}^8}{\{H^+\}^2} = 10^{-15.4^j}$
65	$\{A^z\} = 0.5[A^z]$, $Z = \pm 2$
66	$\{A^z\} = 0.8[A^z]$, $Z = \pm 1$
67	$\{A^z\} = 1.0[A^z]$, $Z = 0$
68	$2[Ca^{++}] + [Mg^{++}] + [Sr^{++}] + [Na^+] + [H^+] = 2[CO_3^{--}] + [SO_4^{--}]$ $+ [HCO_3^-] + [OH^-] + [Cl^-]$

^aH. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 3rd ed. (A. C. S. Monograph 137), New York, N. Y., Reinhold, 1958 p. 638.

^bA. A. Markam and K. A. Kobe, *J. Am. Chem. Soc.* **63**, 449 (1941).

^cH. S. Harned and F. T. Bonner, *ibid* **67**, 1026 (1945).

^dH. S. Harned and S. R. Scholes, *ibid* **63**, 1706 (1941).

^eT. E. Larson and A. M. Buswell, *J. Am. Water Works Assoc.* **34**, 1667 (1942).

^fReference 61

^gW. M. Latimer, "Oxidation Potentials", 2nd ed., New York, N. Y., Prentice Hall, 1952.

^hReference 82

ⁱReference 68

^jReference 58

equation of electroneutrality. To further simplify the calculations, the values for the activity coefficients were assumed as 0.5 for the double charged ions, and as .8 for the single charged ions. These were representative values for solutions of the expected ionic strength. More accurate estimates of the activity coefficients could be made, but the small error introduced by this approximation and the scope of this model did not merit a more exacting treatment. Also, since activities were available from the water analyses of the reservoir for the comparison with the model, the activity coefficients would only influence the equation of electroneutrality. In this equation, the influence of the activity coefficients tend to cancel out. There are some discrepancies in the available values for the equilibrium constants, especially for the silicate minerals. In all cases, the values were chosen to be consistent with those used by other workers for natural water systems.

The system of equations was solved by combining the equations for the individual equilibrium constants to obtain the activity of the individual components in terms of the activity of the hydrogen ion and the partial pressure of carbon dioxide, substituting the results into Equation 65 or 66 to obtain the concentrations, and combining these into the equation for electroneutrality to give a higher degree polynomial equation containing only one unknown, the hydrogen ion. This equation was solved using the well-known Newton's approximation method. The concentration of the remaining components was then readily calculated. For example, Equations 55 and 56 are rearranged to obtain

$$\{\text{OH}^-\} = \frac{10^{-14.35}}{\{\text{H}^+\}} \quad (55)$$

and

$$\{\text{H}_2\text{CO}_3\} = 10^{-1.33} P_{\text{CO}_2} \quad (56)$$

Equation 69 is obtained by combining Equations 56 and 57,

$$\{\text{HCO}_3^-\} = \frac{10^{-7.75} P_{\text{CO}_2}}{\{\text{H}^+\}} \quad (69)$$

Equation 70 from 58 and 69,

$$\{\text{CO}_3^{--}\} = \frac{10^{-18.18} P_{\text{CO}_2}}{\{\text{H}^+\}^2} \quad (70)$$

Equation 71 from 59 and 60,

$$\{\text{Ca}^{++}\} = \frac{10^{9.86} \{\text{H}^+\}^2}{P_{\text{CO}_2}} \quad (71)$$

Equation 72 from 57, 60, and 70,

$$\{\text{Mg}^{++}\} = \frac{10^{-9.73} \{\text{H}^+\}^2}{P_{\text{CO}_2}} \quad (72)$$

Equation 73 from 61 and 71, and

$$\{\text{SO}_4^{--}\} = \frac{10^{-14.40} P_{\text{CO}_2}}{\{\text{H}^+\}^2} \quad (73)$$

Equation 74 from 62 and 73.

$$\{\text{Sr}^{++}\} = \frac{10^{+7.90} \{\text{H}^+\}^2}{P_{\text{CO}_2}} \quad (74)$$

Equations 70 and 71 are combined to obtain Equation 75:

$$\{\text{H}_4\text{SiO}_4\} = 10^{-8.17} P_{\text{CO}_2}^{1.25} \quad (75)$$

and Equations 64 and 75 are combined to obtain Equation 76:

$$\{\text{Na}^+\} = \frac{10^{5.17} \{\text{H}^+\}}{P_{\text{CO}_2}^{1.25}} \quad (76)$$

The activities expressed by Equations 55, 69-74, and 76, are converted to concentrations by substituting into Equations 65 and 66; the results are substituted into the equation for electroneutrality (Equation 68), and both sides are multiplied by $a_{H^+}^2$ to obtain Equation 77.

$$\begin{aligned} & \frac{4}{P_{CO_2}} \left(10^{9.96} + 10^{9.73} + 10^{7.90} \right) \{H^+\}^4 + 1.25 \left(1. + \frac{10^{5.17}}{P_{CO_2}^{1.25}} \right) \{H^+\}^3 \\ & = [Cl^-] \{H^+\}^2 + 1.25 \left(10^{-14.35} + 10^{-7.75} P_{CO_2} \right) \{H^+\} \\ & + 4P_{CO_2} \left(10^{-18.18} + 10^{-14.40} \right) \end{aligned} \quad (77)$$

The partial pressure of carbon dioxide in the gas phase and the concentration of the chloride ion ($10^{-1.5}$ molar) were specified, and the equation was solved for the activity of the hydrogen ion by Newton's approximation method. This approximation method is discussed in many other sources, such as Butler,¹¹⁵ and is not duplicated here. A General Electric Time Sharing Computer system was used for the calculation of the hydrogen ion activity. The activity of the hydrogen ion was substituted into the above equations (Equations 55, 56, 69-76) and the activities of the remaining variables calculated.

The results are shown in Table IX for several values of the partial pressure of carbon dioxide. Water analyses which would be representative of this area for ground waters and small streams were not readily available for a general comparison. However, a survey of the analyses published by the Geological Survey¹⁴ for surface waters in this area suggested that the more saline waters differ

TABLE IX

COMPOSITION OF EVAPORITE EQUILIBRIUM MODELS

All values are in moles/liter except P_{CO_2}
which is in atmospheres.

COMPONENT	CALCULATED CONCENTRATIONS					
pP_{CO_2}	3.5	3.25	3.0	2.75	2.5	2.25
pH	7.8	7.7	7.6	7.4	7.3	7.2
$p\{Ca^{++}\}$	2.2	2.2	2.2	2.2	2.2	2.2
$p[Ca^{++}]$	1.9	1.9	1.9	1.9	1.9	1.9
$p\{Mg^{++}\}$	2.4	2.4	2.4	2.4	2.4	2.5
$p[Mg^{++}]$	2.1	2.1	2.1	2.1	2.1	2.2
$p\{Sr^{++}\}$	4.2	4.2	4.2	4.3	4.3	4.3
$p[Sr^{++}]$	3.9	3.9	3.9	4.0	4.0	4.0
$p\{Na^+\}$	2.2	2.1	2.0	1.9	1.9	1.8
$p[Na^+]$	2.1	2.0	1.9	1.8	1.8	1.7
$p\{HCO_3^-\}$	3.4	3.3	3.2	3.0	2.9	2.8
$p[HCO_3^-]$	3.3	3.2	3.1	2.9	2.8	2.7
$p\{CO_3^{--}\}$	6.1	6.1	6.0	6.0	6.0	6.0
$p[CO_3^{--}]$	5.8	5.8	5.7	5.7	5.7	5.7
$p\{SO_4^{--}\}$	2.3	2.3	2.3	2.2	2.2	2.2
$p[SO_4^{--}]$	2.0	2.0	2.0	1.9	1.9	1.9
$p[H_2CO_3]$	4.8	4.6	4.3	4.1	3.8	4.6
$p[H_4SiO_4]$	3.6	3.6	3.5	3.5	3.5	3.5
pOH	6.2	6.3	6.4	6.6	6.7	6.8

from those predicted by the model by only a few tenths of a log unit or less.

Diluted Clay-Calcite Model

In this model, it was assumed that the waters from the beds of evaporite rocks flowed from the area, were diluted by waters originating from areas where the common evaporite rock forming minerals were either absent or not abundant, and were mixed with the clay minerals and calcite which were present in the suspended solids, the soils, the stream beds, and the reservoir basin.

The model was prepared by removing the solution phase of the evaporite model, diluting it by an appropriate amount, mixing it with the clay minerals and calcite, and exposing it to air containing carbon dioxide. Equilibrium was then assumed, and the composition variables were calculated using a procedure similar to that used in the evaporite model.

The specified phases were (1) solution, (2) gas or atmosphere, (3) calcite, (4) sodium montmorillonite, (5) calcium montmorillonite, and (6) kaolinite. The components which were required to reproduce the system were represented by the same 10 components used previously. According to the phase rule, six variables had to be specified to define the system. The concentration of sulfate, magnesium, strontium, chloride, temperature, and pressure were chosen. The temperature and pressure were defined at 15° C. and one atmosphere, as in the previous model. Chloride concentration was taken as the average observed chloride concentration, $10^{-1.90}$ molar, and the concentration

of magnesium, strontium, and sulfate were defined by diluting the solution phase of the evaporite model. The concentrations of the other components were determined by the new model.

The partial pressure of carbon dioxide in soil gases and in ground and surface waters is generally ten to several hundred times that of air. For the dilution model, the solution phase from an evaporite model with a carbon dioxide partial pressure of $10^{-2.25}$ atmospheres was used. Actually, there would be no significant differences in the final result using any value between $10^{-3.5}$ to $10^{-2.25}$ atmospheres since only the concentrations of sulfate, magnesium and strontium would be affected in the new model. As shown in Table IX, these varied only 0.1 log units over this partial pressure range. The degree of dilution was based on the concentration of sulfate predicted by the model and the average observed value in the reservoir during this study. Average sulfate concentration from all stations was calculated to be $10^{-2.99}$, and that predicted by the evaporite model was $10^{-1.9}$. This gives a dilution factor of $10^{-1.09}$. This factor was used to define the sulfate, magnesium, and strontium concentrations in the diluted model.

Proceeding as in the calculation in the evaporite model, substitution of Equations 55-59 and 63-65 into the equation of electro-neutrality gives equation 78:

$$\begin{aligned} \frac{4}{P_{CO_2}} 10^{9.98} \{H^+\}^4 + 1.25 \left(1 + \frac{10^{5.17}}{P_{CO_2}^{1.25}} \right) \{H^+\}^3 + 2 \left([Mg^{++}] + \right. \\ \left. + [Sr^{++}] \right) \{H^+\}^2 = (2[SO_4^{--}] + [Cl^-]) \{H^+\}^2 + 1.25(10^{-14.35} + \\ + 10^{-7.75} P_{CO_2}) \{H^+\} + 4(10^{-18.18}) P_{CO_2} \end{aligned} \quad (78)$$

Substituting the concentrations of sulfate, strontium, magnesium, and chloride into the equation ($10^{-2.99}$, $10^{-5.07}$, $10^{-3.24}$, and $10^{-1.90}$ molar), rearranging, and multiplying both sides by $\{H^+\}^2$, the final form given in Equation 79 is obtained.

$$\frac{4}{P_{CO_2}} 10^{9.96} \{H^+\}^4 + 1.25 \left(1 + \frac{10^{5.17}}{P_{CO_2}^{1.25}} \right) \{H^+\}^3 =$$

$$\left(2(-10^{-3.24} - 10^{-5.07} + 10^{-2.99}) + 10^{-1.90} \right) \{H^+\}^2$$

$$+ 1.25 (10^{-14.35} + 10^{-7.75} P_{CO_2}) \{H^+\} + 4(10^{-18.18}) P_{CO_2} \quad (79)$$

Equation 79 was solved for the hydrogen ion activity at several partial pressures of carbon dioxide by Newton's approximation method and the results substituted in Equations 55, 56, 69-71, 75 and 76 to obtain the remaining unknown activities and concentrations. The results are given in Table X as well as the average concentrations observed during this study. If a partial pressure of carbon dioxide representative of that of natural waters and of Keystone Reservoir itself is used, the agreement is excellent.

Diluted Clay Model

The x-ray diffraction studies of the reservoir suggest that calcite was very abundant in the sediments but not in the suspended matter. It was not observed in any of the suspended solids samples. In addition, the comparison of the solubility product of calcite with that observed in the reservoir suggests that the waters were usually undersaturated with respect to calcite. Although the results of the diluted clay-calcite model are not unreasonable,

TABLE X

COMPOSITION OF DILUTED CLAY - CALCITE EQUILIBRIUM MODEL

All values are in moles/liter except P_{CO_2}
which is in atmospheres.

COMPONENT	CALCULATED						OBSERVED
pP_{CO_2}	3.5	3.25	3.0	2.75	2.5	2.25	2.9
pH	8.1	8.0	7.9	7.8	7.6	7.5	7.8
$p\{Ca^{++}\}$	2.7	2.7	2.8	2.8	2.8	2.9	3.1
$p[Ca^{++}]$	2.4	2.4	2.5	2.5	2.5	2.6	2.8
$p[Mg^{++}]$	3.2	3.2	3.2	3.2	3.2	3.2	3.2
$p[Sr^{++}]$	5.1	5.1	5.1	5.1	5.1	5.1	5.1
$p\{Na^+\}$	2.5	2.4	2.3	2.2	2.2	2.1	2.0
$p[Na^+]$	2.4	2.3	2.2	2.1	2.1	2.0	1.9
$p\{HCO_3^-\}$	3.2	3.0	2.9	2.8	2.6	2.5	2.8
$p[HCO_3^-]$	3.1	2.9	2.8	2.7	2.5	2.4	2.7
$p\{CO_3^{--}\}$	5.5	5.5	5.5	5.4	5.4	5.4	5.5
$p[CO_3^{--}]$	5.3	5.3	5.3	5.1	5.1	5.1	5.2
$p\{SO_4^{--}\}$	3.3	3.3	3.3	3.3	3.3	3.3	3.3
$p[SO_4^{--}]$	3.0	3.0	3.0	3.0	3.0	3.0	3.0
$p[H_2CO_3]$	4.8	4.6	4.3	4.1	3.8	3.6	4.2
$p[H_2SiO_4]$	3.6	3.6	3.5	3.5	3.5	3.5	3.7
pOH	6.3	6.4	6.5	6.6	6.7	6.8	6.6

considering the uncertainties of the thermodynamic data and the non-ideality of nature, the values predicted for the calcium concentration by the model are about 0.3 logarithm units high. In order to examine the possibility of the insignificant contribution of calcite to the system, a model was prepared using kaolinite, sodium montmorillonite, and calcium montmorillonite as the solid phases.

Including the gas and solution phases with the three solid phases, there are a total of five phases. The same 10 components as before are used and according to the phase rule, seven variables must be, or can be, specified in order to define the system. Temperature, pressure, and the concentrations of magnesium, strontium, sulfate, and chloride are specified as 15° C., one atmosphere, and $10^{-3.24}$, $10^{-5.07}$, $10^{-2.99}$, $10^{-1.90}$ molar as above in the diluted calcite-clay model. The primary object of this model is to attempt to identify some of the regulatory processes. Any of the other concentration variables can be defined as the seventh variable, and essentially the same end result will be obtained. Calcium is chosen as the seventh variable. Based on the same dilution factor as was used for the other components, calcium concentration is set at $10^{-2.85}$ molar. Substituting these values into Equation 68, Equation 80 is obtained and solved in the same manner as above. The results are summarized in Table XI.

$$\begin{aligned}
 1.25 \left(1 + \frac{10^{5.15}}{(P_{CO_2})^{1.25}} \{H^+\}^3 \right) &= \left(2(-10^{-3.24} - 10^{-2.85} - 10^{-5.07} + 10^{-2.99}) \right. \\
 &+ 10^{-1.9} \left. \right) \{H^+\}^2 + 1.25 (10^{-14.85} + 10^{-7.75} P_{CO_2}) \{H^+\} \\
 &+ (4)(10^{-18.15}) P_{CO_2} \qquad (80)
 \end{aligned}$$

TABLE XI

COMPOSITION OF DILUTED CLAY EQUILIBRIUM MODEL
 All values are in moles/liter except P_{CO_2}
 which is in atmospheres.

COMPONENT	CALCULATED						OBSERVED
pP_{CO_2}	3.5	3.25	3.0	2.75	2.5	2.25	2.9
pH	7.6	7.6	7.6	7.5	7.5	7.4	7.8
$p[Ca^{++}]$	2.8	2.8	2.8	2.8	2.8	2.8	2.8
$p[Mg^{++}]$	3.2	3.2	3.2	3.2	3.2	3.2	3.2
$p[Sr^{++}]$	5.1	5.1	5.1	5.1	5.1	5.1	5.1
$p\{Na^+\}$	2.0	2.0	2.0	2.0	2.0	1.9	2.0
$p[Na_+]$	1.9	1.9	1.9	1.9	1.9	1.8	1.9
$p\{HCO_3^-\}$	3.6	3.4	3.2	3.0	2.8	2.6	2.8
$p[HCO_3]$	3.5	3.3	3.1	2.9	2.7	2.5	2.7
$p\{CO_3^{--}\}$	6.4	6.2	6.1	5.9	5.8	5.7	5.5
$p[CO_3^{--}]$	6.1	5.9	5.8	5.6	5.5	5.4	5.2
$p\{SO_4^{--}\}$	3.3	3.3	3.3	3.3	3.3	3.3	3.3
$p[SO_4^{--}]$	3.0	3.0	3.0	3.0	3.0	3.0	3.0
$p[H_2CO_3]$	4.8	4.6	4.3	4.1	3.8	3.6	4.2
$p[H_4SiO_4]$	3.6	3.6	3.5	3.5	3.5	3.5	3.7
pOH	6.8	6.8	6.8	6.9	6.9	7.0	6.6

Variable Dilution Clay-Calcite Model

The degree that the waters from the area of the Permian rocks are diluted will vary depending on the amount of precipitation and runoff. The next expansion of the chemical equilibrium model was to allow the degree of dilution to vary at various times which corresponds to times of observation of the reservoir properties.

The construction of the model was (1) the formulation of an evaporite model which was the same as the one above where the partial pressure of carbon dioxide was specified at $10^{-2.25}$ atmospheres, (2) the solution phase from the evaporite model was diluted by different amounts which was to model the differing degrees of dilution at given times, and (3) the formulation of a diluted clay-calcite model using the concentrations of magnesium, strontium, and sulfate defined by the first two steps.

The dissolved solids of streams can usually be directly related to flow rates. The waters in reservoirs are stored waters so that rates of inflow, outflow, or lake level are only roughly related to the dissolved solids. The chloride originates primarily in the area of the Permian rocks and does not appear to undergo any actions which would regulate its concentration thereafter except dilution. If it is assumed that the chloride ion concentrations in the waters in contact with the evaporite minerals occur in approximately proportional amounts to the other dissolved constituents, a dilution factor can be derived based on the chloride ion concentration. Applying the previously derived dilution factor of $10^{-1.08}$ to the average observed chloride concentration, $10^{-1.90}$ molar, an apparent chloride

saturation value of $10^{-8.2}$ molar is obtained. This factor is used in the proportionality equation,

$$[X] = \frac{[Cl^-_{obs}]}{10^{-8.2}} [X_{sat}] \quad (81)$$

from which the concentrations of magnesium, strontium, and sulfate can be calculated and thus specified for the diluted phase of the formulation. The quantity $[X]$ is the concentrations of magnesium, strontium, or sulfate after dilution, $[X_{sat}]$ is the corresponding concentration predicted from the evaporite model part of the formulation, and $[Cl^-_{obs}]$ is the observed chloride concentration at the particular time that the system of Keystone Reservoir is to be modeled.

The computation procedures were the same as those used above. In order to evaluate the effect of the suggested super-saturation with respect to carbon dioxide, the calculations were done where several partial pressures of carbon dioxide were specified. A tabulation of the results is given in Table XII at various chloride ion concentrations. The values of the average observed monthly concentrations of some of the major ions are plotted in Figures 26 and 27 against time as well as the values predicted by the model.

Variable Dilution Clay Model

In the same manner as the variable dilution clay-calcite model, a model similar to the diluted clay model was prepared by allowing the degree of dilution to vary. The same dilution factors used in the variable dilution clay-calcite model were applied to Ca^{++} , Mg^{++} , Sr^{++} , and SO_4^{--} . The remaining specified variables were unchanged.

TABLE XII

COMPOSITION OF VARIABLE DILUTION CLAY-CALCITE MODEL

pP_{CO_3}	pH	$p\{\text{Ca}^{++}\}$	$p\{\text{Mg}^{++}\}$	$p\{\text{Sr}^{++}\}$	$p\{\text{Na}^+\}$	$p\{\text{OH}^-\}$	$p\{\text{HCO}_3^-\}$	$p\{\text{CO}_3^{--}\}$	$p\{\text{SO}_4^{--}\}$	$p[\text{H}_2\text{CO}_3]$	$p[\text{H}_4\text{SiO}_4]$	$p[\text{Cl}^-]$
2.50	7.47	2.48	2.99	4.82	1.99	6.88	2.78	5.74	2.74	3.83	3.48	1.65
2.50	7.50	2.54	3.04	4.87	2.02	6.85	2.75	5.68	2.79	3.83	3.48	1.70
2.50	7.53	2.59	3.09	4.92	2.04	6.82	2.72	5.62	2.84	3.83	3.48	1.75
2.50	7.55	2.65	3.14	4.97	2.07	6.79	2.69	5.57	2.89	3.83	3.48	1.80
2.50	7.58	2.70	3.19	5.02	2.10	6.77	2.67	5.51	2.94	3.83	3.48	1.85
2.50	7.61	2.76	3.24	5.07	2.13	6.74	2.64	5.46	2.99	3.83	3.48	1.90
2.50	7.63	2.81	3.29	5.12	2.15	6.71	2.62	5.41	3.04	3.83	3.48	1.95
2.50	7.66	2.85	3.34	5.17	2.17	6.69	2.59	5.36	3.09	3.83	3.48	2.00
2.50	7.68	2.90	3.39	5.22	2.20	6.67	2.57	5.32	3.14	3.83	3.48	2.05
2.50	7.70	2.94	3.44	5.27	2.22	6.65	2.55	5.27	3.19	3.83	3.48	2.10
2.50	7.72	2.99	3.49	5.32	2.24	6.63	2.53	5.23	3.24	3.83	3.48	2.15
3.00	7.68	2.40	2.99	4.82	2.13	6.67	3.07	5.82	2.74	4.33	3.54	1.65
3.00	7.71	2.46	3.04	4.87	2.16	6.64	3.04	5.76	2.79	4.33	3.54	1.70
3.00	7.74	2.51	3.09	4.92	2.19	6.61	3.01	5.71	2.84	4.33	3.54	1.75
3.00	7.76	2.57	3.14	4.97	2.22	6.58	2.98	5.65	2.89	4.33	3.54	1.80
3.00	7.79	2.63	3.19	5.02	2.25	6.56	2.96	5.59	2.94	4.33	3.54	1.85
3.00	7.82	2.68	3.24	5.07	2.27	6.53	2.93	5.54	2.99	4.33	3.54	1.90
3.00	7.85	2.73	3.29	5.12	2.30	6.50	2.90	5.48	3.04	4.33	3.54	1.95
3.00	7.87	2.79	3.34	5.17	2.33	6.48	2.88	5.43	3.09	4.33	3.54	2.00
3.00	7.90	2.84	3.39	5.22	2.35	6.45	2.85	5.38	3.14	4.33	3.54	2.05
3.00	7.92	2.89	3.44	5.27	2.38	6.42	2.83	5.33	3.19	4.33	3.54	2.10
3.00	7.95	2.94	3.49	5.32	2.40	6.40	2.80	5.28	3.24	4.33	3.54	2.15
3.50	7.90	2.34	2.99	4.82	2.29	6.45	3.35	5.88	2.74	4.83	3.61	1.65
3.50	7.93	2.40	3.04	4.87	2.32	6.42	3.32	5.82	2.79	4.83	3.61	1.70
3.50	7.95	2.45	3.09	4.92	2.35	6.39	3.29	5.77	2.84	4.83	3.61	1.75
3.50	7.98	2.51	3.14	4.97	2.38	6.36	3.26	5.71	2.89	4.83	3.61	1.80
3.50	8.01	2.56	3.19	5.02	2.40	6.34	3.24	5.66	2.94	4.83	3.61	1.85
3.50	8.04	2.62	3.24	5.07	2.43	6.31	3.21	5.60	2.99	4.83	3.61	1.90
3.50	8.07	2.67	3.29	5.12	2.46	6.28	3.18	5.55	3.04	4.83	3.61	1.95
3.50	8.09	2.73	3.34	5.17	2.49	6.26	3.16	5.49	3.09	4.83	3.61	2.00
3.50	8.12	2.78	3.39	5.22	2.51	6.23	3.13	5.44	3.14	4.83	3.61	2.05
3.50	8.14	2.83	3.44	5.27	2.54	6.20	3.10	5.39	3.19	4.83	3.61	2.10
3.50	8.17	2.88	3.49	5.32	2.56	6.18	3.08	5.34	3.24	4.83	3.61	2.15

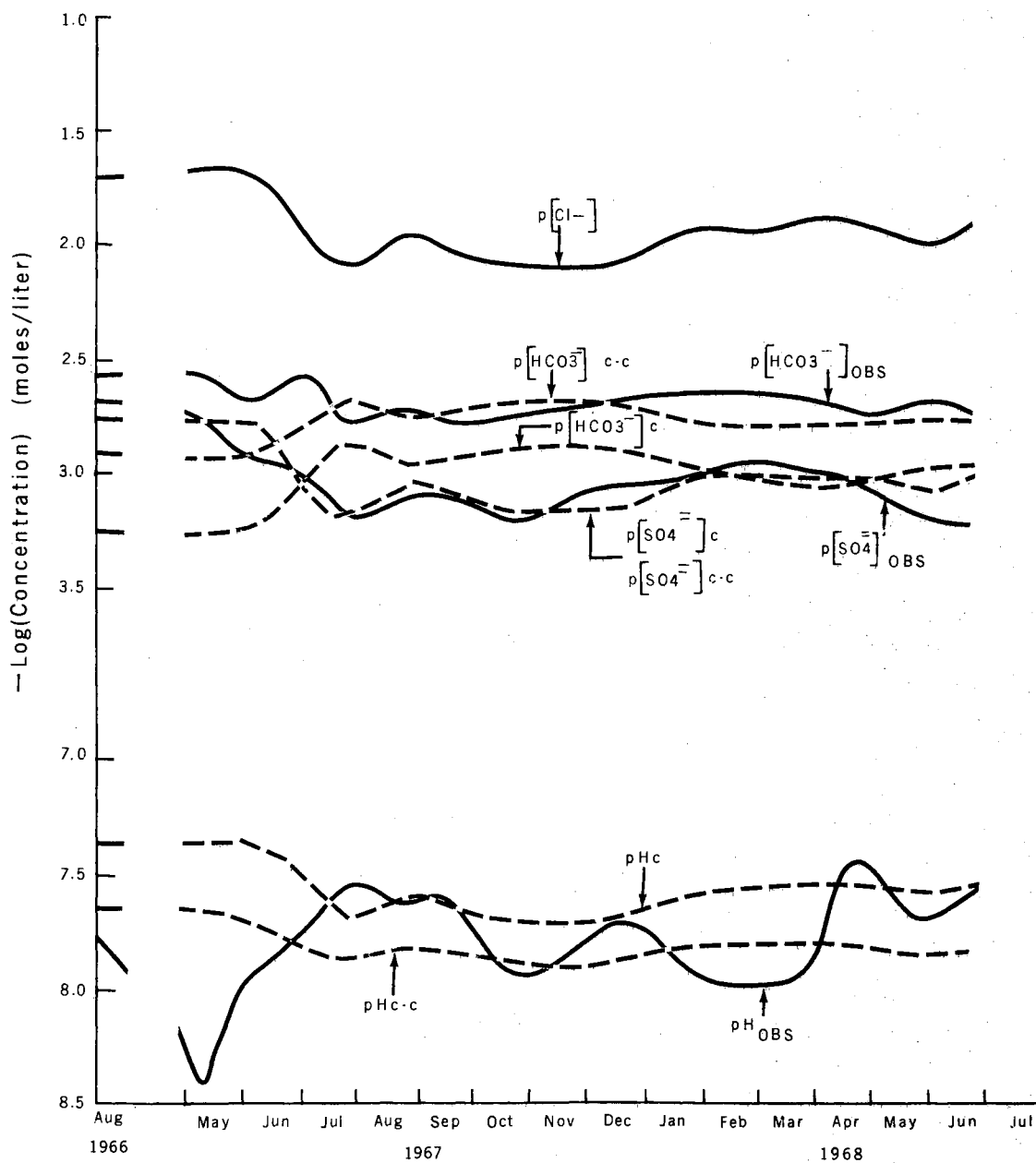


Figure 26. Comparison of Observed Concentrations of Major Anions and pH with Concentrations Calculated from the Variable Dilution Equilibrium Models. Subscripts c-c, c, and OBS refer to clay-calcite model, clay model, and observed values. Partial pressure of carbon dioxide was $10^{-2.9}$ atmospheres.

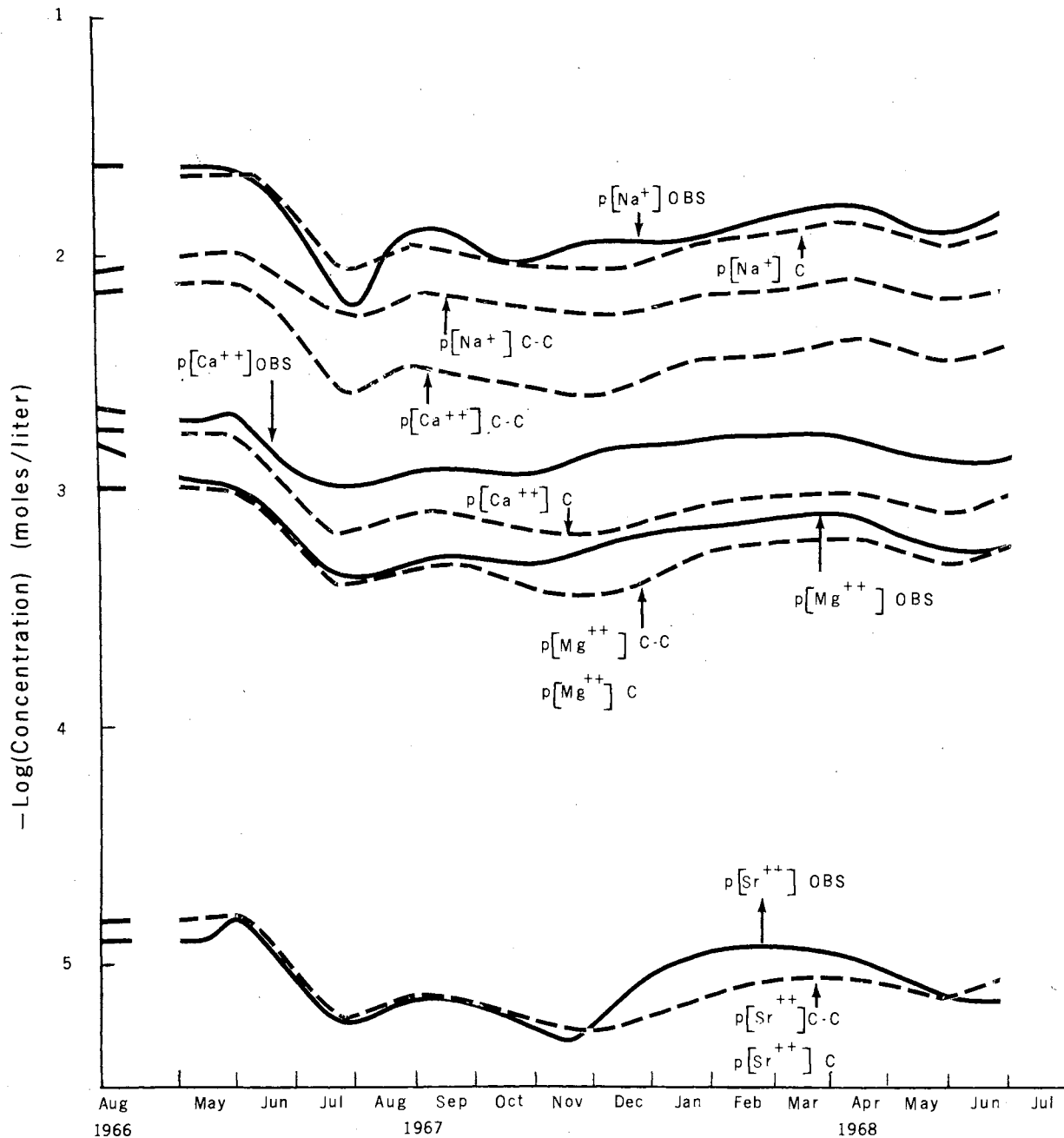


Figure 27. Comparison of Observed Concentrations of the Major Cations with Concentrations Calculated from the Variable Dilution Models. Subscripts OBS, C-C and C refer to the observed, clay-calcite model, and clay model. The partial pressure of carbon dioxide was $10^{-2.9}$ atmospheres.

The results are given in Table XIII and are plotted in Figures 26 and 27.

Discussion of Equilibria of Keystone Reservoir
Natural Water System

Considering the state of our knowledge of the solution chemistry of sedimentary minerals under laboratory conditions, and especially under natural conditions, as well as our capabilities to describe the chemistry of the natural water system of Keystone Reservoir, the agreement between the observed data and either the clay-calcite models or the clay models are quite good. The data probably fit the clay models best; but the widespread occurrence of calcite in the system would suggest that the clay-calcite model would be the one most likely to be approached. In short, the comparison is perhaps better than one could hope for. It would definitely indicate that the composition of the waters is determined by definite chemical reactions, which include the solid phases, that are rapid enough to at least approach a state of chemical equilibrium. There is no indication that the composition of the waters is determined merely by chance. The comparison is actually better than analyses often obtained for water systems from different laboratories.

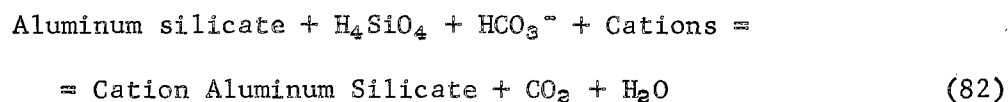
Equilibrium between the carbon dioxide in air, the gas phase, and the solution does not appear to be a good assumption. This is probably due to the slow rate of mixing and the slow exchange between the two phases. In the formulation of the models, a series of solutions using several partial pressures of carbon dioxide in the gas

TABLE XIII

COMPOSITION OF VARIABLE DILUTION CLAY MODEL

pP_{CO_2}	pH	$p[Ca^{++}]$	$p[Mg^{++}]$	$p[Sr^{++}]$	$p[Na^+]$	$p\{OH^-\}$	$p\{HCO_3^-\}$	$p\{CO_3^{--}\}$	$p[SO_4^{--}]$	$p[H_2CO_3]$	$p[H_4SiO_4]$	$p[Cl^-]$
3.50	7.39	2.76	2.99	4.82	1.78	6.96	3.86	6.90	2.74	4.83	3.61	1.65
3.50	7.43	2.81	3.04	4.87	1.83	6.91	3.81	6.81	2.79	4.83	3.61	1.70
3.50	7.48	2.86	3.09	4.92	1.88	6.86	3.76	6.71	2.84	4.83	3.61	1.75
3.50	7.53	2.91	3.14	4.97	1.93	6.81	3.71	6.61	2.89	4.83	3.61	1.80
3.50	7.58	2.96	3.19	5.02	1.98	6.77	3.67	6.51	2.94	4.83	3.61	1.85
3.50	7.63	3.01	3.24	5.07	2.02	6.72	3.62	6.42	2.99	4.83	3.61	1.90
3.50	7.68	3.06	3.29	5.12	2.07	6.67	3.57	6.32	3.04	4.83	3.61	1.95
3.50	7.72	3.11	3.34	5.17	2.12	6.62	3.53	6.23	3.09	4.83	3.61	2.00
3.50	7.77	3.16	3.39	5.22	2.16	6.58	3.48	6.14	3.14	4.83	3.61	2.05
3.50	7.81	3.21	3.44	5.27	2.21	6.53	3.43	6.05	3.19	4.83	3.61	2.10
3.50	7.86	3.26	3.49	5.32	2.25	6.49	3.39	5.96	3.24	4.83	3.61	2.15
2.50	7.24	2.76	2.99	4.82	1.76	7.11	3.01	6.20	2.74	3.83	3.48	1.65
2.50	7.28	2.81	3.04	4.87	1.80	7.06	2.96	6.11	2.79	3.83	3.48	1.70
2.50	7.33	2.86	3.09	4.92	1.85	7.02	2.92	6.02	2.84	3.83	3.48	1.75
2.50	7.37	2.91	3.14	4.97	1.89	6.98	2.88	5.94	2.89	3.83	3.48	1.80
2.50	7.41	2.96	3.19	5.02	1.93	6.94	2.84	5.86	2.94	3.83	3.48	1.85
2.50	7.45	3.01	3.24	5.07	1.96	6.90	2.80	5.78	2.99	3.83	3.48	1.90
2.50	7.48	3.06	3.29	5.12	2.00	6.86	2.76	5.71	3.04	3.83	2.48	1.95
2.50	7.52	3.11	3.34	5.17	2.04	6.83	2.76	5.64	3.09	3.83	3.48	2.00
2.50	7.55	3.16	3.39	5.22	2.07	6.80	2.70	5.58	3.14	2.83	3.48	2.05
2.50	7.58	3.21	3.44	5.27	2.10	6.77	2.67	5.52	3.19	3.83	3.48	2.10
2.50	7.61	3.26	3.49	5.32	2.13	6.74	2.64	5.46	3.24	3.83	3.48	2.15
3.00	7.32	2.76	2.99	4.82	1.77	7.03	3.43	6.54	2.74	4.33	3.54	1.65
3.00	7.36	2.81	3.04	4.87	1.82	6.98	3.38	6.45	2.79	4.33	3.54	1.70
3.00	7.41	2.86	3.09	4.92	1.87	6.94	3.34	6.35	2.84	4.33	3.54	1.75
3.00	7.46	2.91	3.14	4.97	1.92	6.89	3.29	6.26	2.89	4.33	3.54	1.80
3.00	7.51	2.96	3.19	5.02	1.96	6.84	3.24	6.17	2.94	4.33	3.54	1.85
3.00	7.55	3.01	3.24	5.07	2.00	6.80	3.20	6.08	2.99	4.33	3.54	1.90
3.00	7.59	3.06	3.29	5.12	2.05	6.75	3.15	5.99	3.04	4.33	3.54	1.95
3.00	7.63	3.11	3.34	5.17	2.09	6.71	3.11	5.91	3.09	4.33	3.54	2.00
3.00	7.67	3.16	3.39	5.22	2.13	6.67	3.07	5.83	3.14	4.33	3.54	2.05
3.00	7.71	3.21	3.44	5.27	2.17	6.63	3.03	5.75	3.19	4.33	3.54	2.10
3.00	7.75	3.26	3.49	5.32	2.21	6.60	3.00	5.68	3.24	4.33	3.54	2.15

phase were used to allow for this deviation from ideality. Another manner to express this effect, and perhaps a more correct way, is to remove the gas phase from the model and specify the partial pressure of carbon dioxide in the solution phase. The same end result would be obtained either way. Carbon dioxide is used in photosynthesis and is produced by the biological respiratory processes in the soils, sediments, and in the waters during all phases of its development. The influence of the biota on the carbon dioxide concentration cannot be denied. In addition, carbon dioxide can be formed by the dissolution of the carbonate minerals and reactions of the dissolved carbonates. Also, the aluminum silicate clay minerals can act as pH regulators. These silicate reactions have been postulated to approach equilibrium in the ocean and have been postulated to regulate the partial pressure of carbon dioxide in the earth's atmosphere. These reactions can be illustrated by Equation 82.^{76,77}



If this type of reaction is coupled with the slow exchange of carbon dioxide between the liquid and gas phases, it could contribute to the observed super-saturation. As an illustration, waters originating from silicate rocks usually have relatively high concentrations of bicarbonate and dissolved silica. If these waters are mixed with waters containing high concentrations of cations, such as the waters originating from the evaporite rocks, the reaction shown by Equation 82 will be shifted to produce carbon dioxide. If the

exchange with the gas phase is slow, the waters will appear to be super-saturated with carbon dioxide compared to the atmospheric carbon dioxide.

The pH and bicarbonate predicted by the model are definitely within the range of the observed values; but their variations with dilution, or time, are not always in good agreement. At least three factors could contribute to this observation. The first factor is the partial pressure of carbon dioxide which would influence these constituents more directly than the other components. In general, lower concentrations of hydrogen and bicarbonate ions occur with lower observed concentrations of carbon dioxide. A possible exception might be the data from August, 1966, when low concentrations of carbon dioxide occurred in the epilimnion and quite high values occurred in the hypolimnion. Overall, this may be only an indicator rather than the cause of the observed trends. An average temperature was used for the model and comparison data. The equilibrium reactions and the solubility of carbon dioxide are all temperature dependent. An obvious extension of these models would be to allow the temperature to vary as well as the degree of dilution. Due to insufficient data for the complete system, this was not attempted here. Nevertheless, the lower solubility of carbon dioxide at higher temperatures could partially account for some of the deviations, such as the lower hydrogen ion and bicarbonate values in the early observations. The most fundamental explanation for the deviations is the lack of chemical equilibrium in the system or inadequate phases used to model the real system.

The concentrations of sulfate, magnesium, and strontium are modeled quite well by the dilution treatments. Not only do the absolute values agree well, the general trends are followed quite closely.

The values for calcium predicted by the clay-calcite model are higher than the observed values, while those specified by dilution in the clay model are lower. The assumption in the clay model is that the calcium concentration in the waters is determined chiefly by the calcium added to the waters from the Permian rocks; and since the hydrogen ion concentration is a negligible amount compared to the calcium ion concentration, the ion exchange reaction would not influence the calcium concentration significantly. However, there is "fixed acid" present in the carbonate and silicate systems. This could be responsible for the low calcium values calculated by the clay model. If the calcium concentration is specified as that observed in the reservoir, higher bicarbonate and lower sodium and hydrogen concentrations would be predicted by the clay model. The actual situation would be expected to be somewhere between these two models; but the clay-calcite model should be approached more closely much more of the time. The essential features of the trends predicted by the varying degrees of dilution are followed closely, however. The equilibrium constant for the reaction between calcium montmorillonite and kaolinite is probably known with the least certainty. This comparison may suggest an error in the thermochemical data. Also, sodium montmorillonite and calcium montmorillonite are assumed as two separate phases. It may be more appropriate to count these as one phase. The above formulation is

equivalent to the system where there is only one montmorillonite phase with the additional condition specified in order to define the system that the amount of the two forms of montmorillonite are equal. This would seem to be an appropriate assumption.

The dissolved silica appears to be slightly undersaturated with respect to the aluminum silicate minerals by less than .2 logarithm units. This is a reasonably close agreement but may further suggest inadequacies in our knowledge of the silicate system.

Equilibrium calculations suggest that the inorganic phosphate in the system should increase significantly from August, 1966, to August, 1967; but they also suggest that the waters contain a very large excess of phosphate. The equilibrium reactions of the phosphate system have received very little study and much remains to be learned. Considerations of the heterogeneous inorganic phosphate reactions may offer some valuable insight into the phosphorus cycle in natural water systems.

In all the equilibrium treatments above, they must be considered as a rough approximation. The desired equilibrium data is not always available, some is of questionable quality, and where abundant data are available, a wide range of values almost always exist. In all the treatments above, thermochemical data which were consistent with that used by other workers were applied. Also, the methods used to describe the natural system may not be adequate for a rigid thermodynamic treatment. This includes the water analyses, such as the analytical chemical procedures, the instability of stored samples, and the problems and errors of in situ or field analyses, poor

sample representation, such as poor spacial and time representation, and the solid phases used to model the system. For example, the pH and alkalinity are quite critical in the equilibrium calculations used. These can be measured very accurately under carefully controlled laboratory conditions. However, measurements under field conditions are subject to many errors; and if the samples are stored, they are subject to change. Barnes¹¹⁶ has pointed out some of the probable errors in field pH measurements and noted that errors of more than 0.5 pH units can easily result. Examples of the processes causing changes in the bicarbonate ion concentration and pH which readily occur upon storage are the solution or dissolution of carbon dioxide, shifts in the position of the equilibrium of the carbonate due to temperature changes, and the actions of bacteria in a container that provides a large surface area which can promote their action.

In no natural water system is complete equilibrium ever obtained. This is obvious if processes such as the conversion of solar energy into chemical energy by photosynthesis, the action of wind to produce waves and currents, and the large influxes of masses of water and other materials into natural systems are considered. Nevertheless, equilibrium represents the direction that all the chemical reactions must be proceeding. The lack of total equilibrium in nature probably represents the greatest cause of deviations observed above, especially considering the small size and the average lifetime of the system.

Although the treatment may not be as exacting as some may desire, the results are definitely reasonable. Many of the micro-processes

are blurred by this type of treatment, and refinements will be available only when more and better data become available. This also represents what must be a prerequisite for any dynamic model to be developed for the reactions in the system.

CHAPTER VII

MASS TRANSFER MODEL

It was suggested in Chapter V that after August, 1966, the water from the Cimarron River flowed along the bottom layers of the Cimarron arm of the reservoir and out the lower gates of the dam; while the water from the Arkansas River spread out nearly uniformly at all depths in the Arkansas arm and flowed up the Cimarron arm in the upper layers considerable distances before sinking toward the outlet at the bottom of the dam. When it is considered that the water from the Cimarron River contains four times as much dissolved solids and that its flow is generally one-fifth that of the Arkansas River, this flow pattern could account for the observed distribution of the dissolved solids in the reservoir. The observations of the dissolved solids were treated in Chapter V.

In an attempt to model these essential features, a mass transfer model was considered. As a first approximation, it was assumed that the distribution of the conservative chemical constituents could be determined by the flow of water through the reservoir, or the currents in the reservoir, and these currents are a result of the forced convection of water masses into and out of the reservoir. Fluid was forced into the system at locations which correspond to the influxes from the Cimarron and Arkansas Rivers and forced from

the system at the location which corresponds to the release of water through the lower gates of the dam.

This type of mathematical model is limited in several ways. For example, mass transport phenomena alone is extremely complex, and many simplifying assumptions must be made in order to obtain solutions. However, the mathematical simulation of the various mechanisms occurring in natural systems could be a powerful tool to aquatic scientists. In the models, these mechanisms are easy to manipulate and the models facilitate their study. Also, these mathematical models will be the basis of predictive models of the water quality of natural systems.

Formulation of the Problem

Development of the Convection and Continuity Equations

The mass transfer equation of the distribution of a substance in the system is given by Equation 83, where c is the instantaneous concentration of the substance at any point (x, y, z) , V_x , V_y , and V_z are the instantaneous velocities in the x , y , and z directions at the point, D_x , D_y and D_z are the diffusion coefficients and R is the rate of production of c .

$$\frac{\partial c}{\partial t} + V_x \frac{\partial c}{\partial x} + V_y \frac{\partial c}{\partial y} + V_z \frac{\partial c}{\partial z} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} + R \quad (83)$$

The two-dimension convection equation for the conservative substance c in which the convective terms are large compared to the diffusion or turbulent transport terms is given by Equation 84.

$$\frac{\partial c}{\partial t} + V_x \frac{\partial c}{\partial x} + V_y \frac{\partial c}{\partial y} = 0 \quad (84)$$

A good approximation of the flow pattern, that is the velocities in the x and y directions at any point in the system, can frequently be obtained by solving the equations of change for potential flow in the case of irrotational steady flow of an ideal fluid. The equation of continuity for the two-dimensional, irrotational steady flow of an ideal fluid is given by Equation 85.

$$\frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} = 0 \quad (85)$$

It is easier to work in terms of a velocity potential rather than the terms of the velocity components V_x and V_y . The velocity potential, ϕ , is defined by Equations 86 and 87, and it satisfies the two-dimension Laplace Equation (Equation 88).

$$V_x = - \frac{\partial \phi}{\partial x} \quad (86)$$

$$V_y = - \frac{\partial \phi}{\partial y} \quad (87)$$

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0 \quad (88)$$

The Laplace Equation can be used to construct a set of equipotential lines ($\phi(x,y) = \text{constant}$) which describes the ideal flow problem.

The expressions given above are developed in standard texts on transfer phenomena such as that by Bird, Steward, and Lightfoot.¹¹⁷ The ideal fluid used is presumed to be incompressible, to have constant density, and to have no viscosity. This is an idealized situation and does not exist; but the assumption is helpful and is

reasonable for systems the size of Keystone Reservoir. The flow of a real fluid introduces the effect of viscosity which results in the development of shear stresses between neighboring fluid particles. Liquids are relatively incompressible and are generally treated as wholly incompressible. Steady flow is one in which all conditions at any point in a stream remain constant with respect to time, but the conditions may be different at different points. Irrotational flow may be briefly described as flow in which each element of the moving fluid suffers no net rotation from one instant to the next with respect to a given frame of reference.

Geometric Considerations

Figure 28 represents the geometry of the problem. The reservoir was modeled by a basin of a constant width and of depth increasing uniformly from the head to a maximum depth at the dam. The two arms of the reservoir were symmetrical.

Fluid was injected into the head of the Cimarron arm at some rate, Q . At the head of the Arkansas arm, fluid was injected at a rate of five times that of the Cimarron arm ($5Q$). The fluid was removed from the bottom of the basin at a rate to conserve mass ($6Q$).

Plan of Attack

An approach to the problem can be considered as composed of the following steps. These are: (1) determine the velocity potential at any point in the reservoir for the case of irrotational steady

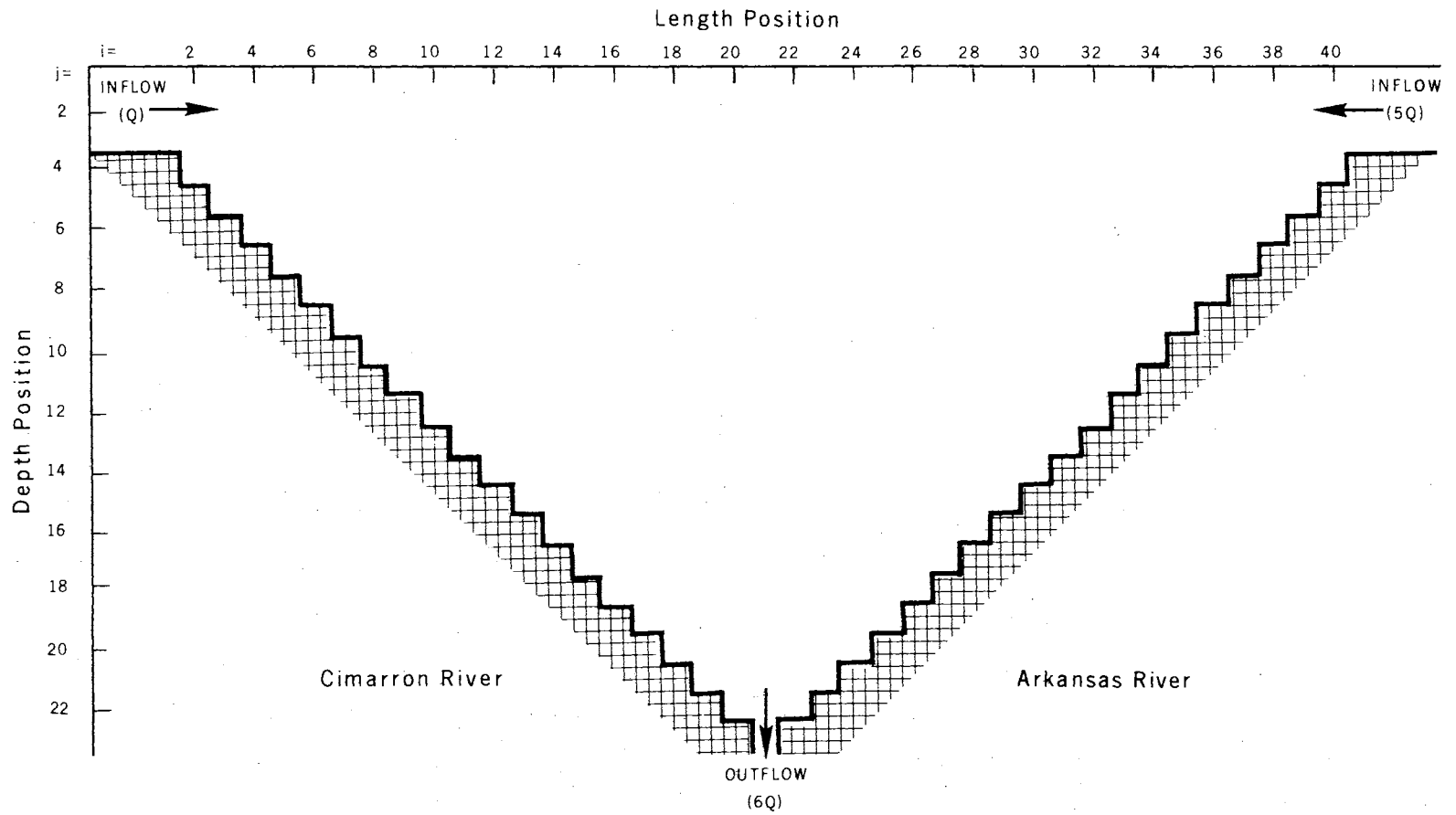


Figure 28. Geometric Configuration of the Mass Transfer Model of Keystone Reservoir.

flow of an ideal fluid using Equation 88, (2) determine the velocity components at any point from the calculated velocity potentials using Equations 86 and 87, and (3) using the velocity components, determine the concentration of the conservative constituent at any point in the reservoir at any time from Equation 84. In this work, the first two steps are completed and an approach to the third is suggested.

Calculation of Velocity Potentials

The partial differential equation which describes the velocity potential at any point in the system was given by Equation 88. The boundary conditions are:

$$\frac{\partial \phi}{\partial y} = 0 \text{ at } j = 1/2, 1 \leq i \leq i_{\max}$$

$$\frac{\partial \phi}{\partial y} = 0 \text{ at } j = j_d, 0 \leq i \leq (21-1/2)$$

$$\frac{\partial \phi}{\partial y} = 0 \text{ at } j = j_d, (21 + 1/2) \leq i \leq i_{\max}$$

$$\frac{\partial \phi}{\partial y} = -\frac{Q_{out}}{\Delta x} \text{ at } j \geq (22+1/2), (21-1/2) < i < (21+1/2) \quad (89)$$

$$\frac{\partial \phi}{\partial x} = -\frac{Q_{in1}}{3\Delta y} \text{ at } i \leq 0, 1/2 < j < 3+1/2$$

$$\frac{\partial \phi}{\partial x} = 0 \text{ at } i = i_d, 3+1/2 \leq j \leq 22+1/2$$

$$\frac{\partial \phi}{\partial x} = -\frac{Q_{in2}}{3\Delta y} \text{ at } i \geq i_{\max}; 1/2 < j < 3+1/2$$

where i and j are the length and depth positions, $i_{\max} = 41$, $j_{\max} = 22$, j_d is the depth position at the bottom of the system at $i = i_d$, and Q_{out} , Q_{in1} , and Q_{in2} are the flow rates out, into the Cimarron arm,

and into the Arkansas arm. The subscript max refers to the maximum length and depth positions. The distances between the length and depth positions are Δx and Δy .

Numerical approximations to solutions of this fluid flow equation in two-space dimensions may be obtained by the stepwise solution of an associated difference equation. Two major schemes are normally employed for the numerical approximations of partial differential equations. These are the explicit scheme and the implicit scheme. The explicit difference equations are simple to solve but require an uneconomically large number of time steps of limited size. Many implicit difference equations do not limit the time step but require at each time step the solution by iteration of large sets of simultaneous equations.

To avoid these difficulties, the alternating direction implicit method (ADI) of Peacemen and Rachford^{11a} was used to iterate to the solution of the Laplace equation. Each stage of the iteration may be regarded as a time step of an unsteady state problem where the starting values used for the first iteration correspond to the initial condition. If one of the second derivatives, for example, $\partial^2 \Phi / \partial x^2$, is replaced by a second difference equation evaluated in terms of the unknown values of Φ , while the other derivative, $\partial^2 \Phi / \partial y^2$, is replaced by a second difference evaluated in terms of known values of Φ , sets of simultaneous equations are formed that can be solved without iteration. In this case, these equations are implicit in the x-direction. If the procedure is then repeated for a second time step of equal size, with the difference equations implicit in the y direction, the overall procedure for the two time steps is stable.

Thus, two difference equations are used--one for the first time step and the other for the second time step of equal size. In the first time step, it is implicit in one direction, e.g. x, and explicit in the other (y). In the next step, the directions are alternated and it becomes implicit in the y direction and explicit in the x direction.

The difference equation for the unsteady state problem (Equation 90) for the first time step, or for odd time steps, is given in Equation 91. Central differences are used to represent the second order differential terms and forward differences are used to represent the first order term.

$$\frac{\partial \phi}{\partial t} = \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \quad (90)$$

$$\begin{aligned} \frac{\phi_{i,j}^{n+1} - \phi_{i,j}^n}{\Delta t} = & \frac{Kr_{i,j} \frac{\phi_{i,j+1}^{n+1} - \phi_{i,j}^{n+1}}{(\Delta x)} - Kl_{i,j} \frac{\phi_{i,j}^{n+1} - \phi_{i,j-1}^{n+1}}{(\Delta x)}}{\Delta x} \\ + & \frac{Ka_{i,j} \frac{\phi_{i,j+1}^n - \phi_{i,j}^n}{\Delta y} + Kb_{i,j} \frac{\phi_{i,j}^n - \phi_{i,j-1}^n}{\Delta y}}{\Delta y} \\ + & G_{i,j} \end{aligned} \quad (91)$$

The values of i and j represent distance positions in the x and y directions and n represents time steps; and i, j, and n are integers. For example, $x = (i-1)\Delta x$, $y = (j-1)\Delta y$, and $t = n\Delta t$.

The equation for the second time step, or all even time steps, is:

$$\begin{aligned}
\frac{\phi_{i,j}^{n+2} - \phi_{i,j}^{n+1} - \phi_{i,j}^{n+1}}{\Delta t} &= Kr_{i,j} \frac{\phi_{i+1,j}^{n+1} - \phi_{i,j}^{n+1}}{\Delta x} - Kl_{i,j} \frac{\phi_{i,j}^{n+1} - \phi_{i-1,j}^{n+1}}{\Delta x} \\
+ \frac{Ka_{i,j} \frac{\phi_{i,j+1}^{n+2} - \phi_{i,j}^{n+2}}{\Delta y} - Kb_{i,j} \frac{\phi_{i,j}^{n+2} - \phi_{i,j}^{n+2}}{\Delta y}}{\Delta y} \\
+ G_{i,j} & \tag{92}
\end{aligned}$$

The terms $Kr_{i,j}$, $Kl_{i,j}$, $Ka_{i,j}$, $Kb_{i,j}$ and $G_{i,j}$ are terms used to define the boundary conditions. $G_{i,j}$ is a source term and is defined at points of inflow and outflow by $G = Q/\Delta x \Delta y \Delta z$ where Q is the volume flow rate and Δz is the width of the system. All other values of $G_{i,j}$ are zero. At the boundaries, $\Delta\phi/\Delta x = \Delta\phi/\Delta y = 0$. For ease of computer programming, this is defined by the dimensionless constants Kr , Kl , Ka , or Kb . At the last grid point inside the system on the right hand side and those to the right of them outside the system, $Kr_{i,j} = 0$. This sets the term $\frac{\phi_{i+1,j} - \phi_{i,j}}{\Delta x} = 0$ at the boundary, that is, defines a no-flow boundary. Similarly, $Kl_{i,j}$, $Ka_{i,j}$, and $Kb_{i,j}$ are set equal to zero at the points inside the system the furthest left, above, and below which are no flow boundaries. All other values inside the system are set equal to one.

The equations may be arranged in the following form which is more suitable for calculation. Equation 91 becomes 93.

$$\begin{aligned}
Kr_{i,j} \phi_{i+1,j}^{n+1} - (Ka_{i,j} + Kb_{i,j} + \rho) \phi_{i,j}^{n+1} + Kl_{i,j} \phi_{i-1,j}^{n+1} &= \\
= - \left(\frac{\Delta x}{\Delta y} \right)^2 (Ka_{i,j} \phi_{i,j+1}^n - (Ka_{i,j} + Kb_{i,j} - \rho \left(\frac{\Delta y}{\Delta x} \right)^2) \phi_{i,j}^n) &+ \\
+ Kb_{i,j} \phi_{i,j-1}^n + G_{i,j} (\Delta y)^2 & \tag{93}
\end{aligned}$$

Equation 92 becomes 94.

$$\begin{aligned}
 & Ka_{i,j} \phi_{i,j}^{n+2} - \left(Ka_{i,j} + Kb_{i,j} + \rho \left(\frac{\Delta y^2}{\Delta x^2} \right) \right) \phi_{i,j}^{n+2} + \\
 & + Kb_{i,j-1}^{n+1} = - \left(\frac{\Delta y}{\Delta x} \right)^2 \left(Kr_{i,j} \phi_{i+1,j}^{n+1} - (Kr_{i,j} + Kl_{i,j} - \rho) \phi_{i,j}^{n+1} + \right. \\
 & \left. + Kl_{i,j} \phi_{i,j-1}^{n+1} + G_{i,j} (\Delta x)^2 \right) \quad (94)
 \end{aligned}$$

The parameter ρ is an iterative parameter and is equal to $\frac{(\Delta x)^2}{\Delta t}$. This sets the size of the time steps. Following the suggestion of Peaceman and Rachford,¹²⁸ the optimum value of ρ for rapid convergence is defined by Equation 95,

$$\rho = 4 \sin \frac{2(2k+1)\pi}{N} \quad (95)$$

where k is the number of iterative cycles completed, that is the number of pairs of time steps, and N is the larger of the number of distance steps in the x or in the y direction. There are $N-2$ iterations (or $2(N-2)$ time steps) required for convergence. In this study, the procedure was repeated several times to improve the approximated solution. The results from one complete calculation were used as the initial condition for the next complete calculation series.

For each mesh point, depending on whether the time step is even or odd, either Equation 93 or Equation 94 can be written in finite difference representation, where the left side of the equation contains three unknowns and the right side contains known values. If there are M mesh point-lines, with N mesh points along each line, and the equation is written for every point, N simultaneous equations for each line, including initial and boundary conditions, are obtained.

For M lines, there are $N \times M$ simultaneous equations and they contain $M \times N$ unknowns. The process thus requires solving N simultaneous equations M times or M simultaneous equations N times. The solution of these equations can be obtained in a straightforward manner. For example, consider that the use of this equation at each time step leads to M sets of N simultaneous equations of the form:

$$B_0 \Phi_0 + C_0 \Phi_1 = D_0,$$

$$A_r \Phi_{r-1} + B_r \Phi_r + C_r \Phi_{r+1} = D_r \quad (1 \leq r \leq N-2) \quad (96)$$

$$A_{N-1} \Phi_{N-2} + B_{N-1} \Phi_{N-1} = D_{N-1}$$

let

$$W_0 = B_0, \quad (1 \leq r \leq N-1) \quad (97)$$

$$W_r = B_r - A_r b_{r-1}$$

$$b_r = \frac{C_r}{W_r} \quad (0 \leq r \leq N-2) \quad (98)$$

$$g_0 = \frac{D_0}{W_0}$$

$$g_r = \frac{D_r - A_r g_{r-1}}{W_r} \quad (1 \leq r \leq N-1) \quad (99)$$

The solution becomes

$$\Phi_{N-1} = g_{N-1}$$

$$\Phi_r = g_r - b_r \Phi_{r+1} \quad (0 \leq r \leq N-2) \quad (100)$$

Thus, w, b, and g are computed in order of increasing r and Φ is computed in order of decreasing r.

In general, Equations 93 and 94, along with associated formulations, were used for alternate stages of the iteration, with n representing the number of stages already carried out, until the approximated

solution was obtained.

The velocities at any point (x, y) can readily be calculated from the velocity potentials by the finite difference representations of Equations 86 and 87. The central difference representations used in this work are given by Equations 101 and 102.

$$V_{x_i, j} = \frac{\Phi_{i+1, j} - \Phi_{i-1, j}}{2(\Delta x)} \quad (101)$$

$$V_{y_i, j} = \frac{\Phi_{i, j+1} - \Phi_{i, j-1}}{2(\Delta y)} \quad (102)$$

The boundary conditions remain as those stated above in Equation 89.

Results and Discussions of Model Calculations

The computer program used for the calculations and the results of the velocity potential and velocity calculations are listed in Appendix D. Subroutines SOLUI and SOLUJ for the solution of the simultaneous equations were derived from that of Kazemi.¹¹⁹ The values for the length, depth and width intervals $(\Delta x, \Delta y, \text{ and } \Delta z)$ were 5., 5., and 5. The flow rates, Q_{in1} , Q_{in2} , and Q_{out} were 10., 50., and 60. These values do not necessarily exactly duplicate the real system but are adequate to illustrate the mechanisms to be modeled.

The velocity potentials shown in Figure 29 illustrate that the essential features of the flow pattern suggested above are retained by the model. The flow is normal to these equipotential lines and the velocities, or the flow rates are inversely proportional to the distances between them. The slower flow of water from the Cimarron

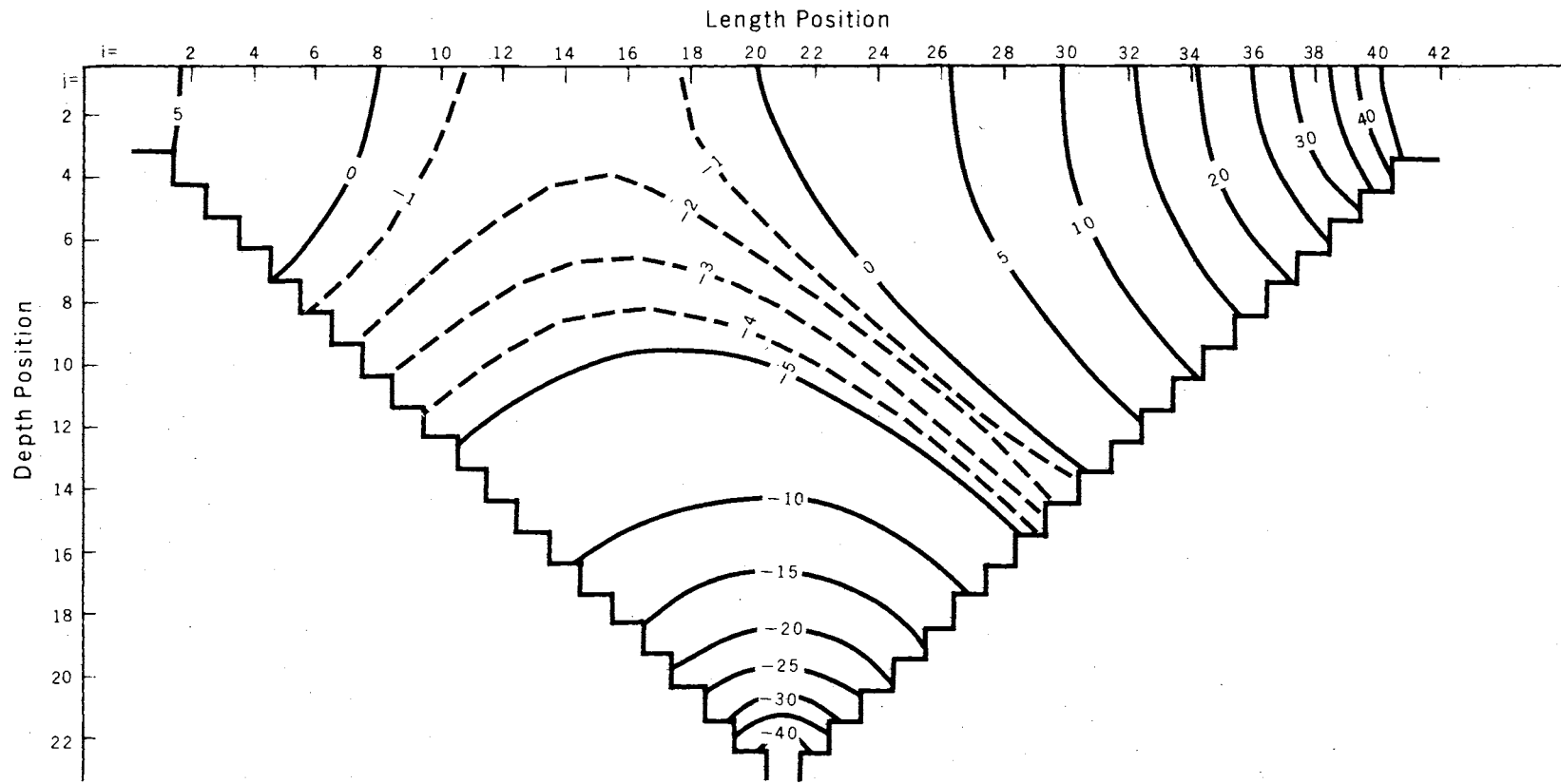


Figure 29. Velocity Potentials of Fluid Transport Model of Keystone Reservoir.

River is forced down and below the water from the Arkansas River. The Arkansas River water flows up the Cimarron arm above the Cimarron water several miles.

This flow pattern could be used to model the distributions of some conservative constituent. For example, the dissolved solids of the Cimarron River water are about five times greater than those in the Arkansas River water. According to this fluid flow model, they would be carried below the Arkansas water, or along the bottom of the Cimarron arm, and out the lower gates of the dam. Although this part of the model was not solved in this work, the following approach is suggested.

Approximate solutions of the convection equation,

$$\frac{\partial c}{\partial t} + V_{x_1, j} \frac{\partial c}{\partial x} + V_{y_1, j} \frac{\partial c}{\partial y} + GC_1^n, j = 0 \quad (103)$$

can be computed with an explicit, four-point, central difference approximation. In this equation, GC_1^n, j is the rate of production of C and is zero except at the locations where dissolved solids are entering or being removed from the system. This corresponds to the influx of waters from the Cimarron and Arkansas Rivers and the release of water through the lower gates of the dam. The central difference equations can be written as,

$$\frac{C_{i, j}^{n+1} - C_{i, j}^{n-1}}{2(\Delta t)} + V_{x_1, j} \frac{C_{i+1, j}^n - C_{i-1, j}^n}{2(\Delta x)} + V_{y_1, j} \frac{C_{i, j+1}^n - C_{i, j-1}^n}{2(\Delta y)} + GC_1^n, j = 0 \quad (104)$$

The concentration at time zero ($C_{i, j}^{n-1}$) is the concentration at the initial time condition. For the first time step, the concentration

at time equal one ($C_{i,j}^n$) must be approximated by another technique. This can be done by the central space difference approximation but a forward time difference approximation. This is given by the equation:

$$\frac{C_{i,j}^n - C_{i,j}^{n-1}}{(\Delta t)} + V_{x1,j} \frac{C_{i+1,j}^n - C_{i-1,j}^n}{2(\Delta x)} + V_{y1,j} \frac{C_{i,j+1}^n - C_{i,j-1}^n}{2(\Delta x)} + GC_{i,j}^n = 0 \quad (105)$$

For stability, the ratios $V_x \Delta t / \Delta x$ and $V_y \Delta t / \Delta y$ should be ≤ 1 , that is, the time step is set by these ratios.

This can be treated as a non-steady state problem but with steady flow. The concentrations in the input waters can be varied by assigning values to $GC_{i,j}^n$ at varied times, n . The values of $GC_{i,j}^n$ are defined as $QC_{i,j}^n / \Delta x \Delta y \Delta z$, where Q is the rate of inflow.

The mechanisms incorporated in the model give results which duplicate the essential features of the observations. However, since the transport phenomena is extremely complex, many factors were neglected. Of primary concern in this system is the effect of salt-induced density differences. This mechanism is not necessary for incorporation into the model to duplicate the major features of the real system; but in nature, it is surely a very important factor. For example, during the time water was released from the upper layers, salt-induced density flows apparently caused the Cimarron water to accumulate and stagnate in the bottom of the reservoir. This model would not be expected to duplicate this system.

If the effect of salt-induced density differences are included in the treatment, the problem becomes grossly more difficult. Not only

must the effect of density be included in the equation of continuity, steady flow can no longer be assumed; and the pressure and gravitational forces must be considered as well as the rate of momentum gain by convection.

Another limitation of the model was the frictional forces such as wind stresses, shear stresses between neighboring fluid particles, and the frictional drag at the surface of the reservoir basin. For example, the direct action of wind-driven currents or waves would be expected to keep the surface layers well mixed.

Other limitations include the assumption concerning the shape of the basin, the steady flow assumption, and neglect of various other forces, such as the coriolis force.

Despite the possible limitations of the model, the excellent agreement of the features of the model with those observed suggest that the currents which result from the convection of water masses into and from the system are important and cannot be neglected.

CHAPTER VIII

SUMMARY

The object of this work was to formulate an adequate experimental and theoretical description of the natural water system of Keystone Reservoir, Oklahoma. A series of theoretical chemical equilibrium models and a theoretical mass transfer model were formulated and compared to the observed real system to achieve this objective. The results of this study could provide the framework for the development of a continual, predictive model of the water quality of the reservoir and the downstream areas.

The analysis of the chemical equilibria involved the careful evaluation of the homogeneous and heterogeneous chemical equilibrium reactions, which could influence the composition of the water throughout its hydrological history and using these reactions to formulate a chemical equilibrium model of the reservoir. The formulation of the mass transfer model was based on the assumption that the spatial distribution of the chemical components was determined by the forced convection of the waters into the reservoir. This analysis involved the solution of second order partial differential equations, which describe the velocity potential at any point in the system. A technique to solve the first order partial differential equation, which describes the convective mass transfer in the reservoir, was suggested.

Both models were compared to the description of the real system derived from chemical and physical observations at monthly intervals from May, 1967, to June, 1968. Periodic observations were made for the preceding year. The water analyses of the samples obtained during this interval not only included the total analytical concentrations of the major inorganic components, it included the concentrations and activities of the free ions and ion pairs formed from these major constituents. The expression of the chemical analyses in this manner shows that many more constituents exist in solutions than are reported in the classical water analysis and allowed a rigorous comparison with the equilibrium models.

The following conclusions have been made as a result of this study:

1. During the major portion of this study, salt-heavy, dense water originating from the Cimarron River underflowed as a density current the stored water in the reservoir, flowed along the bottom of the Cimarron arm, and out through the lower outlet gates of the dam. The density current resulted from salt-induced density differences, and temperature and suspended matter did not contribute significantly to the density differences.

2. This flow pattern prevented the accumulation and putrefication of the dense water which was previously observed in the bottom of the reservoir when surface waters were removed. In comparison, the waters were more dilute, and no stable chemocline, except along the bottom of the Cimarron arm, or thermocline developed. Anoxic conditions did not develop during this period; but the waters in the

deeper portion of the reservoir were undersaturated with respect to oxygen in summer, 1967, and spring, 1968. The dense water along the bottom of the Cimarron arm contained lower concentrations of oxygen except in spring, 1968. In fall, 1967, and winter, 1968, the waters are near saturation with respect to oxygen.

3. The waters of the reservoir were near a state of solubility equilibrium with the solid phases calcite, kaolinite, sodium montmorillonite, and calcium montmorillonite, were super-saturated with respect to the phosphate mineral hydroxapatite, and were under-saturated with respect to magnesium carbonate, strontium carbonate, calcium sulfate, and strontium sulfate. The waters were super-saturated with respect to atmospheric carbon dioxide. The pH buffer action of the heterogeneous silicate system and the slow exchange of carbon dioxide with the atmosphere were suggested to contribute to the super-saturation effect.

4. A 10-component chemical equilibrium model agreed quite well with the observed data. The model was based on the hypothesis that waters originally in equilibrium with the common evaporite and clay minerals in large areas of the Great Salt Plains were diluted by fresher waters not exposed to the evaporite minerals as they flow toward the reservoir and then approached a state of chemical equilibrium with calcite and the clay minerals which adjusted their final concentrations.

5. Except for the concentration of phosphate, the symptoms of eutrophication decreased during this study period compared to those reported for the previous year. Calculations based on the solubility

equilibrium of the solution phase with hydroxyapatite suggested that the phosphate concentration should increase approximately 17 times from August, 1966, to August, 1967. Comparison with the observed data suggested that the waters were super-saturated. Further studies of the heterogeneous inorganic phosphate reactions may offer significant insight into the phosphorus cycle in natural water systems.

6. Many more soluble inorganic chemical species occurred in the natural waters than are normally considered in the classical chemical water analysis. These were primarily ion pairs formed from the major inorganic components.

7. The essential features of the currents which were suggested by the distributions of the major components can be duplicated by a fluid transfer model. The model shows that the waters from the Cimarron River tend to flow under the stored water in the Cimarron arm while the Arkansas River water flows up the Cimarron arm in the upper layers considerable distances before sinking toward the outlet.

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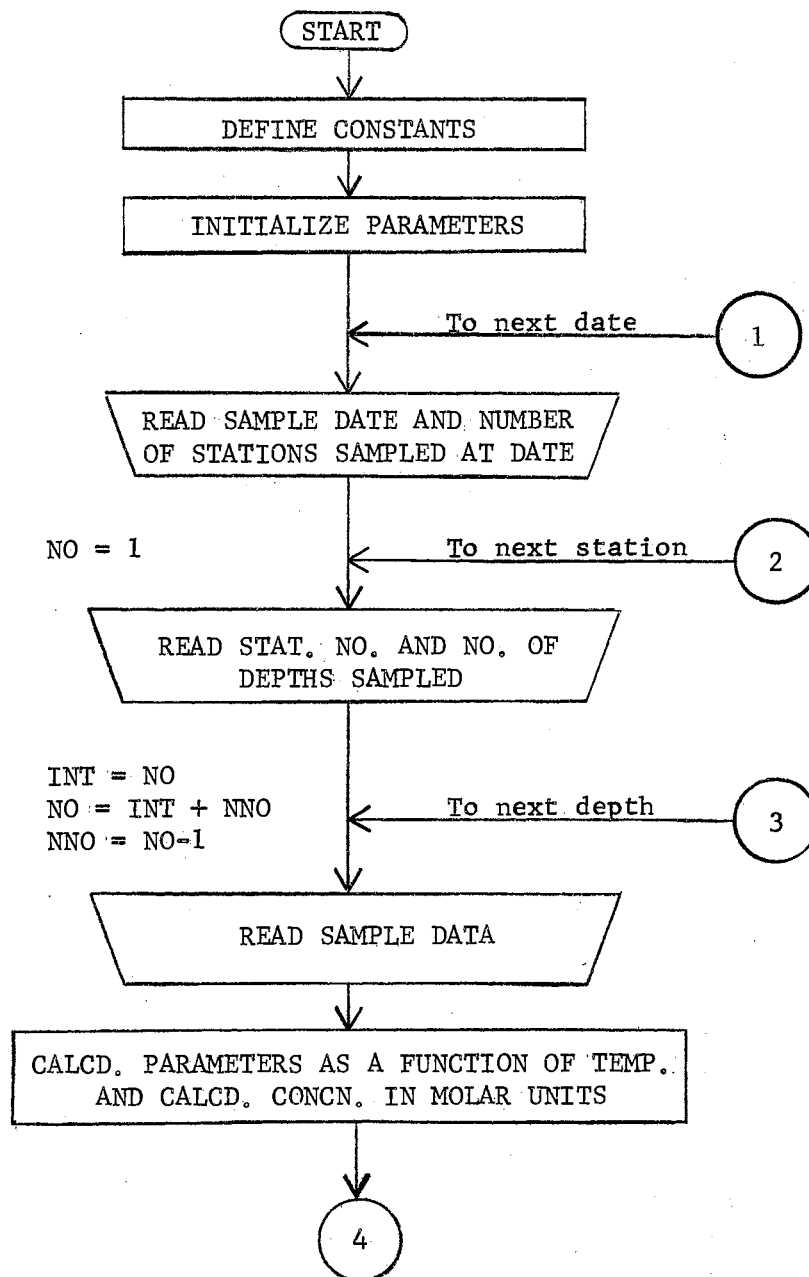
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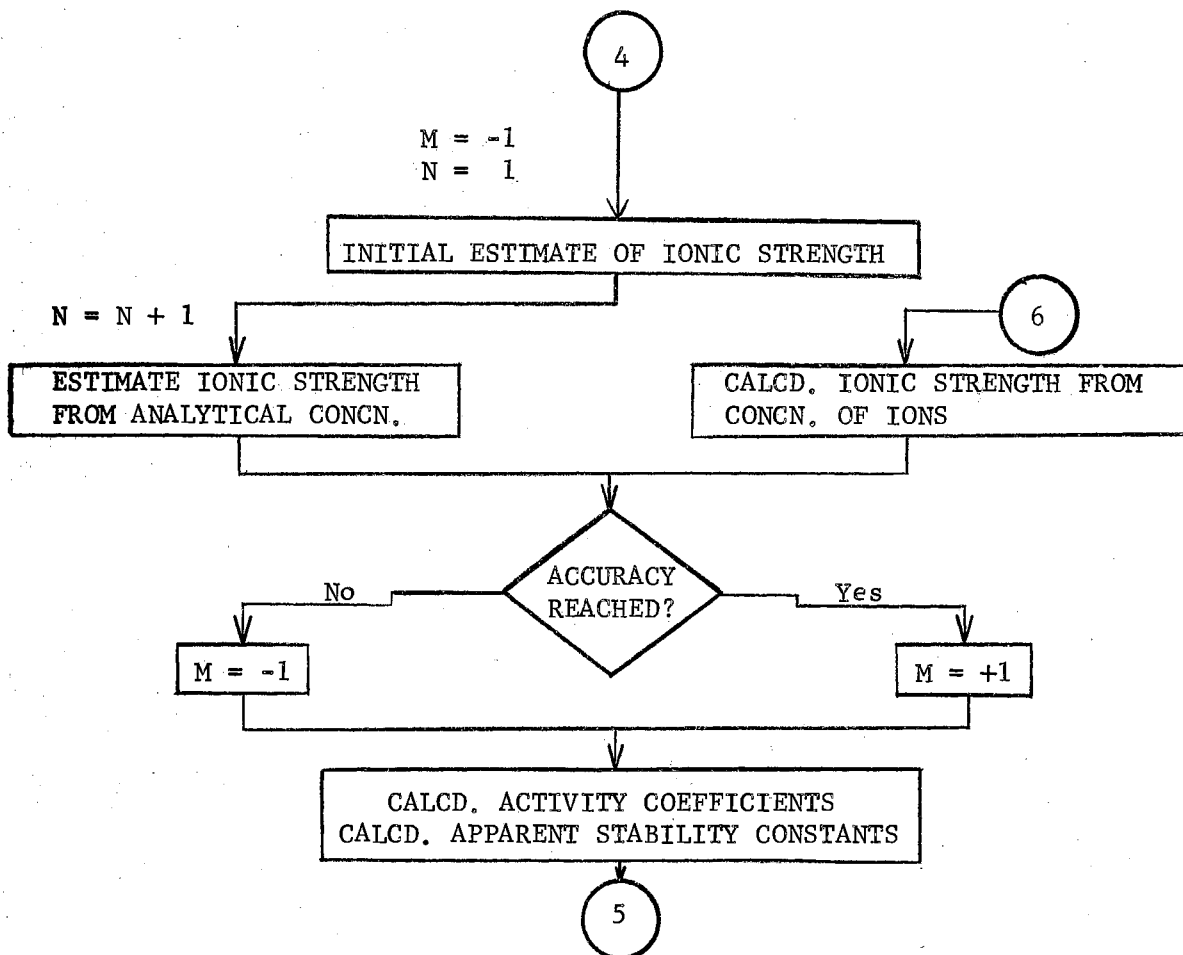
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APPENDIX A

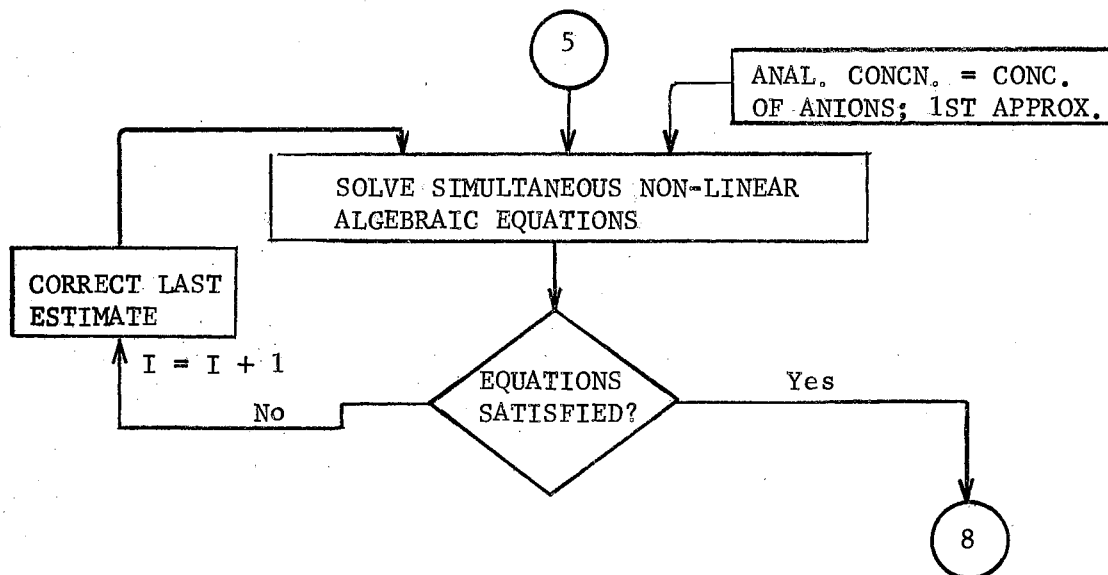
FLOW SHEET, PROGRAM LISTING, AND EXAMPLE OUTPUT OF
DISTRIBUTION OF DISSOLVED SPECIES

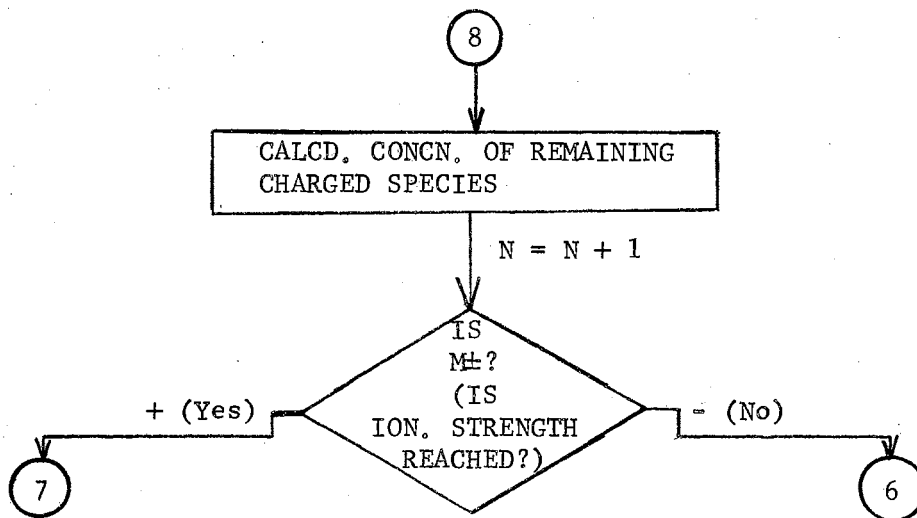
Initialization

Calculation of Ionic Strength

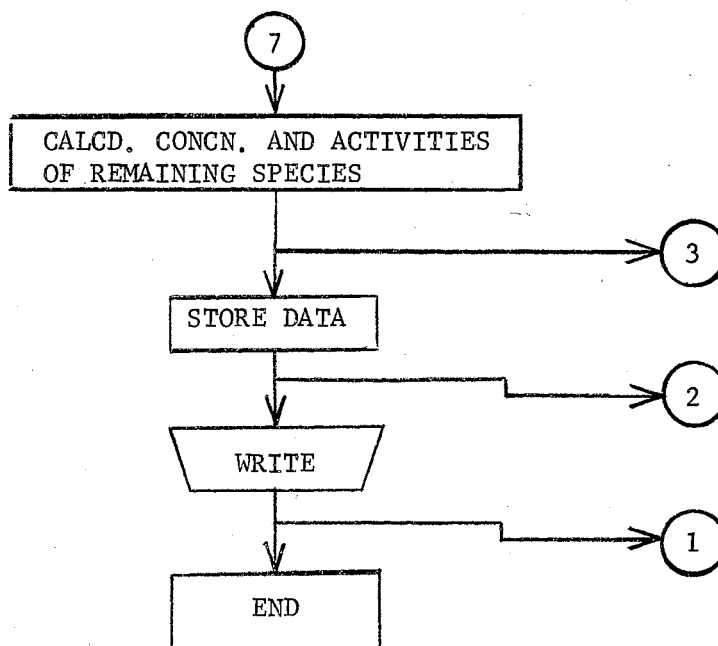


Solution to System of Non-linear Algebraic Equations





Activities and Concentrations




```

Z=50.3E+8*(1./((E*T)**.5))
C CALCULATE MOLES PER LITER
C(5,L)=1./10.**B(5,L)
C(6,L)=B(6,L)/31999.
C(7,L)=B(7,L)/87620.
C(8,L)=B(8,L)/35453.
C(9,L)=B(9,L)/34080.
C(10,L)=B(10,L)/61017.
C(11,L)=B(11,L)/96062.
C(12,L)=B(12,L)/40080.
C(13,L)=B(13,L)/24312.
C(14,L)=B(14,L)/22990.
C(15,L)=B(15,L)/39102.
C(16,L)=B(16,L)/60085.
C CALCULATE IONIC STRENGTH, AIS
M=-1
N=1
AIS(N)=1.
C ESTIMATE IONIC STRENGTH FROM TOTAL CONCENTRATION
AIS(N+1)=(0.5)*(C(8,L)+C(10,L)+C(14,L)+C(15,L)+4.*C(7,L)+C(11,L)+
1C(12,L)+C(13,L))
GO TO 12
C CALCULATE IONIC STRENGTH FROM ION CONCENTRATIONS
13 AIS(N+1)=.5*(C(8,L)+C(18,L)+C(22,L)+C(23,L)+C(25,L)+C(26,L)+C
1(27,L)+C(28,L)+C(29,L)+C(30,L)+C(32,L)+C(37,L)+C(46,L)+
24.*C(7,L)+C(19,L)+C(20,L)+C(21,L)+C(24,L)+C(31,L))
12 CONTINUE
C WAS ACCURACY REACHED
DIF=(AIS(N+1)-AIS(N))**2
IF(DIF-TOLRN)9,9,10
10 M=-1
GO TO 14
9 M=+1
14 CONTINUE
C CALCULATE ACTIVITY COEFFICIENTS
F(7)=1./10.**4.*Y*AIS(N)**.5/(1.+Z*G(7)*AIS(N)**.5)
F(8)=F(23)
F(17)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(17)*AIS(N+1)**.5))
F(18)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(18)*AIS(N+1)**.5))
F(19)=10.**(-Y*.4*AIS(N+1)**.5/(1.+Z*G(19)*AIS(N+1)**.5))
F(20)=10.**(-Y*.4*AIS(N+1)**.5/(1.+Z*G(20)*AIS(N+1)**.5))
F(21)=10.**(-Y*.4*AIS(N+1)**.5/(1.+Z*G(21)*AIS(N+1)**.5))
F(22)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(22)*AIS(N+1)**.5))
F(23)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(23)*AIS(N+1)**.5))
F(24)=10.**(-Y*.4*AIS(N+1)**.5/(1.+Z*G(24)*AIS(N+1)**.5))
F(25)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(25)*AIS(N+1)**.5))
F(26)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(26)*AIS(N+1)**.5))
F(27)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(27)*AIS(N+1)**.5))
F(28)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(28)*AIS(N+1)**.5))
F(29)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(29)*AIS(N+1)**.5))
F(30)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(30)*AIS(N+1)**.5))
F(31)=10.**(-Y*.4*AIS(N+1)**.5/(1.+Z*G(31)*AIS(N+1)**.5))
F(32)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(32)*AIS(N+1)**.5))
F(46)=10.**(-Y*AIS(N+1)**.5/(1.+Z*G(46)*AIS(N+1)**.5))
C CALCULATE APPARENT STABILITY CONSTANTS
A(3)=AA(3)*F(24)/F(18)
A(4)=AA(4)*F(20)/F(18)/F(25)
A(5)=AA(5)*F(20)/F(24)/F(36)
A(6)=AA(6)*F(21)/F(18)/F(26)
A(7)=AA(7)*F(21)/F(24)/F(37)
A(8)=AA(8)*F(22)/F(18)/F(38)
A(9)=AA(9)*F(22)/F(24)/F(27)
A(10)=AA(10)*F(20)/F(19)/F(39)
A(11)=AA(11)*F(21)/F(19)/F(40)
A(12)=AA(12)*F(22)/F(19)/F(28)
A(13)=AA(13)*F(23)/F(19)/F(29)
A(14)=AA(14)*F(30)/F(41)
A(15)=AA(15)*F(31)/F(30)
A(16)=AA(16)*F(32)/F(42)
A(17)=AA(17)*F(21)/F(17)/F(46)
C SOLVE SYSTEM OF NONLINEAR ALGEBRAIC EQUATIONS
I=1

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```

DO 3 K=18,23
3 X(K,I)=0.
C(17,L)=U(17,L)/F(17)
X(18,I)=C(10,L)
X(19,I)=C(11,L)
4 X(20,I+1)=C(12,L)/(1.+A(4)+A(5)/(A(3)*C(5,L)))*X(18,I)+A(10)*X(19
1,I)
X(21,I+1)=C(13,L)/(1.+A(6)+A(7)/(A(3)*C(5,L)))*X(18,I)+A(11)*X(19
1,I)+A(17)*C(17,L)
X(22,I+1)=C(14,L)/(1.+A(8)+A(9)/(A(3)*C(5,L)))*X(18,I)+A(12)*X(19
1,I)
X(23,I+1)=C(15,L)/(1.+A(13)*X(19,I)
X(18,I+1)=C(10,L)/(1.+A(6)*X(21,I+1)+A(4)*X(20,I+1)+A(8)*X(22,I+1)
1)
X(19,I+1)=C(11,L)/(1.+A(11)*X(21,I+1)+A(10)*X(20,I+1)+A(12)*X(22,I
1+1)+A(13)*X(23,I+1))
SUM=0.
DO 5 K=18,23
5 SUM=SUM+(X(K,I+1)-X(K,I))**2
IF(SUM-TOLR)6,6,7
7 I=I+1
GO TO 4
6 CONTINUE
DO 8 K=18,23
8 C(K,I)=X(K,I+1)
C CALCULATE CONCENTRATIONS OF CHARGED COMPONENTS
C(17,L)=U(17,L)/F(17)
C(24,L)=C(18,L)/C(5,L)*A(3)
C(25,L)=C(20,L)*C(18,L)*A(4)
C(26,L)=C(21,L)*C(18,L)*A(6)
C(27,L)=C(22,L)*C(24,L)*A(9)
C(28,L)=C(22,L)*C(19,L)*A(12)
C(29,L)=C(23,L)*C(19,L)*A(13)
C(30,L)=C(19,L)/(1.+C(5,L)*A(14))
C(31,L)=C(30,L)/C(5,L)*A(15)
C(32,L)=C(16,L)/(1.+C(5,L)*A(16))
C(46,L)=AA(17)*C(21,L)*F(21)*U(17,L)/F(46)
N=N+1
C WAS IONIC STRENGTH REACHED
IF(M)13,13,15
15 CONTINUE
8(45,L)=AIS(N)
C CALCULATE CONCENTRATIONS AND ACTIVITIES OF REMAINING COMPONENTS
U(7,L)=C(7,L)*F(7)
U(8,L)=C(8,L)*F(8)
DO 11 K=18,30
11 U(K,L)=C(K,L)*F(K)
U(31,L)=U(30,L)/C(5,L)*AA(15)
U(32,L)=F(32)*C(32,L)
U(33,L)=C(5,L)*U(18,L)*AA(2)
U(35,L)=U(33,L)
U(34,L)=U(35,L)*AA(1)
U(36,L)=U(20,L)*U(24,L)*AA(5)
U(37,L)=U(21,L)*U(24,L)*AA(17)
U(38,L)=U(22,L)*U(18,L)*AA(8)
U(39,L)=U(20,L)*U(19,L)*AA(10)
U(40,L)=U(21,L)*U(19,L)*AA(11)
U(41,L)=C(5,L)*U(30,L)*AA(14)
U(42,L)=C(5,L)*U(32,L)*AA(16)
DO 16 K=33,42
16 C(K,L)=U(K,L)/F(K)
U(46,L)=AA(17)*U(17,L)*U(21,L)
C(46,L)=U(46,L)/F(46)
B(17,L)=C(17,L)*18998.
B(18,L)=C(18,L)*61017.
B(19,L)=C(19,L)*96062.
B(20,L)=C(20,L)*40080.
B(21,L)=C(21,L)*24312.
B(22,L)=C(22,L)*22990.
B(23,L)=C(23,L)*39102.
B(24,L)=C(24,L)*60085.
B(25,L)=C(25,L)*101097.

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B(26,L)=C(26,L)*85329.
B(27,L)=C(27,L)*82999.
B(28,L)=C(28,L)*119052.
B(29,L)=C(29,L)*135164.
B(30,L)=C(30,L)*33072.
B(31,L)=C(31,L)*32064.
B(32,L)=C(32,L)*95108.
B(33,L)=C(33,L)*62025.
B(34,L)=C(34,L)*62025.
B(35,L)=C(35,L)*44010.
B(36,L)=C(36,L)*100089.
B(37,L)=C(37,L)*84321.
B(38,L)=C(38,L)*84007.
B(39,L)=C(39,L)*136142.
B(40,L)=C(40,L)*120374.
B(41,L)=C(41,L)*34080.
B(42,L)=C(42,L)*96116.
B(46,L)=C(46,L)*43310.
C(47,L)=C(46,L)+C(17,L)
B(47,L)=C(47,L)*18998.
DO 90 K=6,42
90 C(K,L)=C(K,L)*1000.
C CALCULATE TOTAL DISSOLVED SOLIDS
SUM=B(7,L)+B(8,L)-B(33,L)+B(46,L)
DO 19 K=17,42
19 SUM=SUM+B(K,L)
B(43,L)=SUM
C CALCULATE TOTAL CARBONATE
C(44,L)=C(24,L)+C(27,L)+C(36,L)+C(37,L)
B(44,L)=C(44,L)*60.009
DO 18 K=6,42
18 U(K,L)=U(K,L)*1000.
C UNIT CONVERSION FOR TABULATION
B(46,L)=B(46,L)*1000.
C(7,L)=C(7,L)*1000.
C(17,L)=C(17,L)*1000.
C(24,L)=C(24,L)*1000.
C(25,L)=C(25,L)*1000.
C(26,L)=C(26,L)*1000.
C(27,L)=C(27,L)*1000.
C(29,L)=C(29,L)*1000.
C(31,L)=C(31,L)*10.**6.
C(32,L)=C(32,L)*1000.
C(36,L)=C(36,L)*1000.
C(37,L)=C(37,L)*1000.
C(38,L)=C(38,L)*1000.
C(41,L)=C(41,L)*1000.
C(44,L)=C(44,L)*1000.
C(46,L)=C(46,L)*1000.
C(46,L)=C(46,L)*1000.
C(47,L)=C(47,L)*1000.
C(47,L)=C(47,L)*1000.
U(7,L)=U(7,L)*1000.
U(17,L)=U(17,L)*1000.
U(24,L)=U(24,L)*1000.
U(25,L)=U(25,L)*1000.
U(26,L)=U(26,L)*1000.
U(27,L)=U(27,L)*1000.
U(29,L)=U(29,L)*1000.
U(31,L)=U(31,L)*1000.
U(32,L)=U(32,L)*1000.
U(36,L)=U(36,L)*1000.
U(37,L)=U(37,L)*1000.
U(38,L)=U(38,L)*1000.
U(41,L)=U(41,L)*1000.
U(46,L)=U(46,L)*1000.
U(46,L)=U(46,L)*1000.
ISN(L)=ISNN
C GO TO NEXT DEPTH
2 CONTINUE
C GO TO NEXT STATION
404 CONTINUE
C WRITE RESULTS IN TABULAR FORM
WRITE(6,21)
WRITE(6,402)
WRITE(6,604)
WRITE(6,600)(ISN(L),B(1,L),B(2,L),B(3,L),B(43,L),B(4,L),B(5,L),
1B(6,L),B(8,L),B(11,L),B(10,L),B(44,L),B(47,L),B(9,L),
2B(14,L),B(12,L),B(13,L),B(15,L),B(7,L),B(16,L),B(19,L),
3B(18,L),B(24,L),B(17,L),B(30,L),L=1,NOO)
WRITE(6,21)
WRITE(6,605)
WRITE(6,601)(B(31,L),B(22,L),B(20,L),B(21,L),B(23,L),B(42,L),
1B(32,L),B(35,L),B(41,L),B(25,L),B(26,L),B(27,L),B(28,L),
2B(29,L),B(36,L),B(37,L),B(38,L),B(39,L),B(40,L),B(46,L),
3B(45,L),L=1,NOO)
WRITE(6,21)
WRITE(6,402)
WRITE(6,606)
WRITE(6,602)(ISN(L),B(1,L),B(2,L),B(3,L),B(43,L),B(4,L),B(5,L),
1C(6,L),C(8,L),C(11,L),C(10,L),C(44,L),C(47,L),C(9,L),
2C(14,L),C(12,L),C(13,L),C(15,L),C(7,L),C(16,L),C(19,L),
3C(18,L),C(24,L),C(17,L),C(30,L),L=1,NOO)
WRITE(6,21)
WRITE(6,607)
WRITE(6,603)(C(31,L),C(22,L),C(20,L),C(21,L),C(23,L),C(42,L),
1C(32,L),C(35,L),C(41,L),C(25,L),C(26,L),C(27,L),C(28,L),
2C(29,L),C(36,L),C(37,L),C(38,L),C(39,L),C(40,L),C(46,L),
3B(45,L),L=1,NOO)
WRITE(6,21)
WRITE(6,402)
WRITE(6,606)
WRITE(6,602)(ISN(L),B(1,L),B(2,L),B(3,L),B(43,L),B(4,L),B(5,L),
1C(6,L),U(8,L),C(11,L),C(10,L),C(44,L),C(47,L),C(9,L),
2C(14,L),C(12,L),C(13,L),C(15,L),U(7,L),C(16,L),U(19,L),
3U(18,L),U(24,L),U(17,L),U(30,L),L=1,NOO)
WRITE(6,21)
WRITE(6,607)
WRITE(6,603)(U(31,L),U(22,L),U(20,L),U(21,L),U(23,L),U(42,L),
1U(32,L),U(35,L),U(41,L),U(25,L),U(26,L),U(27,L),U(28,L),
2U(29,L),U(36,L),U(37,L),U(38,L),U(39,L),U(40,L),U(46,L),
3B(45,L),L=1,NOO)
WRITE(6,21)
C GO TO NEXT SAMPLING DATE
GO TO 17
END

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APPENDIX B

ANALYSES OF WATER FROM KEYSTONE RESERVOIR

ACTIVITY — MOLARITY

AUGUST 20, 1966																																							
ST NO	DPHT (M)	TEMP (C)	CUND UMHO	DISS. SULID	SUSP. SOLID	PH	DISS. O2	CL- SR++	SO4=	HCO3	CO3=	F-	HS-	S=	NA+	CA++	MG++	K+	H4-	H3-	DISS	DISS	CAH-	MGH-	NA-	NA-	KSO4	CA-	MG-	NA-	CA-	MG-	MGF+	ION STR					
				MG/L	MM/L		MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L				
5	0.0	27.1	2200.	1609.	2.0	8.45	.212	15.04	7.1	0.98	2.13	29.3	3.8	.0	.0	16.1	1.01	0.61	.149	.147	8.2	.016	0.0	38.9	18.8	8.77	.083	1.06	46.6	44.9	19.3	.202	.144	0.15	.030				
5	1.0	27.1	2200.	1625.	2.0	8.35	.217	15.04	6.9	1.01	2.29	25.0	6.8	.0	.0	16.1	1.01	0.59	.158	.136	6.1	.022	0.0	42.2	19.4	7.50	.085	1.16	40.1	36.8	20.7	.210	.143	0.26	.030				
5	2.0	27.1	2200.	1593.	2.0	8.27	.212	14.89	7.0	1.00	2.29	20.8	7.0	.0	.0	15.4	0.98	0.64	.145	.126	4.7	.027	0.0	41.0	21.2	5.97	.081	1.06	32.4	33.5	19.8	.202	.155	0.30	.029				
5	4.0	26.7	2180.	1605.	5.0	8.25	.212	15.55	7.1	1.00	2.13	18.3	7.0	.0	.0	15.4	0.96	0.67	.145	.096	3.4	.026	0.0	37.4	20.5	5.24	.081	1.05	28.0	30.6	18.4	.198	.159	0.31	.030				
5	6.0	26.6	2180.	1612.	5.0	8.23	.211	15.39	7.0	1.00	2.29	18.8	7.0	.0	.0	15.2	1.00	0.64	.147	.147	5.0	.030	0.0	41.8	21.1	5.32	.080	1.06	29.8	30.0	19.6	.205	.152	0.29	.030				
5	8.0	26.6	2180.	1606.	5.0	8.20	.204	15.13	7.0	1.01	2.13	16.3	6.3	.0	.0	15.9	0.99	0.64	.156	.112	3.5	.029	0.0	38.5	19.6	4.82	.084	1.13	25.6	26.1	19.0	.207	.153	0.27	.030				
5	10.0	26.5	2200.	1593.	2.0	8.15	.203	15.31	7.0	1.00	2.13	14.5	8.0	.0	.0	15.2	0.96	0.68	.145	.151	4.3	.033	0.0	37.2	20.9	4.10	.080	1.05	22.0	24.8	18.2	.197	.162	0.36	.029				
5	12.0	25.5	2320.	1619.	3.5	7.92	.111	15.38	7.1	1.02	2.37	9.3	8.0	.0	.0	15.2	0.96	0.72	.145	.134	2.2	.064	0.0	41.4	24.8	2.63	.081	1.04	14.1	16.9	20.3	.198	.169	0.38	.030				
5	14.0	21.0	2750.	1920.	2.5	7.45	.0	19.04	6.7	1.02	2.42	2.9	10.0	.0	.0	18.8	0.98	0.79	.144	.192	1.1	.206	0.0	43.4	27.6	1.02	.101	0.96	4.5	5.8	25.7	.197	.161	0.52	.035				
5	16.0	20.0	2950.	2108.	6.5	7.42	.0	20.40	7.0	1.07	2.64	2.9	10.0	.030	.094	20.8	1.12	0.74	.143	.317	1.7	.245	12.9	54.0	28.2	1.12	.117	0.98	5.1	5.4	31.0	.235	.154	0.49	.038				
5	18.0	18.0	3250.	2384.	6.5	7.32	.0	23.66	7.1	0.96	2.78	2.3	10.0	.061	.139	25.0	1.10	0.76	.139	.375	1.6	.336	35.3	55.7	30.6	1.07	.126	0.83	4.0	4.4	39.1	.203	.133	0.50	.043				
5	20.0	16.7	3750.	2503.	6.5	7.30	.0	25.14	6.9	0.93	3.00	2.3	10.0	.103	.214	25.9	1.15	0.76	.147	.410	1.6	.389	66.3	63.0	32.8	1.11	.126	0.83	4.2	4.4	43.7	.203	.123	0.50	.045				
5	22.0	15.8	3750.	2577.	39.5	7.30	.0	26.06	7.0	0.92	3.00	2.3	10.0	.117	.234	26.7	1.18	0.76	.153	.431	1.7	.394	78.0	64.2	32.7	1.12	.129	0.84	4.2	4.3	45.0	.205	.118	0.50	.046				
MAY 14, 1967																																							
5	0.0	18.7	2460.	1759.	2.5	8.43	.293	17.25	6.5	0.85	2.62	28.4	7.0	.0	.0	18.5	1.00	0.55	.153	.017	6.9	.024	0.0	47.6	20.8	9.77	.083	0.82	45.0	39.2	27.2	.165	.087	0.25	.032				
5	2.0	18.7	2500.	1766.	2.0	8.45	.292	17.56	6.3	0.84	2.37	27.0	6.2	.0	.0	18.5	1.08	0.58	.145	.017	1.0	.021	0.0	46.7	19.9	9.32	.082	0.77	46.3	39.3	24.7	.176	.091	0.24	.033				
5	4.0	18.7	2500.	1779.	2.0	8.45	.297	17.81	6.4	0.84	2.41	27.4	6.0	.0	.0	18.6	1.05	0.58	.145	.017	0.9	.021	0.0	46.1	20.3	9.48	.082	0.77	45.6	40.2	25.2	.171	.092	0.23	.033				
5	6.0	18.7	2500.	1775.	2.0	8.47	.297	17.55	6.4	0.84	2.21	26.3	6.0	.0	.0	19.3	1.07	0.57	.149	.031	1.8	.019	0.0	43.1	18.1	9.47	.085	0.79	44.7	37.4	24.0	.174	.089	0.22	.033				
5	8.0	18.0	2500.	1737.	2.0	8.48	.306	17.42	7.2	0.85	2.21	26.5	6.0	.0	.0	18.2	1.06	0.60	.147	.030	1.8	.019	0.0	42.9	19.1	8.99	.081	0.77	44.7	39.9	22.6	.173	.092	0.24	.032				
5	10.0	18.0	2500.	1747.	2.5	8.48	.294	17.92	7.2	0.87	2.25	27.0	5.8	.0	.0	17.5	1.05	0.59	.153	.031	1.9	.019	0.0	43.0	19.2	8.80	.080	0.83	44.9	40.1	22.2	.176	.094	0.23	.032				
5	12.0	17.0	2500.	1762.	2.5	8.50	.285	17.91	6.7	0.86	2.23	27.3	5.8	.0	.0	18.2	1.06	0.59	.149	.011	0.7	.018	0.0	43.2	18.9	9.29	.083	0.78	46.1	40.3	22.9	.175	.089	0.23	.033				
5	14.0	17.0	2500.	1739.	2.5	8.56	.287	17.59	6.9	0.85	2.20	31.0	5.8	.0	.0	18.1	1.06	0.60	.147	.014	1.0	.016	0.0	42.3	19.0	10.42	.081	0.76	51.9	46.4	22.4	.171	.090	0.23	.032				
5	16.0	16.0	3000.	2088.	5.6	8.10	.139	21.91	6.4	0.81	2.40	11.4	5.8	.0	.0	23.0	1.03	0.60	.152	.022	6.6	.050	0.0	45.0	20.8	4.88	.098	0.73	18.7	17.2	30.9	.158	.083	0.23	.038				
5	18.0	13.0	3750.	2531.	64.8	8.02	.037	27.89	6.7	0.83	2.38	8.8	5.0	.0	.0	27.8	1.02	0.62	.154	.114	2.4	.063	0.0	44.0	21.2	4.53	.121	0.72	14.1	13.6	37.1	.156	.079	0.20	.046				
MAY 27, 1967																																							
5	0.0	19.5	2480.	1840.	7.7	8.30	.321	18.47	7.1	0.60	1.77	14.6	30.0	.0	.0	23.4	1.07	0.57	.142	.017	0.7	.022	0.0	34.6	14.5	6.35	.074	0.54	24.7	20.7	23.4	.125	.065	1.12	.035				
5	2.0	19.5	2564.	1691.	1.4	8.35	.324	18.52	7.6	0.65	1.71	15.7	26.0	.0	.0	18.1	1.11	0.58	.145	.017	0.8	.019	0.0	34.4	14.4	5.31	.062	0.60	27.6	23.0	17.4	.139	.072	1.00	.032				
5	4.0	19.5	2547.	1683.	0.7	8.20	.291	18.26	8.0	0.64	1.88	12.3	26.0	.0	.0	17.8	1.13	0.60	.152	.017	0.5	.029	0.0	38.6	16.3	4.06	.059	0.61	21.9	18.4	18.8	.139	.073	1.03	.032				
5	6.0	19.5	2564.	1733.	2.4	8.25	.247	18.40	7.6	0.63	1.88	13.7	26.0	.0	.0	19.2	1.12	0.61	.160	.032	1.1	.026	0.0	38.4	16.5	4.90	.063	0.64	24.4	20.9	20.2	.137	.073	1.04	.033				
5	8.0	19.5	2564.	1714.	2.6	8.10	.220	18.42	7.9	0.64	1.92	9.9	26.0	.0	.0	18.3	1.15	0.61	.164	.032	0.8	.038	0.0	40.1	16.9	3.38	.061	0.67	18.1	15.2	19.7	.143	.075	1.05	.032				
5	10.0	19.5	2564.	1699.	0.4	8.05	.216	18.35	8.4	0.64	1.93	8.9	24.0	.0	.0	17.9	1.14	0.60	.162	.032	0.7	.042	0.0	40.0	16.7	2.98	.061	0.66	16.1	13.4	19.5	.142	.073	0.95	.032				
5	12.0	19.0	2481.	1696.	3.7	8.00	.199	18.35	8.3	0.64	1.95	7.9	24.0	.0	.0	17.9	1.14	0.60	.166	.012	0.2	.048	0.0	40.4	16.9	2.63	.060	0.68	14.3	11.9	19.6	.142	.073	0.95	.032				
5	14.0	18.5	2564.	1734.	5.6	7.95	.179	18.57	8.4	0.64	1.97	7.1	26.0	.0	.0	18.7	1.14	0.61	.173	.015	0.3	.055	0.0	40.8	17.5	2.46	.063	0.69	12.7	10.9	20.7	.140	.073	1.05	.033				
5	16.0	18.0	2564.	1776.	3.8	7.90	.132	19.13	8.2	0.64	1.97	6.2	26.0	.0	.0	19.3	1.12	0.61	.172	.023	0.4	.063	0.0	40.1	17.4	2.24	.065	0.68	11.0	9.5	21.4	.137	.071	1.05	.033				
5	18.0	16.5	2849.	1936.	34.1	7.65	.082	21.09	8.5	0.60	1.93	3.3	24.0	.0	.0	22.0	1.11	0.61	.174	.030	0.3	.112	0.0	39.0	16.9	1.35	.070	0.63	5.8	5.0	23.9	.127	.064	0.96	.036				
5	20.0	15.0	3077.	2043.	379.5	7.45	.007	22.94	8.3	0.60	1.98	2.1	24.0	.0	.0	22.3	1.11	0.62	.173	.116	0.7																		

JULY 29, 1967																																			
ST NO	OPTH (M)	TEMP (C)	COND UHMO	DISS SOLID	SUSP. MG/L	PH	DISS. O2	CL-	SR++	S04=	HC03	CO3=	F-	HS-	Σ	NA+	CA++	MG++	K+	H4-SiO4	H3-SiO3	DISS CO2	OISS H2S	CAH-CO3+	MGH-CO3+	NA-CO3-	NA-SO4-	KSO4	CA-CO3	MG-CO3	NA-HCO3	CA-SO4	MG-SO4	MGF+	ION STR
4	0.0	27.0	938.	683.	18.0	7.75	.210	6.00	3.5	0.36	1.62	4.4	14.7	.0	.0	6.9	0.65	0.25	.143	.260	2.9	.063	0.0	19.3	5.9	0.57	.013	0.38	4.6	2.8	6.3	.049	.022	0.25	.012
4	2.0	26.0	927.	667.	20.0	7.70	.191	5.74	3.5	0.37	1.63	3.9	14.4	.0	.0	6.5	0.66	0.26	.143	.265	2.6	.072	0.0	19.7	6.1	0.48	.013	0.38	4.1	2.5	6.0	.051	.022	0.25	.012
4	5.0	25.0	962.	695.	20.0	7.68	.191	6.23	3.5	0.36	1.63	3.6	15.8	.0	.0	6.9	0.66	0.27	.143	.264	2.5	.077	0.0	19.6	6.3	0.47	.013	0.37	3.8	2.5	6.3	.049	.022	0.28	.012
4	7.0	25.0	974.	699.	20.0	7.62	.184	6.31	3.5	0.37	1.63	3.2	16.5	.0	.0	6.9	0.66	0.28	.143	.256	2.1	.088	0.0	19.5	6.5	0.40	.013	0.37	3.3	2.2	6.3	.049	.023	0.30	.012
4	10.0	25.0	1040.	723.	21.0	7.58	.170	6.54	3.6	0.37	1.62	2.9	18.8	.0	.0	7.3	0.66	0.28	.142	.266	2.0	.096	0.0	19.5	6.7	0.39	.014	0.37	3.0	2.1	6.7	.050	.024	0.35	.013
4	14.0	25.0	1148.	825.	23.0	7.48	.093	8.01	3.6	0.42	1.70	2.4	20.0	.0	.0	8.2	0.67	0.30	.137	.212	1.3	.126	0.0	20.8	7.3	0.37	.018	0.41	2.5	1.8	7.8	.057	.028	0.39	.015
4	16.0	25.0	1221.	1119.	39.0	7.30	.044	11.10	4.0	0.45	1.73	1.6	20.0	.0	.0	13.2	0.71	0.33	.130	.199	0.8	.195	0.0	22.4	8.3	0.39	.031	0.41	1.8	1.3	12.8	.064	.034	0.44	.020
4	18.0	25.0	1789.	1309.	43.0	7.24	.028	13.43	4.9	0.47	1.78	1.4	20.0	.0	.0	15.7	0.73	0.34	.122	.176	0.6	.230	0.0	23.7	8.8	0.42	.039	0.41	1.7	1.2	15.7	.070	.037	0.45	.024
5	0.0	25.5	962.	698.	47.0	8.20	.191	6.22	3.5	0.37	1.65	12.3	19.2	.0	.0	7.0	0.67	0.24	.147	.242	7.6	.023	0.0	20.2	5.7	1.61	.014	0.39	13.1	7.3	6.5	.050	.020	0.30	.012
5	2.0	25.0	947.	691.	78.0	7.98	.189	6.31	3.5	0.37	1.94	6.8	18.2	.0	.0	7.0	0.64	0.26	.147	.244	4.7	.036	0.0	17.9	5.7	0.89	.014	0.38	7.0	4.4	6.1	.048	.022	0.31	.012
5	4.0	25.0	968.	685.	77.0	7.76	.184	6.24	3.3	0.36	1.61	4.3	15.8	.0	.0	6.7	0.66	0.25	.136	.254	2.9	.063	0.0	19.2	5.9	0.54	.013	0.35	4.5	2.7	6.1	.048	.021	0.26	.012
5	6.0	25.0	950.	698.	72.0	7.68	.170	6.44	3.4	0.36	1.61	3.6	17.9	.0	.0	6.8	0.66	0.25	.147	.260	2.5	.074	0.0	19.2	5.9	0.46	.013	0.37	3.7	2.3	6.2	.048	.021	0.30	.012
5	8.0	25.0	927.	706.	87.0	7.62	.157	6.53	3.4	0.36	1.60	3.1	17.9	.0	.0	6.9	0.65	0.25	.147	.260	2.3	.086	0.0	19.1	5.9	0.40	.013	0.37	3.2	2.0	6.2	.047	.021	0.30	.012
5	11.0	25.0	950.	707.	88.0	7.40	.136	6.49	3.4	0.36	1.59	1.9	17.0	.0	.0	6.8	0.66	0.25	.147	.311	1.6	.142	0.0	19.0	5.8	0.24	.013	0.37	1.9	1.2	6.1	.048	.021	0.29	.012
5	14.0	25.0	1061.	797.	126.0	7.38	.121	7.71	3.9	0.38	1.58	1.8	17.8	.0	.0	8.0	0.66	0.28	.144	.312	1.5	.148	0.0	19.1	6.4	0.26	.016	0.38	1.9	1.2	7.1	.051	.024	0.33	.014
5	16.0	25.0	1166.	962.	70.0	7.34	.085	9.55	3.9	0.39	1.67	1.7	19.2	.0	.0	10.5	0.69	0.26	.145	.306	1.3	.172	0.0	21.1	6.4	0.33	.022	0.40	1.9	1.1	9.9	.055	.023	0.34	.017
5	18.0	25.0	1451.	1026.	55.0	7.30	.049	10.52	4.8	0.45	1.70	1.6	19.8	.0	.0	11.4	0.71	0.32	.135	.070	0.3	.191	0.0	21.9	7.9	0.34	.027	0.43	1.8	1.3	10.9	.064	.033	0.42	.019
5	20.0	24.0	1947.	1291.	57.0	7.30	.048	12.05	5.7	0.75	1.66	1.5	23.2	.0	.0	14.1	1.07	0.43	.141	.070	0.3	.190	0.0	32.4	10.3	0.40	.056	0.73	2.6	1.6	13.2	.162	.071	0.66	.024
5	23.0	23.0	5495.	4274.	60.0	7.38	.043	47.54	6.9	0.78	1.65	1.8	29.5	.0	.0	52.8	1.13	0.50	.148	.075	0.4	.160	0.0	34.0	11.9	0.74	.216	0.78	3.2	2.2	49.1	.176	.083	0.97	.077
6	0.0	26.0	1131.	727.	56.0	7.88	.184	6.38	4.4	0.39	1.61	5.8	18.8	.0	.0	7.6	0.63	0.25	.145	.323	4.9	.047	0.0	18.4	5.9	0.82	.016	0.41	5.8	3.7	6.8	.050	.023	0.31	.013
6	2.0	26.0	932.	720.	60.0	7.62	.142	6.30	3.6	0.38	1.69	3.2	13.8	.0	.0	7.6	0.63	0.26	.145	.327	2.7	.084	0.0	18.3	5.9	0.44	.015	0.39	3.2	2.0	6.8	.049	.023	0.23	.013
6	5.0	25.0	932.	722.	74.0	7.58	.142	6.34	3.7	0.38	1.99	2.8	14.4	.0	.0	7.6	0.63	0.25	.140	.334	2.5	.094	0.0	18.2	5.6	0.40	.015	0.37	2.8	1.7	6.8	.048	.021	0.23	.013
6	7.0	25.0	855.	687.	105.0	7.48	.142	5.92	3.0	0.34	1.56	2.2	13.8	.0	.0	7.4	0.62	0.22	.134	.313	1.9	.116	0.0	17.5	5.1	0.30	.013	0.32	2.1	1.2	6.5	.043	.018	0.20	.012
6	10.0	25.0	818.	601.	172.0	7.36	.105	5.15	3.1	0.30	1.50	1.6	13.1	.0	.0	6.5	0.60	0.23	.119	.169	0.8	.147	0.0	16.4	5.0	0.19	.010	0.25	1.5	0.9	5.5	.037	.016	0.20	.011
6	12.0	24.0	855.	565.	180.0	7.18	.105	4.44	3.2	0.30	1.54	1.1	13.8	.0	.0	6.1	0.60	0.23	.135	.155	0.5	.232	0.0	16.7	5.0	0.12	.010	0.28	1.0	0.6	5.3	.036	.015	0.21	.010
6	15.0	24.0	950.	667.	195.0	7.11	.022	6.07	4.4	0.32	1.56	0.9	16.5	.0	.0	6.4	0.79	0.26	.134	.148	0.4	.276	0.0	22.4	5.8	0.11	.011	0.29	1.1	0.6	5.6	.051	.018	0.28	.012
7	0.0	26.0	962.	706.	64.0	7.70	.194	6.32	3.1	0.37	1.59	3.8	14.4	.0	.0	7.4	0.64	0.25	.145	.245	2.5	.070	0.0	18.4	5.8	0.52	.014	0.38	3.8	2.4	6.6	.047	.022	0.24	.013
7	2.0	26.0	927.	696.	80.0	7.62	.181	6.31	3.1	0.34	1.55	3.1	13.8	.0	.0	7.4	0.61	0.24	.143	.252	2.1	.082	0.0	17.3	5.3	0.43	.013	0.34	3.0	1.8	6.5	.042	.019	0.22	.012
7	5.0	25.0	874.	644.	121.0	7.43	.163	5.76	3.2	0.31	1.55	1.9	13.1	.0	.0	6.6	0.61	0.24	.128	.254	1.4	.129	0.0	17.3	5.3	0.24	.011	0.28	1.9	1.2	5.7	.039	.017	0.20	.011
7	7.0	25.0	855.	635.	140.0	7.40	.141	5.63	3.2	0.32	1.55	1.8	13.8	.0	.0	6.5	0.60	0.23	.128	.249	1.2	.139	0.0	17.0	5.3	0.22	.011	0.28	1.7	1.1	5.6	.039	.017	0.21	.011
7	10.0	25.0	827.	622.	161.0	7.39	.126	5.47	3.2	0.31	1.53	1.8	16.5	.0	.0	6.3	0.60	0.24	.128	.246	1.2	.140	0.0	16.7	5.3	0.21	.010	0.28	1.7	1.0	5.4	.038	.017	0.26	.011
7	12.0	25.0	827.	595.	170.0	7.38	.099	5.11	3.2	0.30	1.50	1.7	14.4	.0	.0	6.0	0.59	0.23	.128	.249	1.2	.141	0.0	16.2	5.0	0.19	.010	0.27	1.6	1.0	5.1	.036	.016	0.22	.011
7	15.0	25.0	818.	555.	180.0	7.32	.092	4.59	3.2	0.29	1.49	1.5	13.8	.0	.0	5.6	0.57	0.21	.119	.257	1.1	.160	0.0	15.5	4.6	0.15	.008	0.24	1.3	0.8	4.7	.034	.014	0.20	.010
7	17.0	26.0	600.	458.	389.0	7.30	.086	3.81	3.4	0.14	1.49	1.4	12.3	.0	.0	4.1	0.60	0.22	.104	.257	1.0	.165	0.0	16.3	4.6	0.11	.003	0.10	1.4	0.8	3.5	.017	.007	0.17	.008
AUGUST 20, 1967																																			
3	0.0	25.6	1250.	851.	23.0	7.70	.133	8.15	3.9	0.40	1.62	3.8	12.7	.0	.0	9.6	0.64	0.31	.132	.176	1.8	.072	0.0	18.7	7.1	0.68	.020	0.37	3.8	2.9	8.7	.051	.028	0.26	.015
3	4.0	23.9	1250.	856.	22.0	7.70	.161	8.34	3.9	0.41	1.62	3.7	11.5	.0	.0	9.4	0.65	0.30	.132	.184	1.8	.074	0.0	19.2	7.0	0.65	.020	0.37	3.8	2.8	8.6	.053	.027	0.23	.015
3	8.0	23.9	1300.	865.	22.0	7.70	.159	8.51	3.9	0.41	1.62	3.7	11.7	.0	.0	9.5	0.66	0.28	.132	.176	1.8	.074	0.0	19.4	6.5	0.65	.020	0.37	3.8	2.6	8.7	.053	.025	0.21	.016
3	10.0	23.9	1400.	870.	23.0	7.69	.157	8.60	3.9	0.41	1.63	3.6	11.7	.0	.0	9.5	0.66	0.27	.130	.172	1.7	.076	0.0	19.5	6.4	0.64	.020	0.37	3.8	2.5	8.7	.054	.025	0.21	.016
3	12.0	24.4	1800.	948.	24.0	7.65	.156	10.48	4.0	0.41	1.63	3.4	11.7	.0	.0	9.3	0.65	0.29	.129	.174	1.6	.083	0.0	19.4	6.8	0.58	.020	0.37	3.5	2.4	8.6	.054	.026	0.22	.017
3	14.0	24.4	2200.	981.	26.0	7.60</																													

SEPTEMBER 15, 1967																																				
ST NO	DPH (M)	TEMP (C)	COND UMHO	DISS. SOLID MG/L	SUSP. SOLID MG/L	PH	DISS. O2 MM/L	CL- MM/L	SR+++ MM/L	SO4= MM/L	HCO3= MM/L	CO3= MM/L	F- MM/L	HS- MM/L	S= MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- MM/L	H3- MM/L	DISS. CO2 MM/L	DISS. H2S MM/L	CAH- CO3+ MM/L	MGH- CO3+ MM/L	NA- CO3+ MM/L	KA- SO4= MM/L	KSO4 MM/L	CA- Cl-3 MM/L	MG- CO3 MM/L	NA- HCO3 MM/L	CA- SO4 MM/L	MG- SO4 MM/L	MGF+ MM/L	ICN STR	
2	0.5	25.5	1351.	1075.	18.8	8.40	3.19	11.22	3.6	0.40	1.37	16.2	11.9	0	0	13.6	0.63	0.78	0.205	0.044	3.2	0.12	0	0	15.7	5.4	4.10	0.28	0.57	16.2	11.5	10.5	0.51	0.26	0.22	0.20
2	4.5	23.2	1432.	1125.	30.0	8.20	2.03	11.43	3.6	0.39	1.36	9.7	12.0	0	0	15.1	0.63	0.28	0.196	0.069	3.1	0.20	0	0	15.6	5.4	2.71	0.31	0.52	9.6	6.7	11.4	0.49	0.23	0.22	0.21
2	8.5	22.9	2174.	1450.	107.2	7.40	0.51	15.72	3.6	0.37	1.68	1.9	13.2	0	0	18.5	0.68	0.36	0.130	0.144	1.0	0.156	0	0	20.7	8.4	0.64	0.36	0.45	2.0	1.7	14.0	0.50	0.28	0.31	0.26
3	0.5	25.3	1939.	850.	9.2	7.80	2.57	7.86	3.8	0.42	1.34	4.1	10.7	0	0	10.2	0.70	0.79	0.199	0.161	2.0	0.049	0	0	17.6	5.8	0.78	0.23	0.60	4.6	3.0	7.9	0.60	0.29	0.21	0.19
3	4.5	23.2	1117.	871.	13.2	7.60	2.05	8.10	3.9	0.43	1.34	2.4	10.5	0	0	10.5	0.69	0.50	0.212	0.200	1.6	0.078	0	0	16.8	5.9	0.47	0.23	0.61	2.6	1.9	7.9	0.58	0.28	0.21	0.16
3	8.5	23.2	1314.	954.	17.2	7.40	1.71	9.14	3.8	0.47	1.33	1.5	10.8	0	0	11.3	0.69	0.30	0.227	0.256	1.3	0.123	0	0	16.6	5.9	0.32	0.28	0.72	1.6	1.1	8.5	0.64	0.30	0.22	0.17
3	12.5	22.6	2230.	1633.	56.4	7.60	1.59	17.84	4.1	0.45	1.73	1.9	14.1	0	0	21.7	0.73	0.36	0.221	0.194	1.0	0.161	0	0	23.0	7.0	0.77	0.51	0.66	2.2	1.7	21.1	0.65	0.34	0.33	0.30
4	0.5	23.6	1168.	820.	11.2	7.80	2.44	7.02	4.1	0.45	1.52	4.3	9.6	0	0	9.5	0.71	0.31	0.231	0.284	3.2	0.095	0	0	10.5	6.8	0.76	0.22	0.71	4.8	2.4	8.1	0.63	0.30	0.20	0.15
4	4.5	23.0	1156.	822.	10.4	7.60	2.01	6.94	4.0	0.45	1.63	2.9	9.7	0	0	10.0	0.76	0.31	0.202	0.250	2.0	0.095	0	0	21.5	7.2	0.49	0.22	0.61	3.3	2.2	8.5	0.65	0.29	0.20	0.15
4	8.5	22.8	1156.	837.	10.4	7.40	1.64	6.84	4.1	0.46	1.54	1.7	9.5	0	0	10.0	0.69	0.31	0.198	0.169	0.8	0.131	0	0	17.7	6.4	0.33	0.24	0.54	2.1	1.3	8.6	0.69	0.30	0.19	0.15
4	12.5	22.5	1270.	907.	12.8	7.40	1.27	8.41	3.8	0.40	1.41	1.6	10.2	0	0	11.3	0.69	0.31	0.198	0.169	0.8	0.131	0	0	17.7	6.4	0.33	0.24	0.54	2.1	1.2	9.0	0.56	0.27	0.21	0.17
4	16.5	22.3	2866.	1800.	39.6	7.40	0.81	19.62	4.6	0.47	1.78	2.0	10.3	0	0	22.5	0.75	0.40	0.192	0.134	0.7	0.167	0	0	25.8	10.4	0.82	0.55	0.60	2.5	2.0	22.5	0.73	0.39	0.27	0.33
5	0.5	23.0	1156.	806.	13.6	7.80	2.28	6.98	3.6	0.47	1.42	4.0	9.6	0	0	9.1	0.73	0.30	0.220	0.269	3.4	0.052	0	0	18.8	6.1	0.67	0.22	0.69	4.6	3.0	7.2	0.68	0.30	0.19	0.15
5	4.5	23.0	1156.	814.	13.6	7.80	2.28	7.07	3.9	0.49	1.43	4.0	9.7	0	0	9.1	0.73	0.30	0.220	0.269	3.4	0.052	0	0	18.9	6.2	0.68	0.23	0.72	4.6	3.0	7.3	0.70	0.31	0.19	0.15
5	8.5	23.0	1156.	840.	10.8	7.80	2.22	7.12	3.9	0.46	1.41	4.0	9.5	0	0	10.1	0.72	0.31	0.217	0.277	3.5	0.053	0	0	18.5	6.3	0.75	0.24	0.68	4.5	3.1	8.0	0.66	0.30	0.19	0.16
5	12.5	23.0	1156.	825.	14.8	7.60	1.90	7.22	4.0	0.46	1.46	2.6	10.2	0	0	9.3	0.74	0.30	0.202	0.271	2.1	0.088	0	0	19.6	6.3	0.45	0.22	0.63	3.0	2.0	7.6	0.68	0.30	0.20	0.15
5	16.5	22.5	1156.	832.	14.8	7.60	1.04	7.08	4.0	0.46	1.50	2.6	10.3	0	0	9.7	0.72	0.31	0.220	0.262	2.1	0.089	0	0	19.7	6.7	0.47	0.23	0.68	3.0	2.0	8.2	0.66	0.30	0.21	0.15
6	0.5	23.0	1030.	794.	15.6	7.40	2.10	6.10	4.3	0.49	1.59	1.8	10.5	0	0	8.9	0.76	0.33	0.229	0.312	1.6	0.147	0	0	21.9	7.5	0.30	0.23	0.76	2.1	1.5	8.0	0.74	0.34	0.23	0.15
6	4.5	22.8	1039.	759.	12.4	7.60	2.06	6.19	4.5	0.48	1.56	2.8	10.8	0	0	8.0	0.78	0.29	0.225	0.285	2.3	0.092	0	0	22.1	6.5	0.41	0.20	0.72	3.4	2.0	7.0	0.74	0.29	0.21	0.14
6	8.5	22.8	1070.	803.	20.4	7.60	2.00	6.22	4.4	0.46	1.59	2.8	10.3	0	0	8.4	1.05	0.31	0.224	0.316	2.5	0.093	0	0	30.3	7.1	0.44	0.21	0.70	4.7	2.2	7.5	0.97	0.31	0.21	0.15
6	12.5	22.8	1156.	803.	10.0	7.40	1.83	6.34	4.4	0.48	1.67	1.9	10.3	0	0	8.9	0.78	0.30	0.249	0.311	1.6	0.156	0	0	23.8	7.3	0.31	0.22	0.81	2.3	1.4	8.3	0.75	0.31	0.21	0.15
7	0.5	23.1	1023.	762.	16.0	7.40	1.93	5.85	4.5	0.49	1.59	1.8	10.8	0	0	8.7	0.78	0.30	0.236	0.313	1.6	0.147	0	0	22.6	7.0	0.27	0.21	0.79	2.2	1.4	7.3	0.77	0.32	0.22	0.14
7	4.5	23.1	1029.	759.	18.0	7.60	1.93	5.94	4.5	0.48	1.59	2.8	10.7	0	0	8.1	0.78	0.34	0.234	0.299	2.4	0.093	0	0	22.6	7.7	0.42	0.20	0.76	3.5	2.4	7.2	0.74	0.34	0.24	0.14
7	8.5	23.0	1075.	805.	10.0	7.40	1.77	5.90	4.6	0.51	1.71	1.9	10.4	0	0	9.1	0.79	0.33	0.222	0.297	1.5	0.158	0	0	24.6	8.2	0.32	0.24	0.77	2.4	1.6	8.7	0.80	0.36	0.23	0.15
7	12.5	22.5	1278.	817.	20.0	7.40	0.91	6.21	5.0	0.58	1.85	2.0	11.1	0	0	8.1	0.82	0.36	0.231	0.260	1.3	0.173	0	0	27.6	9.8	0.31	0.25	0.90	2.7	1.9	8.5	0.90	0.44	0.27	0.15
8	0.5	23.2	1025.	752.	23.6	7.40	2.13	5.97	5.0	0.55	1.73	1.9	10.9	0	0	8.0	0.84	0.37	0.222	0.261	1.3	0.159	0	0	26.5	9.1	0.29	0.23	0.83	2.6	1.8	7.8	0.93	0.43	0.26	0.15
8	4.5	23.2	1133.	767.	26.4	7.80	2.13	5.99	5.0	0.58	1.64	4.6	11.3	0	0	8.0	0.85	0.34	0.222	0.258	3.2	0.060	0	0	25.4	8.0	0.69	0.24	0.87	6.2	3.9	7.4	0.98	0.42	0.25	0.15
8	8.5	23.2	1133.	800.	27.2	7.80	2.00	6.03	5.0	0.59	1.64	4.6	11.2	0	0	8.3	0.85	0.32	0.240	0.262	3.3	0.060	0	0	25.3	7.6	0.72	0.26	0.97	6.2	3.7	7.7	1.00	0.41	0.24	0.15
9	0.5	23.0	2012.	1202.	122.8	7.40	1.55	11.25	5.0	0.64	1.70	1.9	11.2	0	0	13.4	0.86	0.38	0.245	0.250	1.3	0.157	0	0	26.6	9.4	0.47	0.45	1.06	2.2	1.8	12.8	1.09	0.52	0.28	0.22
9	4.5	23.0	2012.	1226.	132.0	7.20	2.16	11.24	5.0	0.57	1.69	1.2	11.3	0	0	14.4	0.87	0.40	0.245	0.258	1.0	0.248	0	0	26.7	9.8	0.32	0.43	0.94	1.6	1.2	13.7	0.98	0.49	0.30	0.22

OCTOBER 21, 1967																																				
2	0.5	17.0	2000.	1278.	23.9	8.60	3.23	14.28	5.5	0.45	1.28	19.8	20.5	0	0	15.6	0.71	0.34	0.131	0.037	2.9	0.008	0	0	16.6	6.3	5.75	0.37	0.36	22.3	16.8	11.3	0.61	0.27	0.46	0.24
2	4.5	17.0	2000.	1283.	27.5	8.60	3.06	14.34	5.8	0.44	1.29	20.0	15.7	0	0	15.8	0.71	0.34	0.131	0.026	2.1	0.008	0	0	16.8	6.3	5.87	0.36	0.35	22.6	17.0	11.5	0.60	0.26	0.35	0.24
2	8.5	16.6	3200.	2081.	89.0	8.40	2.26	24.24	8.0	0.51	1.48	14.3	18.0	0	0	25.3	0.86	0.46	0.127	0.048	2.4	0.015	0	0	23.3	5.8	6.73	0.67	0.39	19.6	16.4	21.1	0.63	0.40	0.54	0.38
3	0.5	18.4	1550.	1019.	17.5	8.20	2.92	10.61	5.4	0.44	1.39	8.8	13.2	0	0	11.8	0.71	0.33	0.135	0.169	5.4	0.022	0	0	18.1	6.6	1.94	0.27	0.37	10.0	7.2	9.3	0.60	0.26	0.28	0.19
3	4.5	18.2	1550.	1011.	20.0	8.20	2.81	10.52	5.6	0.44	1.39	8.8	14.5	0	0	11.7	0.72	0.33	0.133	0.155	4.5	0.022	0	0	18.2	6.5	1.91	0.27	0.36	10.0	7.2	9.1	0.60	0.26	0.31	0.19
3	8.5	18.1	1550.	1006.	18.0	8.20	2.78	10.50	5.6	0.43	1.39	8.7	14.1	0	0	11.7	0.71	0.33	0.133	0.125	3.9	0.022	0	0	18.0	6.6	1.91	0.27	0.36	9.9	7.2	9.1	0.59	0.26	0.31	0.19
3	12.5	18.1	1650.	1077.	32.0	8.20	2.55	11.39	5.7	0.43	1.45	9.1	12.2	0	0	12.6	0.71	0.33	0.128	0.137	4.3	0.023	0	0	18.8	6.9	2.15	0.29	0.35	10.3	7.5	10.3	0.59	0.26	0.26	0.20
4	0.5	18.8	1175.	791.	18.0	7.80	2.56	7.87																												

NOVEMBER 18, 1967																																					
ST NO	DPH (M)	TEMP (C)	COND UHMO	DISS SOLID	SUSP. MG/L	PH	UISS. O2 MM/L	CL- MM/L	SR++ UM/L	SD4+ MM/L	HC03- MM/L	CO3= MM/L	F- MM/L	HS- MM/L	S= MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- MM/L	H3- MM/L	DISS SIO4- MM/L	DISS SIO3- MM/L	DISS CO2 MM/L	DISS H2S MM/L	CAH- CO3+ MM/L	MGH- CO3+ MM/L	NA- CO3+ MM/L	NA- SO4- MM/L	KS04- MM/L	CA- CO3 MM/L	MG- CO3 MM/L	NA- HCO3 MM/L	CA- SO4 MM/L	MG- SO4 MM/L	MGF+ MM/L	ION STR
2	0.5	13.1	1540.	1622.	12.7	8.10	4.28	10.47	2.6	0.50	1.50	6.7	19.5	0	0	11.6	0.77	0.32	122	118	2.9	0.03	0.0	20.9	6.8	1.43	0.30	0.34	8.1	5.3	9.7	0.70	0.24	0.41	0.19		
2	4.5	12.5	1590.	1016.	17.3	8.15	3.71	10.68	2.3	0.47	1.40	6.1	15.6	0	0	11.6	0.76	0.34	126	103	2.6	0.031	0.0	19.4	6.6	1.32	0.29	0.33	7.4	5.0	9.1	0.66	0.23	0.34	0.19		
2	8.5	12.8	3140.	2022.	38.0	8.50	0.56	24.58	0.9	0.59	1.66	18.4	16.8	0	0	21.6	0.95	0.44	0.69	0.52	3.1	0.015	0.0	28.8	11.1	7.42	0.07	0.16	27.8	21.4	20.2	1.03	0.62	0.51	0.37		
3	0.5	13.6	1180.	808.	12.0	7.70	4.91	7.51	4.6	0.43	1.55	2.8	15.0	0	0	8.5	0.77	0.32	128	209	2.1	0.084	0.0	21.6	7.3	0.44	0.19	0.32	3.4	2.3	7.4	0.62	0.22	0.32	0.15		
3	4.5	12.9	1200.	836.	11.3	7.70	4.65	7.54	4.2	0.44	1.50	2.6	15.3	0	0	9.6	0.76	0.33	128	200	2.0	0.083	0.0	20.8	7.3	0.47	0.22	0.32	3.2	2.2	8.1	0.62	0.23	0.34	0.16		
3	8.5	13.0	1340.	904.	11.7	7.90	4.55	8.89	3.9	0.48	1.48	4.1	13.5	0	0	9.8	0.76	0.32	130	188	3.0	0.051	0.0	20.5	6.8	0.75	0.25	0.35	5.0	3.3	8.1	0.68	0.24	0.28	0.17		
3	12.5	12.5	1790.	1139.	21.0	7.90	4.05	12.77	2.3	0.50	1.39	3.8	14.2	0	0	12.4	0.77	0.35	0.77	1.07	1.7	0.049	0.0	19.4	7.0	0.89	0.33	0.22	4.7	3.3	9.7	0.70	0.26	0.33	0.21		
4	0.5	13.3	1050.	759.	17.3	7.70	3.05	6.43	3.6	0.44	1.55	2.8	12.8	0	0	8.3	0.78	0.30	120	249	2.5	0.085	0.0	21.9	6.7	0.43	0.19	0.30	3.4	2.1	7.3	0.63	0.21	0.25	0.14		
4	4.5	13.3	1050.	770.	10.0	7.90	3.05	6.43	4.0	0.44	1.61	4.5	13.5	0	0	8.5	0.77	0.32	122	251	4.0	0.055	0.0	22.6	7.5	0.72	0.20	0.30	5.5	3.7	7.7	0.62	0.22	0.29	0.16		
4	8.5	13.1	1060.	791.	11.8	7.90	3.03	6.84	3.7	0.48	1.58	4.4	12.9	0	0	8.5	0.74	0.32	117	257	4.1	0.055	0.0	21.1	7.4	0.70	0.22	0.33	5.2	3.6	7.6	0.65	0.24	0.28	0.15		
4	12.5	13.1	1640.	1129.	13.0	7.70	2.62	12.10	2.3	0.44	1.47	2.6	13.0	0	0	13.1	0.75	0.34	115	140	1.4	0.081	0.0	20.2	7.3	0.64	0.30	0.29	3.1	2.2	10.9	0.62	0.27	0.28	0.21		
4	16.5	12.3	2564.	1727.	17.8	7.90	1.89	20.86	1.4	0.51	1.58	4.3	14.7	0	0	19.0	0.87	0.41	0.06	0.71	1.1	0.055	0.0	25.0	9.3	1.54	0.51	0.10	6.0	4.4	16.9	0.82	0.32	0.40	0.31		
5	0.5	13.2	1130.	821.	12.2	7.70	3.10	7.04	4.2	0.49	1.64	2.9	12.8	0	0	9.1	0.75	0.34	106	231	2.3	0.090	0.0	22.6	8.1	0.49	0.23	0.29	3.5	2.5	8.4	0.68	0.26	0.29	0.15		
5	4.5	13.2	1130.	846.	13.5	7.70	3.10	8.00	3.6	0.44	1.51	2.7	11.5	0	0	9.2	0.75	0.32	119	223	2.2	0.083	0.0	20.7	7.1	0.46	0.21	0.30	3.2	2.2	7.8	0.61	0.22	0.24	0.16		
5	8.5	13.1	1130.	846.	11.8	7.80	3.12	7.87	4.3	0.49	1.50	3.7	13.9	0	0	9.0	0.71	0.38	119	241	3.0	0.065	0.0	19.3	8.2	0.56	0.23	0.33	3.8	3.2	7.6	0.66	0.29	0.35	0.16		
5	12.5	13.0	1400.	973.	11.5	7.50	2.49	9.91	4.5	0.43	1.56	1.7	13.1	0	0	10.8	0.72	0.43	116	187	1.1	0.136	0.0	20.4	9.6	0.35	0.24	0.28	2.0	1.9	9.5	0.57	0.28	0.37	0.19		
5	16.5	12.1	1590.	1148.	11.8	7.90	2.23	11.72	4.5	0.51	1.76	4.8	13.9	0	0	12.4	0.70	0.37	0.88	1.45	2.9	0.062	0.0	28.7	9.4	1.11	0.33	0.25	6.9	4.5	12.3	0.84	0.28	0.34	0.21		
6	0.5	13.0	920.	705.	13.0	7.70	2.93	6.07	3.5	0.41	1.57	2.8	12.0	0	0	6.9	0.76	0.35	122	261	2.6	0.087	0.0	21.9	7.9	0.36	0.14	0.27	3.4	2.4	6.2	0.54	0.21	0.28	0.13		
6	4.5	12.0	930.	707.	14.2	7.70	2.98	6.02	3.7	0.41	1.57	2.7	12.4	0	0	7.1	0.72	0.38	127	274	2.7	0.086	0.0	20.7	8.6	0.37	0.15	0.30	3.2	2.6	6.3	0.55	0.24	0.30	0.13		
6	8.5	11.8	1050.	808.	25.0	7.80	2.43	6.83	3.6	0.46	1.94	4.2	13.8	0	0	7.1	0.73	0.38	116	243	2.4	0.088	0.0	20.8	8.6	0.36	0.15	0.26	3.1	2.6	6.3	0.55	0.23	0.31	0.13		
6	16.5	11.6	1240.	970.	17.8	7.90	2.1E	9.15	4.2	0.50	2.23	6.0	14.7	0	0	7.8	0.74	0.35	115	222	2.8	0.086	0.0	33.3	9.7	0.60	0.19	0.29	3.3	3.6	8.4	0.78	0.23	0.32	0.15		
7	0.5	12.8	820.	639.	14.5	7.70	3.01	5.09	3.0	0.40	1.61	2.8	11.8	0	0	9.7	0.78	0.44	118	208	3.7	0.079	0.0	43.8	14.1	1.05	0.25	0.32	17.3	6.6	12.1	0.98	0.32	0.43	0.19		
7	4.5	12.8	800.	643.	13.8	7.70	3.01	5.36	2.8	0.38	1.55	2.7	11.7	0	0	6.1	0.75	0.30	123	307	3.1	0.089	0.0	22.1	7.1	0.32	0.13	0.28	3.4	2.2	5.5	0.55	0.19	0.24	0.12		
7	8.5	12.0	790.	628.	17.2	7.70	2.88	5.03	2.8	0.37	1.64	2.8	10.5	0	0	6.2	0.75	0.30	123	286	1.9	0.086	0.0	21.2	6.8	0.32	0.12	0.28	3.3	2.1	5.4	0.52	0.17	0.23	0.12		
7	12.5	11.5	1140.	911.	21.8	7.70	2.23	6.76	3.9	0.49	2.36	4.0	14.7	0	0	5.9	0.78	0.30	126	284	2.8	0.092	0.0	23.3	7.2	0.31	0.11	0.25	3.5	2.1	5.5	0.52	0.16	0.21	0.12		
8	0.5	12.0	800.	624.	26.8	7.70	2.57	4.60	2.8	0.38	1.71	3.0	11.8	0	0	6.1	0.82	0.30	123	244	2.4	0.096	0.0	25.5	7.4	0.33	0.12	0.26	1.8	2.2	5.3	0.56	0.17	0.23	0.12		
8	4.5	12.0	810.	623.	17.5	7.70	2.57	4.54	2.8	0.40	1.67	2.9	12.7	0	0	6.1	0.82	0.30	123	276	2.8	0.093	0.0	24.9	7.3	0.32	0.13	0.29	1.7	2.2	5.7	0.60	0.18	0.25	0.12		
8	8.5	12.1	860.	634.	20.8	7.70	2.89	4.73	3.0	0.31	1.76	3.1	11.6	0	0	6.4	0.86	0.31	128	278	2.8	0.099	0.0	27.8	8.0	0.36	0.10	0.27	4.2	2.4	6.3	0.49	0.14	0.24	0.12		
9	0.5	12.6	1490.	1114.	46.8	8.10	3.31	9.62	4.8	0.73	1.56	6.9	16.0	0	0	11.3	1.27	0.54	114	214	5.4	0.034	0.0	36.0	12.1	1.45	0.44	0.47	13.8	9.2	10.0	1.71	0.60	0.57	0.22		
9	4.5	12.6	1450.	1113.	51.0	8.10	3.36	8.52	4.5	0.72	2.32	10.2	16.0	0	0	11.2	1.24	0.53	108	206	5.2	0.051	0.0	52.2	17.8	2.13	0.47	0.43	20.0	13.6	14.6	1.63	0.58	0.56	0.21		

DECEMBER 23, 1967																																			
2	0.5	5.0	1790.	1186.	4.5	7.90	3.41	12.34	2.5	0.51	1.57	3.6	14.2	0	0	13.9	0.81	0.37	0.99	1.93	2.4	0.063	0.0	23.2	8.3	0.93	0.37	0.24	4.6	3.3	12.2	0.71	0.22	0.35	0.22
2	4.5	5.7	1750.	1177.	5.2	7.80	3.26	12.46	2.3	0.51	1.68	3.1	14.0	0	0	13.2	0.81	0.36	0.90	1.28	1.6	0.084	0.0	24.8	8.7	0.76	0.35	0.23	4.0	2.8	12.4	0.72	0.22	0.33	0.22
2	8.5	6.0	2850.	1881.	8.8	7.70	2.58	22.37	1.3	0.55	1.62	2.4	16.0	0	0	21.1	0.92	0.46	0.51	0.83	0.8	0.101	0.0	27.1	10.7	0.95	0.61	0.14	3.5	2.8	19.2	0.88	0.31	0.48	0.34
3	0.5	7.8	1400.	944.	6.8	7.80	3.59	9.40	4.4	0.45	1.53	3.0	13.2	0	0	10.6	0.80	0.35	118	212	2.7	0.074	0.0	23.0	8.2	0.59	0.27	0.30	3.9	2.8	9.1	0.71	0.24	0.33	0.18
3	4.5	7.8	1420.	960.	7.8	7.80	3.59	9.39	4.9	0.49	1.54	3.0	13.7	0	0	10.4	0.80	0.35	118	192	2.4	0.073	0.0	22.4	7.7	0.59	0.25	0.27	3.8	2.6	9.1	0.64	0.20	0.32	0.18
3	8.5	7.8	1390.	945.	7.8	7.80	3.54	9.27	4.7	0.45	1.53	3.0	13.7	0	0	10.6	0.80	0.35	118	192	2.4	0.073	0.0	22.4	7.7	0.59	0.25	0.27	3.8	2.6	9.1	0.64	0.20	0.32	0.18
3	12.5	7.8	1770.	1224.	7.8	7.80	3.27	13.56	3.2	0.53	1.54	3.0	14.0	0	0	13.1	0.82	0.37	0.75	1.62	2.0	0.074	0.0	22.9	8.2	0.74	0.37	0.20	3.9	2.8	11.3	0.77	0.26	0.34	0.22
4	0.5	7.3	1190.	845.	7.5	7.70	3.33	7.80	5.0	0.48	1.77	2.7	13.8	0	0	8.2	0.84	0.35	119	234	2.3	0.108	0.0	27.2	9.0	0.41	0.21	0.29	3.6	2.4	8.2	0.71	0.21	0.32	0.16
4	4.5	7.2	1190.</																																

		JANUARY 24, 1968																																	
ST NO	DPTH (M)	TEMP (C)	COND UMHO	DISS. SOLID	SUSP. SOLID	PH	DISS. O2	CL- MM/L	SR++ MM/L	SO4= MM/L	HC03- MM/L	CO3= MM/L	F- MM/L	HS- MM/L	S= MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- S104 MM/L	H3- S103- MM/L	DISS CO2	DISS H2S	CAH- CO3+ MM/L	MGH- CO3+ MM/L	M- CO3- MM/L	NA- SO4- MM/L	KSO4 MM/L	CA- CO3 MM/L	MG- CO3 MM/L	NA- HC03 MM/L	CA- SO4 MM/L	MG- SO4 MM/L	MGF+ MM/L	ION STR
2	0.5	3.9	166.0	1125.	4.8	8.00	4.06	12.29	5.5	0.46	1.60	4.5	17.8	0	0	12.1	0.82	0.36	0.133	0.152	3.0	0.052	0.0	23.9	8.3	1.01	0.029	0.29	5.8	4.1	10.9	0.64	0.019	C.42	0.021
2	4.5	3.8	166.0	1103.	4.6	8.10	4.0E	11.72	6.3	0.47	1.53	5.4	18.4	0	0	12.3	0.84	0.37	0.124	0.154	3.9	0.040	0.0	23.3	8.1	1.23	0.030	0.27	7.1	4.9	10.6	0.66	0.019	C.44	0.020
2	8.5	3.8	166.0	1103.	14.4	3.00	4.0E	28.08	6.5	0.63	1.40	3.9	20.4	0	0	25.0	1.04	0.52	0.113	0.126	2.5	0.046	0.0	26.4	10.4	1.90	0.085	0.35	6.4	5.1	20.5	1.10	0.037	C.70	0.042
3	0.5	3.3	142.0	997.	4.2	7.60	3.93	9.74	5.2	0.47	1.68	2.9	14.4	0	0	10.7	0.83	0.37	0.125	0.146	2.5	0.088	0.0	25.4	9.1	0.58	0.026	0.28	3.9	2.7	10.1	0.67	0.019	C.35	0.018
3	4.5	3.3	142.0	994.	5.4	7.80	4.06	9.88	5.0	0.51	1.56	2.7	15.2	0	0	10.8	0.83	0.36	0.125	0.196	2.5	0.081	0.0	23.4	8.1	0.55	0.029	0.29	3.6	2.5	9.5	0.71	0.020	C.36	0.018
3	8.5	3.3	142.0	996.	5.2	7.80	3.93	9.97	5.0	0.48	1.53	2.7	14.8	0	0	11.0	0.83	0.37	0.134	0.195	2.5	0.080	0.0	23.1	8.1	0.55	0.028	0.30	3.5	2.5	9.5	0.67	0.019	C.36	0.018
3	12.5	3.0	171.0	1165.	4.8	8.00	4.00	12.81	4.9	0.48	1.60	4.4	16.2	0	0	12.4	0.84	0.38	0.126	0.160	3.2	0.053	0.0	24.3	8.8	1.01	0.031	0.28	5.8	4.2	11.2	0.68	0.020	C.41	0.021
4	0.5	4.1	128.0	925.	8.2	7.80	3.91	8.32	6.1	0.51	1.81	3.2	14.2	0	0	9.7	0.90	0.38	0.125	0.220	2.8	0.093	0.0	29.8	10.0	0.58	0.026	0.30	4.6	3.1	9.9	0.78	0.022	C.36	0.017
4	4.5	3.9	132.0	942.	7.4	8.00	3.96	8.31	6.1	0.59	1.75	4.9	15.4	0	0	9.9	0.89	0.38	0.125	0.217	4.3	0.057	0.0	28.5	9.5	0.91	0.031	0.35	7.0	4.7	9.8	0.90	0.025	C.38	0.018
4	8.5	3.9	128.0	932.	7.8	7.80	3.96	8.32	6.6	0.53	1.75	3.1	13.8	0	0	9.9	0.90	0.38	0.121	0.223	2.8	0.091	0.0	28.7	9.7	0.57	0.028	0.30	4.4	3.0	9.8	0.82	0.023	C.35	0.017
4	12.5	3.9	128.0	919.	7.6	7.80	3.96	8.22	5.7	0.49	1.69	3.0	14.2	0	0	9.7	0.91	0.38	0.121	0.222	2.8	0.087	0.0	27.8	9.4	0.54	0.025	0.28	4.3	2.9	9.2	0.76	0.021	C.36	0.017
4	16.5	3.0	175.0	1192.	6.0	7.80	4.15	12.47	5.5	0.50	1.61	2.8	15.8	0	0	13.5	0.87	0.37	0.121	0.173	2.2	0.084	0.0	25.4	8.6	0.70	0.035	0.28	3.8	2.6	12.2	0.73	0.020	C.39	0.022
5	0.5	4.0	129.0	933.	9.2	7.70	3.96	8.49	6.3	0.48	1.80	2.5	13.8	0	0	9.9	0.90	0.39	0.121	0.223	2.2	0.116	0.0	29.5	10.1	0.47	0.025	0.27	3.6	2.5	10.0	0.74	0.021	C.35	0.017
5	4.5	3.9	128.0	931.	9.2	7.70	3.96	8.48	6.0	0.48	1.73	2.4	14.2	0	0	10.3	0.90	0.37	0.118	0.224	2.2	0.112	0.0	28.3	9.2	0.47	0.026	0.27	3.5	2.3	10.0	0.73	0.020	C.35	0.017
5	8.5	3.9	132.0	926.	8.4	7.80	3.96	8.48	6.0	0.48	1.73	3.1	13.8	0	0	9.9	0.90	0.38	0.116	0.224	2.8	0.089	0.0	28.4	9.5	0.57	0.025	0.26	4.4	2.9	9.6	0.74	0.021	C.35	0.017
5	12.5	3.9	132.0	936.	8.2	8.00	3.98	8.40	5.4	0.49	1.81	5.1	13.8	0	0	10.1	0.90	0.38	0.116	0.224	4.5	0.059	0.0	29.6	9.9	0.96	0.026	0.27	7.2	4.8	10.3	0.75	0.021	C.35	0.017
5	16.5	4.0	132.0	966.	8.0	7.80	3.96	8.43	5.5	0.67	1.74	3.1	13.8	0	0	10.1	0.87	0.38	0.120	0.219	2.8	0.089	0.0	27.6	9.5	0.58	0.036	0.38	4.3	2.9	9.9	1.00	0.029	C.34	0.018
6	0.5	3.5	124.0	928.	6.4	7.80	4.11	7.57	6.3	0.52	2.07	3.6	13.0	0	0	9.7	1.02	0.40	0.118	0.216	2.7	0.108	0.0	38.5	12.0	0.66	0.026	0.29	5.9	3.6	11.3	0.90	0.023	C.34	0.017
6	4.5	3.2	124.0	914.	8.2	8.00	4.19	7.53	5.8	0.54	1.93	5.3	12.8	0	0	9.5	1.01	0.43	0.118	0.219	4.4	0.064	0.0	35.4	11.9	0.95	0.027	0.30	8.5	5.7	10.4	0.92	0.025	C.36	0.017
6	8.5	3.2	124.0	912.	8.6	3.20	4.19	7.47	8.3	0.55	1.92	8.4	13.0	0	0	9.5	1.01	0.44	0.116	0.213	6.7	0.060	0.0	35.4	12.1	1.49	0.027	0.30	13.5	9.2	10.3	0.94	0.026	C.37	0.017
6	12.5	3.2	129.0	946.	8.2	3.00	4.19	7.86	8.1	0.57	1.91	5.3	13.4	0	0	9.9	1.02	0.44	0.116	0.219	4.4	0.063	0.0	35.6	12.1	0.97	0.029	0.31	8.5	5.8	10.7	0.98	0.027	C.39	0.018
6	16.5	2.8	149.0	1072.	6.4	8.00	4.01	9.07	5.6	0.61	2.16	5.9	13.2	0	0	11.1	1.12	0.46	0.115	0.225	4.5	0.072	0.0	44.1	14.4	1.22	0.036	0.32	10.5	6.8	13.5	1.15	0.030	C.40	0.020
7	0.5	3.0	124.0	922.	8.6	7.70	4.18	7.64	6.3	0.54	2.04	2.8	12.8	0	0	9.1	1.06	0.43	0.116	0.214	2.1	0.135	0.0	39.4	12.6	0.48	0.026	0.29	4.7	3.0	10.5	0.96	0.025	C.36	0.017
7	4.5	3.1	124.0	929.	7.8	7.70	4.29	7.52	8.1	0.57	2.04	2.8	11.9	0	0	9.3	1.05	0.44	0.116	0.215	2.1	0.135	0.0	38.9	12.9	0.49	0.028	0.31	4.7	3.1	10.7	1.01	0.027	C.36	0.018
7	8.5	3.1	124.0	937.	8.2	7.70	4.15	7.54	6.3	0.57	2.04	2.8	12.8	0	0	9.5	1.06	0.44	0.116	0.222	2.2	0.135	0.0	39.5	12.9	0.50	0.029	0.31	4.7	3.1	10.9	1.03	0.027	C.37	0.018
8	0.5	2.4	133.0	980.	8.2	7.90	4.50	7.81	6.3	0.62	2.17	4.7	14.2	0	0	9.9	1.09	0.47	0.111	0.223	3.2	0.092	0.0	43.2	14.7	0.86	0.032	0.31	8.1	5.5	12.1	1.13	0.031	C.44	0.019
8	4.5	2.5	133.0	1003.	7.6	7.70	4.48	7.98	6.4	0.62	2.17	2.9	14.8	0	0	10.2	1.11	0.46	0.111	0.207	2.1	0.145	0.0	43.7	14.4	0.56	0.034	0.32	5.2	3.4	12.5	1.16	0.031	C.45	0.019
8	8.5	2.7	133.0	977.	7.8	8.00	4.42	7.74	6.2	0.63	2.12	5.8	14.6	0	0	9.9	1.10	0.46	0.111	0.207	4.1	0.070	0.0	42.5	14.0	1.06	0.033	0.32	10.1	6.6	11.7	1.18	0.031	C.44	0.019
9	0.5	6.2	185.0	1341.	16.8	8.10	3.57	11.57	8.8	0.67	2.51	9.4	14.2	0	0	13.8	1.20	0.61	0.091	0.237	6.0	0.062	0.0	59.9	22.2	2.41	0.048	0.30	19.6	14.5	19.4	1.52	0.050	C.57	0.026
9	4.5	6.2	185.0	1390.	17.0	8.40	3.87	12.02	8.7	0.76	2.58	19.3	14.2	0	0	13.9	1.24	0.60	0.083	0.242	12.1	0.032	0.0	58.3	22.4	5.00	0.056	0.31	38.0	29.1	20.2	1.65	0.056	C.56	0.026

		FEBRUARY 27, 1968																																	
ST NO	DPTH (M)	TEMP (C)	COND UMHO	DISS. SOLID	SUSP. SOLID	PH	DISS. O2	CL- MM/L	SR++ MM/L	SO4= MM/L	HC03- MM/L	CO3= MM/L	F- MM/L	HS- MM/L	S= MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- S104 MM/L	H3- S103- MM/L	DISS CO2	DISS H2S	CAH- CO3+ MM/L	MGH- CO3+ MM/L	M- CO3- MM/L	NA- SO4- MM/L	KSO4 MM/L	CA- CO3 MM/L	MG- CO3 MM/L	NA- HC03 MM/L	CA- SO4 MM/L	MG- SO4 MM/L	MGF+ MM/L	ION STR
2	0.5	5.0	175.0	1173.	4.8	8.00	4.47	11.89	5.0	0.50	1.57	4.5	17.8	0	0	14.0	0.93	0.37	0.115	0.165	3.3	0.050	0.0	23.6	8.5	1.19	0.037	0.27	5.9	4.3	12.4	0.71	0.022	C.44	0.022
2	4.5	5.2	178.0	1185.	4.6	7.80	4.50	12.10	5.5	0.50	1.56	2.9	18.4	0	0	14.1	0.83	0.38	0.119	0.158	2.0	0.079	0.0	23.6	8.6	0.75	0.037	0.29	3.8	2.7	12.4	0.71	0.022	C.46	0.022
2	8.5	4.3	202.0	1382.	8.0	7.80	4.01	14.95	5.0	0.50	1.58	2.8	19.4	0	0	16.6	0.81	0.40	0.105	0.122	1.5	0.081	0.0	25.2	9.2	0.87	0.044	0.25	3.6	2.9	14.7	0.69	0.023	C.52	0.025
3	0.5	5.0	151.0	1009.	4.0	8.00	4.38	9.83	5.1	0.51	1.62	3.0	14.2	0	0	11.0	0.95	0.37	0.124	0.208	2.6	0.082	0.0	25.2	8.8	0.61	0.030	0.31	4.0	2.8	10.0	0.75	0.022	C.35	0.019
3	4.5	5.2	142.0	1001.	4.4	8.00	4.53	9.83	5.1	0.51	1.54	4.5	14.4	0	0	11.0	0.85	0.37	0.120	0.207	4.1	0.049	0.0	23.8	8.3	0.92	0.030	0.30	3.7	2.7	10.0	0.73	0.023	C.37	0.019
3	8.5	5.2	157.0	1041.	4.2	7.80	4.53	10.37	4.9	0.51	1.54	2.8	14.6	0	0	11.6	0.84	0.38	0.124	0.204	2.6	0.077	0.0	23.4	8.4	0.61</									

MARCH 21, 1968																																					
ST	DPH	TEMP	COND	DISS.	SUSP.	PH	DISS.	CL-	SR++	SO4=	HCO3	CO3=	F-	HS-	S-	NA+	CA++	MG++	K+	H4-	H3-	DISS.	DISS.	CAH-	MGH-	NA-	NA-	KS04	CA-	MG-	NA-	CA-	MG-	MGF+	ION		
NO	(M)	(C)	UMHO	SOLID	MG/L	MM/L	O2	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L	MM/L
2	0.5	10.5	2390.	1537.	60.4	7.30	.185	18.87	5.1	0.42	1.24	0.8	17.4	.0	.0	17.6	0.72	0.39	.102	.093	0.4	.179	0.0	16.3	7.1	0.27	.039	.023	0.9	0.8	12.3	.055	.024	0.45	.028		
2	4.5	10.1	3020.	1947.	35.0	7.9C	.197	23.62	4.8	0.51	1.49	3.9	17.2	.0	.0	21.9	0.90	0.48	.085	.128	2.0	.055	0.0	24.3	10.3	1.59	.058	.023	5.5	4.7	18.4	.081	.034	0.54	.035		
2	8.5	10.1	3100.	1991.	25.4	7.9C	.210	24.00	5.4	0.53	1.54	4.0	17.7	.0	.0	22.4	0.91	0.49	.091	.110	1.7	.056	0.0	25.6	10.9	1.68	.062	.026	5.8	4.9	19.4	.086	.036	0.57	.036		
3	0.5	8.0	1630.	1187.	8.2	8.10	.325	12.25	5.5	0.49	1.58	6.2	15.3	.0	.0	13.5	0.87	0.39	.106	.249	6.2	.038	0.0	24.9	8.8	1.56	.035	.026	8.5	6.0	12.0	.075	.024	0.39	.022		
3	4.5	8.0	1810.	1181.	6.8	8.30	.325	12.37	6.1	0.53	1.35	8.4	15.8	.0	.0	13.3	0.85	0.43	.106	.252	10.0	.020	0.0	21.0	8.5	2.09	.037	.028	11.4	9.2	10.2	.079	.030	0.45	.022		
3	8.5	8.0	1820.	1185.	6.8	8.30	.325	12.33	5.3	0.46	1.53	9.5	15.7	.0	.0	13.5	0.89	0.40	.112	.239	9.5	.023	0.0	24.9	8.9	2.40	.033	.026	13.5	9.6	11.6	.073	.024	0.42	.022		
3	12.5	9.4	3200.	2056.	16.4	8.20	.289	24.59	5.6	0.55	1.99	10.2	16.9	.0	.0	23.2	0.93	0.50	.093	.158	5.0	.037	0.6	33.7	14.4	4.40	.067	.027	15.0	12.8	26.0	.092	.038	0.56	.038		
4	0.5	7.1	1540.	1077.	3.0	7.90	.356	9.40	5.6	0.52	1.98	4.8	14.0	.0	.0	12.1	1.02	0.48	.106	.238	3.8	.076	0.0	36.7	13.6	1.08	.033	.028	7.7	5.7	13.5	.093	.031	0.44	.020		
4	4.5	7.1	1540.	1092.	4.0	7.90	.356	9.65	5.8	0.58	1.94	4.7	15.2	.0	.0	11.9	1.01	0.47	.102	.230	3.6	.075	0.0	35.6	13.3	1.04	.036	.030	7.5	5.6	12.9	.103	.035	0.48	.021		
4	8.5	7.1	1540.	1103.	4.1	7.90	.356	9.65	5.8	0.57	1.95	4.7	15.8	.0	.0	12.3	1.02	0.47	.102	.254	4.0	.075	0.0	36.1	13.4	1.08	.036	.029	7.6	5.6	13.4	.101	.034	0.49	.021		
4	12.5	7.1	1540.	1104.	5.0	7.90	.356	9.60	5.6	0.59	1.98	4.8	14.0	.0	.0	12.1	1.02	0.47	.106	.256	4.1	.076	0.0	36.9	13.5	1.08	.038	.032	7.8	5.7	13.4	.106	.035	0.44	.021		
4	16.5	7.1	2020.	1362.	8.2	7.90	.356	13.90	7.0	0.56	1.94	4.7	16.5	.0	.0	15.1	0.99	0.45	.089	.187	3.0	.075	0.0	35.0	12.7	1.32	.044	.025	7.4	5.3	16.5	.097	.032	0.49	.025		
5	0.5	7.1	1540.	1084.	5.0	7.90	.338	9.53	6.1	0.60	1.99	4.8	15.2	.0	.0	11.5	1.07	0.47	.102	.232	3.7	.077	0.0	38.4	13.4	1.03	.035	.030	8.1	5.6	12.8	.109	.034	0.46	.020		
5	4.5	7.1	1540.	1094.	5.2	7.90	.338	9.31	6.2	0.56	1.97	4.8	14.0	.0	.0	12.1	1.03	0.47	.099	.241	3.8	.076	0.0	37.5	13.6	1.08	.038	.030	7.9	5.7	13.5	.109	.036	0.47	.021		
5	8.5	7.1	1520.	1093.	4.6	7.90	.338	9.39	6.1	0.59	1.95	4.7	15.8	.0	.0	12.1	1.08	0.50	.102	.238	3.6	.076	0.0	38.9	14.2	1.07	.036	.029	8.2	6.0	13.4	.107	.035	0.46	.021		
5	12.5	7.1	1860.	1101.	6.6	7.80	.338	9.52	6.1	0.59	1.95	4.7	15.8	.0	.0	11.9	1.09	0.50	.101	.249	4.0	.075	0.0	38.7	14.0	1.04	.037	.030	8.2	5.9	13.0	.113	.037	0.52	.021		
5	16.5	7.2	1620.	1146.	5.8	8.00	.341	9.40	6.2	0.58	2.00	3.8	13.6	.0	.0	12.1	1.09	0.50	.101	.248	3.1	.097	0.0	39.5	14.4	0.86	.037	.030	6.6	4.8	13.6	.110	.036	0.45	.021		
6	0.5	7.2	1620.	1162.	5.8	8.00	.341	9.57	6.1	0.65	2.12	6.5	14.8	.0	.0	12.0	1.17	0.55	.112	.258	5.1	.065	0.0	45.1	16.8	1.45	.041	.037	12.0	8.9	14.3	.133	.045	0.54	.022		
6	4.5	7.2	1620.	1162.	5.0	8.00	.341	9.53	6.1	0.67	2.16	6.6	14.6	.0	.0	12.4	1.17	0.52	.116	.263	5.2	.066	0.0	45.9	16.3	1.52	.044	.039	12.2	8.8	15.0	.137	.044	0.50	.022		
6	8.5	7.2	1640.	1154.	5.4	8.00	.351	9.40	6.3	0.67	2.17	6.6	15.4	.0	.0	12.2	1.17	0.53	.112	.264	5.3	.066	0.0	46.3	16.7	1.51	.043	.038	12.3	8.8	14.9	.139	.045	0.54	.022		
6	12.5	7.2	1590.	1161.	5.0	8.00	.351	9.57	6.0	0.67	2.18	6.7	14.8	.0	.0	12.2	1.18	0.53	.105	.256	5.1	.067	0.0	46.8	16.6	1.52	.043	.036	12.4	8.8	15.0	.138	.045	0.51	.022		
6	16.5	7.2	1670.	1141.	5.8	8.00	.351	9.47	6.2	0.64	2.16	6.6	14.5	.0	.0	12.0	1.16	0.53	.097	.263	5.2	.066	0.0	45.6	16.6	1.48	.040	.031	12.1	8.8	14.6	.130	.043	0.51	.022		
7	0.5	8.0	1660.	1169.	5.9	8.10	.341	9.54	5.3	0.64	2.25	8.8	15.8	.0	.0	12.4	1.20	0.55	.101	.255	6.4	.084	0.0	49.0	17.9	2.04	.042	.033	16.8	12.2	15.7	.136	.046	0.57	.022		
7	4.5	8.0	1640.	1170.	6.3	8.10	.341	9.60	5.3	0.65	2.27	8.9	15.4	.0	.0	12.2	1.19	0.56	.101	.262	6.6	.084	0.0	49.2	18.3	2.02	.042	.034	16.8	12.5	15.6	.138	.048	0.57	.022		
7	8.5	8.0	1580.	1157.	10.2	8.20	.341	9.57	4.1	0.66	2.18	10.8	15.1	.0	.0	12.0	1.18	0.56	.112	.254	8.0	.042	0.0	47.1	17.7	2.41	.041	.038	20.3	15.2	14.8	.137	.048	0.56	.022		
8	0.5	9.0	1730.	1258.	7.6	7.90	.320	10.33	5.4	0.69	2.38	6.1	16.8	.0	.0	13.1	1.23	0.63	.116	.268	4.3	.089	0.0	53.2	21.5	1.47	.048	.042	11.8	9.5	17.5	.152	.059	0.69	.024		
8	4.5	9.0	1770.	1290.	10.6	8.10	.320	10.61	6.0	0.69	2.38	9.6	15.8	.0	.0	13.6	1.26	0.64	.113	.269	6.8	.086	0.0	54.4	21.9	2.42	.049	.041	11.9	15.3	18.2	.154	.059	0.66	.025		
8	8.5	9.0	1690.	1222.	16.4	8.10	.320	10.13	5.3	0.69	2.35	9.4	15.1	.0	.0	12.3	1.21	0.63	.125	.254	6.4	.085	0.0	51.9	21.4	2.17	.045	.045	18.2	15.0	16.3	.149	.059	0.63	.023		
9	0.5	7.3	860.	652.	236.0	7.70	.271	4.57	4.2	0.43	1.79	2.7	11.3	.0	.0	6.6	0.83	0.43	.123	.182	1.8	.109	0.0	26.9	11.1	0.34	.015	.027	3.6	3.0	6.6	.063	.024	0.32	.013		
9	4.5	7.1	940.	712.	246.0	7.70	.275	5.05	3.9	0.51	1.78	2.7	12.0	.0	.0	7.3	0.89	0.43	.113	.176	1.8	.109	0.0	28.8	11.1	0.37	.020	.029	3.8	2.9	7.3	.079	.028	0.34	.014		

APRIL 23, 1968

2	0.5	17.5	1560.	1053.	51.0	7.40	.199	10.12	6.6	0.60	1.37	1.3	14.4	.0	.0	12.5	0.71	0.41	.102	.126	0.6	.138	0.0	17.6	8.0	0.31	.039	.037	1.5	1.4	9.6	.081	.044	0.39	.020
2	4.5	17.0	2120.	1326.	102.0	7.40	.188	14.94	3.9	0.41	1.50	1.5	15.8	.0	.0	15.6	0.69	0.40	.094	.144	0.7	.153	0.0	19.0	8.7	0.43	.033	.024	1.6	1.5	13.2	.054	.029	0.42	.024
2	8.5	16.9	1640.	1126.	146.0	7.4C	.146	12.50	3.9	0.36	1.55	1.5	15.2	.0	.0	13.0	0.64	0.39	.095	.152	0.9	.158	0.0	17.9	8.8	0.36	.025	.021	1.5	1.5	11.3	.044	.025	0.39	.020
3	0.5	16.2	2320.	1471.	11.0	7.6C	.279	16.36	4.3	0.47	1.57	2.4	16.8	.0	.0	17.3	0.82	0.41	.101	.159	1.3	.102	0.0	23.3	9.3	0.76	.043	.028	3.1	2.5	15.2	.072	.033	0.46	.027
3	4.5																																		

MAY 29, 1968

ST NO	DEPTH (M)	TEMP (C)	COND UMHO	DISS. SOLID MG/L	SUSP. SOLID MG/L	PH	DISS. O2 MM/L	CL- SR++ MM/L	SR++ MM/L	S04- MM/L	HCO3 MM/L	CO3- MM/L	F- MM/L	HS- MM/L	S- MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- MM/L	H3- MM/L	DISS CO2 MM/L	DISS H2S MM/L	CO3+ MM/L	CO3- MM/L	CO3- MM/L	SO4- MM/L	CA- MM/L	MG- MM/L	NA- MM/L	CA- MM/L	MG- MM/L	MGF+ MM/L	ION STR	
2	0.5	20.8	1750.	1202.	63.0	7.80	.691	12.11	5.4	0.36	1.54	4.1	15.4	0.0	0.0	16.3	0.59	0.33	.105	.195	2.46	.059	0.0	16.5	7.4	1.25	.031	0.25	3.8	3.4	14.1	.041	.024	0.34	.022
2	4.5	20.1	1860.	1257.	68.0	7.60	.559	14.41	5.4	0.41	1.50	2.5	15.9	0.0	0.0	14.0	0.66	0.45	.105	.169	1.34	.092	0.0	18.2	9.8	0.65	.030	0.27	2.6	2.8	11.9	.052	.036	0.47	.023
2	8.5	19.9	2960.	1859.	48.0	7.60	.431	22.23	5.5	0.47	1.47	2.4	17.9	0.0	0.0	21.4	0.82	0.34	.092	.225	1.79	.091	0.0	22.0	7.2	0.97	.053	0.28	3.2	2.1	17.7	.075	.031	0.40	.033
3	0.5	21.6	2020.	1322.	11.6	8.20	.308	14.70	5.8	0.43	1.62	1.1	16.1	0.0	0.0	14.8	0.77	0.41	.100	.223	2.05	.024	0.0	22.7	9.7	3.06	.033	0.28	13.5	11.5	13.5	.065	.036	0.44	.024
3	4.5	20.2	1970.	1296.	2.0	8.00	.258	14.48	6.0	0.43	1.57	6.5	15.9	0.0	0.0	14.5	0.77	0.42	.100	.218	4.35	.038	0.0	22.0	9.6	1.76	.032	0.28	6.0	6.9	12.7	.065	.035	0.44	.024
3	8.5	20.0	2000.	1260.	13.0	7.80	.228	13.47	6.0	0.43	1.51	4.0	15.6	0.0	0.0	14.5	0.79	0.42	.101	.201	2.53	.059	0.0	21.8	9.1	1.10	.034	0.28	5.0	4.2	12.7	.066	.035	0.43	.023
4	0.5	20.0	1540.	1063.	10.8	8.00	.284	10.16	5.4	0.49	2.15	8.9	14.3	0.0	0.0	10.3	0.96	0.43	.106	.237	4.72	.053	0.0	37.6	13.2	1.72	.026	0.33	13.6	9.6	12.5	.091	.040	0.40	.019
4	4.5	20.0	1510.	1046.	9.6	8.00	.280	9.94	5.2	0.48	2.08	8.7	14.1	0.0	0.0	10.2	0.96	0.42	.102	.243	4.86	.051	0.0	36.5	12.8	1.65	.026	0.32	13.2	9.2	12.0	.091	.040	0.39	.019
4	8.5	19.5	1400.	988.	4.8	7.90	.222	9.12	5.9	0.49	2.02	6.6	13.8	0.0	0.0	9.6	0.97	0.43	.102	.240	3.81	.063	0.0	35.7	12.5	1.18	.025	0.32	10.1	7.1	10.9	.092	.040	0.39	.018
4	12.5	19.2	1875.	1298.	11.9	7.80	.209	13.44	5.7	0.47	1.74	5.5	15.4	0.0	0.0	14.9	0.89	0.42	.102	.233	2.93	.068	0.0	28.3	10.6	1.24	.036	0.30	6.4	4.7	14.5	.081	.037	0.43	.024
4	16.5	19.2	2050.	1368.	17.8	7.60	.167	15.09	5.7	0.46	1.60	2.6	16.1	0.0	0.0	15.3	0.85	0.42	.100	.222	1.76	.099	0.0	24.8	9.8	0.74	.037	0.29	3.5	2.8	13.8	.076	.037	0.45	.025
5	8.5	19.5	1400.	962.	15.2	7.80	.210	9.02	5.3	0.48	1.79	4.6	13.6	0.0	0.0	9.6	0.96	0.42	.102	.234	2.94	.070	0.0	31.3	10.9	0.83	.024	0.31	7.1	4.9	9.7	.090	.039	0.38	.018
5	12.5	19.5	1400.	974.	14.2	7.80	.206	9.24	5.3	0.48	1.81	4.7	13.8	0.0	0.0	9.8	0.96	0.42	.100	.237	2.98	.071	0.0	31.8	10.9	0.89	.024	0.31	7.2	4.9	9.8	.090	.038	0.38	.018
5	16.5	19.5	1730.	1225.	37.4	7.60	.206	12.20	5.3	0.48	1.72	2.8	15.1	0.0	0.0	14.0	0.93	0.43	.103	.227	1.80	.106	0.0	29.2	10.7	0.73	.036	0.32	4.2	3.1	13.5	.088	.040	0.43	.023
6	0.5	20.1	1260.	900.	30.8	7.60	.184	8.50	5.3	0.43	1.75	2.9	12.9	0.0	0.0	9.0	0.90	0.38	.103	.236	1.87	.107	0.0	28.9	9.7	0.49	.020	0.28	4.2	2.8	8.9	.076	.032	0.33	.017
6	4.5	20.0	1260.	894.	45.0	7.60	.165	8.24	5.3	0.42	1.75	2.9	13.0	0.0	0.0	9.3	0.87	0.42	.103	.233	1.85	.108	0.0	27.7	10.7	0.50	.020	0.28	4.0	3.1	9.1	.071	.034	0.36	.017
6	8.5	19.8	1200.	868.	61.0	7.60	.150	8.12	4.7	0.37	1.76	2.9	12.6	0.0	0.0	9.0	0.84	0.40	.107	.240	1.91	.108	0.0	27.0	10.2	0.49	.018	0.26	3.9	2.9	8.9	.061	.029	0.33	.016
6	12.5	19.8	1350.	928.	53.0	7.60	.142	8.73	5.2	0.43	1.75	2.9	14.1	0.0	0.0	9.5	0.90	0.41	.107	.233	1.85	.108	0.0	28.7	10.3	0.51	.022	0.30	4.1	2.9	9.4	.076	.034	0.38	.017
6	16.5	18.8	1420.	988.	30.0	7.40	.119	9.20	5.2	0.47	1.81	1.8	14.1	0.0	0.0	10.0	0.97	0.44	.106	.239	1.20	.180	0.0	32.0	11.4	0.34	.025	0.32	2.8	2.0	10.2	.089	.039	0.41	.018
7	0.5	19.4	690.	516.	246.0	7.60	.162	3.91	2.9	0.22	1.60	2.6	7.8	0.0	0.0	5.1	0.69	0.29	.111	.237	1.88	.099	0.0	20.2	6.7	0.25	.006	0.15	2.9	1.9	4.6	.029	.012	0.15	.009
7	4.5	19.0	830.	588.	156.5	7.60	.137	5.13	3.0	0.27	1.62	2.6	8.2	0.0	0.0	5.5	0.68	0.28	.110	.231	1.83	.101	0.0	20.0	6.0	0.27	.008	0.19	2.8	1.9	5.0	.036	.015	0.34	.011
7	8.5	19.2	1150.	802.	89.5	7.40	.135	7.45	4.1	0.37	1.67	1.7	12.1	0.0	0.0	8.2	0.79	0.39	.112	.230	1.15	.165	0.0	24.2	8.3	0.26	.016	0.27	2.2	1.5	7.7	.057	.024	0.27	.015
8	0.5	19.2	670.	477.	219.0	7.60	.153	3.82	3.1	0.22	1.55	2.5	5.9	0.0	0.0	4.4	0.64	0.27	.112	.155	1.23	.096	0.0	17.9	6.0	0.20	.005	0.17	2.5	1.7	3.8	.028	.011	0.10	.009
8	4.5	18.8	670.	480.	228.0	7.40	.125	4.08	3.1	0.20	1.55	1.6	6.3	0.0	0.0	4.3	0.64	0.27	.110	.124	0.62	.154	0.0	18.0	6.0	0.13	.004	0.15	1.6	1.1	3.7	.025	.010	0.11	.009
8	8.5	18.8	1050.	715.	138.0	7.40	.108	6.84	4.1	0.34	1.40	1.4	10.8	0.0	0.0	7.6	0.76	0.32	.115	.105	0.53	.139	0.0	19.3	6.5	0.20	.014	0.24	1.7	1.2	6.0	.049	.020	0.23	.013
9	0.5	21.0	490.	378.	411.0	7.60	.198	2.97	2.8	0.16	1.60	2.7	5.1	0.0	0.0	2.9	0.60	0.23	.114	.052	0.41	.096	0.0	17.4	5.3	0.14	.002	0.12	2.6	1.6	2.6	.019	.007	0.08	.007
9	4.5	20.3	490.	377.	393.0	7.60	.198	2.84	2.5	0.21	1.58	2.6	3.9	0.0	0.0	2.7	0.62	0.22	.110	.049	0.39	.094	0.0	17.9	5.0	0.13	.003	0.15	2.6	1.5	2.4	.026	.009	0.06	.007

JUNE 21, 1968

ST NO	DEPTH (M)	TEMP (C)	COND UMHO	DISS. SOLID MG/L	SUSP. SOLID MG/L	PH	DISS. O2 MM/L	CL- SR++ MM/L	SR++ MM/L	S04- MM/L	HCO3 MM/L	CO3- MM/L	F- MM/L	HS- MM/L	S- MM/L	NA+ MM/L	CA++ MM/L	MG++ MM/L	K+ MM/L	H4- MM/L	H3- MM/L	DISS CO2 MM/L	DISS H2S MM/L	CO3+ MM/L	CO3- MM/L	CO3- MM/L	SO4- MM/L	CA- MM/L	MG- MM/L	NA- MM/L	CA- MM/L	MG- MM/L	MGF+ MM/L	ION STR	
2	0.5	29.1	2230.	1447.	17.0	8.10	.380	17.04	4.2	0.60	1.53	9.8	15.6	0.0	0.0	16.0	0.77	0.39	.104	.174	4.38	.025	0.0	21.4	8.6	2.91	.034	0.32	12.0	9.6	13.7	.065	.041	0.40	.026
2	4.5	26.6	2080.	1394.	20.0	7.70	.311	15.42	4.2	0.41	1.56	3.8	15.7	0.0	0.0	15.3	0.77	0.38	.117	.158	1.58	.068	0.0	21.9	8.7	1.07	.033	0.35	4.6	3.6	13.4	.065	.038	0.40	.025
2	8.5	26.7	4400.	2915.	54.5	7.60	.198	35.10	5.2	0.59	1.77	3.4	19.7	0.0	0.0	32.5	1.02	0.53	.135	.085	0.67	.097	0.0	32.8	13.6	2.06	.100	0.57	5.5	4.5	32.3	.123	.075	0.69	.052
3	0.5	28.6	1460.	969.	7.6	8.00	.375	10.00	4.2	0.40	1.51	7.6	12.7	0.0	0.0	10.5	0.76	0.35	.102	.231	4.61	.032	0.0	20.8	7.7	1.48	.022	0.30	9.1	6.7	8.9	.062	.035	0.29	.018
3	4.5	27.0	1340.	919.	11.0	8.00	.258	9.18	4.1	0.38	1.53	7.5	12.6	0.0	0.0	10.1	0.76	0.34	.102	.232	4.63	.033	0.0	21.2	7.5	1.40	.020	0.28	9.0	6.3	8.7	.060	.031	0.28	.017
3	8.5	25.5	1970.	1360.	8.5	7.50	.065	14.58	4.3	0.44	2.00	3.0	14.8	0.0	0.0	15.0	0.78	0.38	.111	.223	1.41	.141	0.0	28.5	11.0	0.84	.035	0.35	3.7	2.8	17.0	.070	.039	0.37	.024
3	12.5	25.2	5130.	3414.	25.0	7.60	.102	40.																											

MISCELLANEOUS DATA
Water Analyses

Date	5-5-66	Station No.	Date	Depth	Temp. °C	Conductivity	Dissolved Solids (mg/l)
Station Number	4	5	11-66	0	14.2	2200	1510
Depth (meters)	20			2	14.2	2200	1510
Conductivity (mhos)				4	14.1	2200	1510
Dissolved Solids (mg/l)	5,243			6	14.1	2200	1510
pH	7.75			8	14.1	2200	1510
Sodium (mg/l)	1,748			10	14.1	2200	1510
Calcium (mg/l)	148			12	14.1	2200	1510
Magnesium (mg/l)	53			14	14.1	2400	1640
CO (mg/l)	0			16	13.8	3100	2110
HCO (mg/l)	366			18	13.7	3600	2450
SO (mg/l)	180						
Cl (mg/l)	2,748						

Station No.	Date	Depth	Fe	mn (mg/l)	Station No.	Date	Depth	Temp. °C	Conductivity	Dissolved Solids (mg/l)
5	8-20-66	0	0	.057	5	10-66	0	19	2100	1440
		1	0	.057			2	19	2100	1440
		2	0	.043			4	19	2100	1440
		4	0	.014			6	19	2100	1440
		6	0	.072			8	19	2100	1440
		8	0	.043			10	19	2100	1440
		10	0	.043			12	19	2100	1440
		12	0	.072			14	19	2400	1640
		14	.1	.092			16	18	3000	2050
		16	.1	.076			18	18	3200	2180
		18	.1	1.00			20	18	3300	2250
		20	.1	1.18						
		22	.1	1.70						

APPENDIX C

DESCRIPTIONS AND ANALYSES OF SEDIMENT SAMPLES

DESCRIPTIONS OF SEDIMENT SAMPLES

SAMPLE NAME	DATE	SEDIMENT DEPTH	
5-5-66	5-66	0"	Solids at water-sediment interface, Station 4, 20 meters depth; black, fine grain solids, odor of hydrogen sulfide.
KU	8-66	0-2"	Station 4, 18 meters depth; black, fine grain solids, odor of hydrogen sulfide.
KL	8-66	8-10"	Station 4, 18 meters depth; black, fine grain solids, odor of hydrogen sulfide.
NU	8-66	0-2"	Obtained from center of reservoir below convergence of two rivers, 20 meters; black, hydrogen sulfide odor.
NL	8-66	10-12"	From same core as NU; black clay.
D	8-66	0-6"	Station 5, 20 meters depth; black, fine grain, no hydrogen sulfide odor.
41066	11-66	0-2.5"	Station 4, 18 meters; black sediments.
41066	11-66	2.5-8"	Red-brown clay-like sediments.
41066	11-66	8-11"	Black-brown fine grain sediments.
41066	11-66	11-14"	Black fine grain sediments.
41066	11-66	14-15"	Hard, red clay plug.
1S-1	11-66	0-2"	Hard yellow clay; off south bank at center of reservoir just below the convergence of two rivers.
2S-1	11-66	0-3"	From 1/5 distance across reservoir from south bank, 15 meters, below convergence; black fine grain sediment.
2S-2	11-66	3-10"	Red-brown clay.
3S-1	11-66	0-2"	Center of reservoir, 2/5 across from south bank, 17 meters; black sediments.
3S-2	11-66	2"	Interface between red and black sediments.
3S-3	11-66	2-8"	Red sediments.
3S-4	11-66	8"	Hard red plug.
4C-1	11-66	0-20"	Center of reservoir, 3/5 distance across, 20 meters; black fine grain sediments, H ₂ S odor.
4C-1	11-66	20"	Soft, fine grain black sediments.
5N-1	11-66	0-2"	Center of reservoir, 4/5 distance across from south bank, 13 meters depth; hard black sediments mixed with dead grass and straw.
5N-2	11-66	2"	Hard black plug.

APPENDIX D

MASS TRANSFER MODEL

PROGRAM LISTING AND

EXAMPLE OUTPUT DATA

VANDW

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SUBROUTINE VANDW (DX,DY,DZ,Q11,Q12,Q0,EPS,VX,VY,PHIG
1  ,IMAX,JMAX,K,L)
DIMENSION VX(41,22),VY(41,22),PHIO(41,22),G(41,22),PHII(41,22),
1B(41,22),DI(41,22),CIL(41,22),CIR(41,22),CJA(41,22),CJB(41,22),
2IS(22),IL(22),JS(41),JL(41),A1(41,22),C1(41,22)
C   CALCULATE VELOCITY POTENTIALS
C   INITIALIZE
K=0
L=1
BETA=(DX/DY)**2.
IM1=IMAX-1
JM1=JMAX-1
DO 1 I=1,IMAX
DO 1 J=1,JMAX
G(I,J)=0.
PHIO(I,J)=0.
PHII(I,J)=0.
B(I,J)=0.
DI(I,J)=0.
CIL(I,J)=0.
CIR(I,J)=0.
CJA(I,J)=0.
CJB(I,J)=0.
1 CONTINUE
C   CALCULATE VELOCITY POTENTIAL SOURCE TERMS
G(1,1)=Q11*2./((3.*DX*DY*DZ)
G(1,2)=Q11*2./((3.*DX*DY*DZ)
G(1,3)=Q11*2./((3.*DX*DY*DZ)
G(4,1)=Q12*2./((3.*DX*DY*DZ)
G(4,2)=Q12*2./((3.*DX*DY*DZ)
G(4,3)=Q12*2./((3.*DX*DY*DZ)
G(21,22)=Q0*2./((DX*DY*DZ*3.)
C   DEFINE DISTANCE POSITIONS OF BOUNDARIES
DO 3 J=1,2
IS(J)=1
3 IL(J)=41
DO 4 J=3,22
IS(J)=J-2
4 IL(J)=44-J
C   DEFINE DISTANCE POSITIONS OF BOUNDARIES
DO 5 I=1,20
JS(I)=1
5 JS(I)=I+2
JS(21)=1
JL(21)=22
DO 6 I=22,41
JS(I)=1
6 JL(I)=44-I
C   DEFINE CONSTANTS TO SET BOUNDARIES
DO 14 J=1,JMAX
ISJP1=IS(J)+1
ILJ=IL(J)
DO 15 I=ISJP1,ILJ
15 CIL(I,J)=+1.
ISJ=IS(J)
ILJM1=IL(J)-1
DO 16 I=ISJ,ILJM1
16 CIR(I,J)=+1.
14 CONTINUE
DO 17 I=1,IMAX
JSIP1=JS(I)+1
JLI=JL(I)
DO 18 J=JSIP1,JLI
18 CJB(I,J)=+1.
JS=JS(I)
JLIM1=JL(I)-1
DO 19 J=JSI,JLIM1
19 CJA(I,J)=+1.
17 CONTINUE
100 CONTINUE
C   DEFINE ITERATION PARAMETER RHO
ARG=(2.*K+1.)*3.1415/(4.*IM1)
S=SIN(ARG)
RHO=4.*S*S
RHO=RHO/BETA

```

```

C   SOLVE THE EQUATION
A*PHI(I-1,J)+B*PHI(I,J)+C*PHI(I+1,J)=D
DO 20 I=1,IMAX
DO 20 J=1,JMAX
B(I,J)=-(CIR(I,J)+CIL(I,J)*RHO)
20 CONTINUE
DO 21 I=1,IMAX
DO 21 J=1,JMAX
PHIB=PHIC(I,J-1)
PHIC=PHIG(I,J)
PHIA=PHIG(I,J+1)
D(I,J)=-BETA*(CJA(I,J)*PHIA-(CJA(I,J)+CJB(I,J))-RHO/BETA)*PHIC
1+CJB(I,J)*PHIB+G(I,J)*DY*DY)
21 CCNTINUE
C   CALL SUBROUTINE TO SOLVE SIMULTANEOUS EQUATIONS
DO 22 J=1,JMAX
I1=IS(J)
I2=IL(J)
DO 26 I=1,IMAX
A1(I,J)=CIL(I,J)
26 C1(I,J)=CIR(I,J)
22 CALL SOLU(A1,B,C1,D,I1,I2,J,J,PHI1)
C   SOLVE THE EQUATION
C   A*PHI(I,J-1)+B*PHI(I,J)+C*PHI(I,J+1)=D
DO 23 J=1,JMAX
DO 23 I=1,IMAX
H(I,J)=-(CJA(I,J)+CJB(I,J)*RHO/BETA)
23 CONTINUE
DO 24 J=1,JMAX
DO 24 I=1,IMAX
PHIL=PHI1(I-1,J)
PHIC=PHI1(I,J)
PHIB=PHI1(I+1,J)
D(I,J)=(-1./BETA)*(CIR(I,J)*PHIB-(CIR(I,J)+CIL(I,J))-RHO)*PHIC
1+CIL(I,J)*PHIL+G(I,J)*DX*DX)
24 CCNTINUE
C   CALL SUBROUTINE TO SOLVE SIMULTANEOUS EQUATIONS
DO 25 I=1,IMAX
J1=JS(I)
J2=JL(I)
DO 27 J=1,JMAX
A1(I,J)=CJB(I,J)
27 C1(I,J)=CJA(I,J)
25 CALL SOLU(A1,B,C1,D,I,J1,J2,PHIG)
DO 7 I=1,IMAX
DO 7 J=1,JMAX
IF (ABS(PHI1(I,J)-PHIG(I,J))-EPS)7,7,8
7 CONTINUE
GO TO 9
8 IF(K-(IMAX-2))10,10,11
10 K=K+1
GO TO 100
11 IF(L-10)12,9,9
12 L=L+1
K=0
GO TO 10
9 CONTINUE
VELOCITY CALCULATIONS
DO 2 J=1,JMAX
DO 2 I=1,IMAX
VX(I,J)=0.
VY(I,J)=0.
DO 13 J=1,JMAX
I1=IS(J)
I2=IL(J)
DO 13 I=I1,I2
VX(I,J)=(CIR(I,J)*PHIO(I+1,J)+CIL(I,J)-CIR(I,J))*PHIO(I,J)
1-CIL(I,J)*PHIO(I-1,J))/(DX*2.)*(-1.)
VY(I,J)=(CJA(I,J)*PHIO(I,J+1)+CJB(I,J)-CJA(I,J))*PHIO(I,J)
1-CJB(I,J)*PHIO(I,J-1))/(DY*2.)*(-1.)
13 CONTINUE
DO 28 J=1,3
VX(1,J)=2.*VX(1,J)
28 VX(41,J)=2.*VX(41,J)
VY(21,22)=2.*VY(21,22)
RETURN
END

```


SOLUI

```
SUBROUTINE SOLUI (A1,B1,C1,D1,I1,IMAX,J1,JMAX,XX)
DIMENSION A1(41,22),B1(41,22),C1(41,22),D1(41,22),XX(41,22),G(41,
122),W(41,22)
DO 1 J=J1,JMAX
DO 9 K=I1,IMAX
IF (K-I1) 2,2,3
2 C1(K,J)=C1(K,J)+A1(K,J)
A1(K,J)=0.
GO TO 9
3 IF (K-IMAX) 9,5,5
5 A1(K,J)=A1(K,J)+C1(K,J)
C1(K,J)=0.
9 CONTINUE
10 W(I1,J)=C1(I1,J)/B1(I1,J)
G(I1,J)=D1(I1,J)/B1(I1,J)
I2=I1+1
DO 20 I=I2,IMAX
DENOM=B1(I,J)-A1(I,J)*W(I-1,J)
IF (DENOM) 18,15,18
15 PRINT 50
50 FORMAT (18H ZERO DENOMINATOR.)
GO TO 800
18 W(I,J)=C1(I,J)/DENOM
20 G(I,J)=(D1(I,J)-A1(I,J)*G(I-1,J))/DENOM
XX(IMAX,J)=G(IMAX,J)
DO 30 I=I2,IMAX
II=IMAX+I1-I
30 XX(II,J)=G(II,J)-W(II,J)*XX(II+1,J)
1 CONTINUE
800 RETURN
END
```

SOLUJ

```
SUBROUTINE SOLUJ (A1,B1,C1,D1,I1,IMAX,J1,JMAX,XX)
DIMENSION A1(41,22),B1(41,22),C1(41,22),D1(41,22),XX(41,22),G(41,
122),W(41,22)
DO 1 I=I1,IMAX
DO 9 K=J1,JMAX
IF (K-J1)2,2,3
2 C1(I,K)=C1(I,K)+A1(I,K)
A1(I,K)=0.
GO TO 9
3 IF(K-JMAX)9,5,5
5 A1(I,K)=A1(I,K)+C1(I,K)
C1(I,K)=0.
9 CONTINUE
10 W(I,J1)=C1(I,J1)/B1(I,J1)
G(I,J1)=D1(I,J1)/B1(I,J1)
J2=J1+1
DO 20 J=J2,JMAX
DENOM=R1(I,J)-A1(I,J)*W(I,J-1)
IF(DENOM)18,15,18
15 PRINT 50
50 FORMAT(18H ZERO DENOMINATOR.)
GO TO 800
18 W(I,J)=C1(I,J)/DENOM
20 G(I,J)=(D1(I,J)-A1(I,J)*G(I,J-1))/DENOM
XX(I,JMAX)=G(I,JMAX)
DO 30 J=J2,JMAX
JJ=JMAX+J1-J
30 XX(I,JJ)=G(I,JJ)-W(I,JJ)*XX(I,JJ+1)
1 CONTINUE
800 RETURN
END
```


VITA 3

Clinton Paul Falls

Candidate for the Degree of

Doctor of Philosophy

Thesis: CHEMICAL EQUILIBRIA AND DYNAMICS OF KEYSTONE RESERVOIR

Major Field: Chemistry

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